



US007194801B2

(12) **United States Patent**
Jenson et al.(10) **Patent No.:** **US 7,194,801 B2**
(45) **Date of Patent:** **Mar. 27, 2007**(54) **THIN-FILM BATTERY HAVING
ULTRA-THIN ELECTROLYTE AND
ASSOCIATED METHOD**(75) Inventors: **Mark Lynn Jenson**, Princeton, MN
(US); **Victor Henry Weiss**, Wayzata,
MN (US)(73) Assignee: **Cymbet Corporation**, Elk River, MN
(US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 427 days.(21) Appl. No.: **09/815,983**(22) Filed: **Mar. 23, 2001**(65) **Prior Publication Data**

US 2002/0001747 A1 Jan. 3, 2002

Related U.S. Application Data(60) Provisional application No. 60/191,774, filed on Mar.
24, 2000, provisional application No. 60/225,134,
filed on Aug. 14, 2000, provisional application No.
60/238,673, filed on Oct. 6, 2000.(51) **Int. Cl.**
B23P 17/00 (2006.01)(52) **U.S. Cl.** **29/730**; 29/623.1; 29/623.4;
29/623.5; 429/231.8; 429/231.95; 429/124;
429/126; 429/162; 117/92; 117/117; 117/902;
118/715; 118/720; 118/723 FE; 118/723 FI(58) **Field of Classification Search** 429/204,
429/302, 450, 86, 231.8, 300, 162, 124, 126,
429/231.95; 29/730, 623.1, 623.4, 623.5;
117/92, 117, 902; 118/715, 720, 723 FE,
118/723 FI

See application file for complete search history.

(56) **References Cited****U.S. PATENT DOCUMENTS**

3,419,487 A 12/1968 Robbins et al.
4,207,119 A 6/1980 Tyan 136/89 TF
4,299,890 A 11/1981 Rea et al. 429/124
4,328,262 A 5/1982 Kurahashi et al.
4,333,808 A * 6/1982 Bhattacharyya
et al. 204/192.22
4,353,160 A 10/1982 Armini et al. 29/572
4,365,107 A 12/1982 Yamauchi 136/258
4,435,445 A 3/1984 Allred et al.
4,440,108 A 4/1984 Little et al. 118/719
4,481,265 A 11/1984 Ezawa et al. 429/9
4,520,039 A 5/1985 Ovshinsky 427/35
4,633,129 A 12/1986 Cuomo et al. 313/153
4,645,726 A 2/1987 Hiratani et al. 429/191
4,684,848 A 8/1987 Kaufman et al. 315/111.81
4,696,671 A 9/1987 Epstein et al.
4,730,383 A 3/1988 Balkanski 29/623.5
4,740,431 A 4/1988 Little 429/9
4,832,463 A 5/1989 Goldner et al.
4,862,032 A 8/1989 Kaufman et al. 313/359.1
5,017,550 A 5/1991 Shioya et al. 505/1

5,022,930 A 6/1991 Ackerman et al. 136/251
5,051,274 A 9/1991 Goldner et al. 427/38
5,064,520 A 11/1991 Miyake et al. 204/192.11
5,089,104 A 2/1992 Kanda et al. 204/192.11
5,098,737 A 3/1992 Collins et al. 427/53.1
5,115,378 A 5/1992 Tsuchiya et al. 361/502
5,151,848 A 9/1992 Finello 361/502
5,171,413 A 12/1992 Arntz et al. 204/192.15
5,180,645 A 1/1993 More 429/127
5,189,550 A 2/1993 Goldner et al. 359/273
5,192,947 A 3/1993 Neustein 340/825.44
5,202,196 A * 4/1993 Wang et al. 429/86
5,261,968 A 11/1993 Jordan 136/244
5,273,837 A 12/1993 Aitken et al. 249/30
5,296,122 A 3/1994 Katsube et al. 204/298.04
5,314,765 A 5/1994 Bates 429/194
5,338,625 A 8/1994 Bates et al. 429/193
5,348,703 A 9/1994 Bishop et al. 420/590
5,393,572 A 2/1995 Dearnaley 427/523
5,411,592 A 5/1995 Ovshinsky et al. 118/718
5,415,717 A 5/1995 Perneborn
5,425,966 A 6/1995 Winter et al. 427/255.1
5,426,561 A 6/1995 Yen et al. 361/502
5,433,096 A 7/1995 Janssen et al.
5,445,126 A 8/1995 Graves, Jr.
5,445,906 A 8/1995 Hobson et al. 429/162
5,448,110 A 9/1995 Tuttle et al. 257/723
5,449,994 A 9/1995 Armand et al. 429/304
5,455,126 A 10/1995 Bates et al. 429/127
5,468,521 A 11/1995 Kanai et al. 427/575
5,482,611 A 1/1996 Helmer et al. 204/298.17

(Continued)

FOREIGN PATENT DOCUMENTS

DE 19948742 12/2000

(Continued)

OTHER PUBLICATIONSShukla, A.K., Sampath, S., Vijayamohan—Electrochemical
Capacitors: Energy Storage beyond batteries—Current Science, vol.
79, No. 12,— Dec. 25, 2000.*

(Continued)

Primary Examiner—Bruce F. Bell(74) *Attorney, Agent, or Firm*—Charles A. Lemaire;
Lemaire Patent Law Firm, P.L.L.C.(57) **ABSTRACT**

A method and system for fabricating solid-state energy-storage devices including fabrication films for devices without an anneal step. A film of an energy-storage device is fabricated by depositing a first material layer to a location on a substrate. Energy is supplied directly to the material forming the film. The energy can be in the form of energized ions of a second material. Supplying energy directly to the material and/or the film being deposited assists in controlling the growth and stoichiometry of the film. The method allows for the fabrication of ultrathin films such as electrolyte films and dielectric films.

103 Claims, 46 Drawing Sheets

US 7,194,801 B2

Page 2

U.S. PATENT DOCUMENTS

5,494,762 A 2/1996 Isoyama et al.
5,501,175 A 3/1996 Tanaka et al. 117/108
5,501,924 A 3/1996 Swierbut et al. 429/224
5,510,209 A 4/1996 Abraham et al.
5,512,147 A 4/1996 Bates et al. 204/192.15
5,523,179 A 6/1996 Chu
5,528,222 A 6/1996 Moskowitz et al. 340/572
5,529,671 A 6/1996 Debley et al. 204/192.34
5,536,333 A 7/1996 Foote et al. 136/260
5,549,989 A 8/1996 Anani 429/193
5,558,953 A 9/1996 Matsui et al. 429/194
5,561,004 A 10/1996 Bates et al. 429/162
5,567,210 A 10/1996 Bates et al. 29/623.5
5,569,520 A 10/1996 Bates 429/162
5,569,564 A 10/1996 Swierbut et al. 424/224
5,571,749 A 11/1996 Matsuda et al. 437/113
5,582,623 A 12/1996 Chu
5,585,999 A 12/1996 De Long et al. 361/505
5,593,551 A 1/1997 Lai 204/192.12
5,597,660 A 1/1997 Bates et al. 429/191
5,599,644 A 2/1997 Swierbut et al. 429/224
5,601,652 A 2/1997 Mullin et al. 118/723 EB
5,612,152 A 3/1997 Bates 429/152
5,626,976 A 5/1997 Blanton et al. 429/9
5,644,207 A 7/1997 Lew et al. 320/5
5,654,084 A 8/1997 Egert 428/215
5,686,201 A 11/1997 Chu
5,695,873 A 12/1997 Kumar et al. 428/325
5,695,885 A 12/1997 Malhi 429/7
5,705,293 A * 1/1998 Hobson 429/162
5,714,404 A 2/1998 Mitlitsky et al.
5,763,058 A 6/1998 Isen et al. 428/209
5,789,108 A 8/1998 Chu
5,814,420 A 9/1998 Chu
5,830,331 A 11/1998 Kim et al. 204/192.15
5,849,426 A 12/1998 Thomas et al.
5,863,337 A 1/1999 Neuman et al. 118/718
5,868,914 A 2/1999 Landsbergen et al. . 204/298.06
5,872,080 A 2/1999 Arendt et al. 505/238
5,914,507 A 6/1999 Polla et al. 257/254
5,935,727 A 8/1999 Chiao 429/32
5,953,677 A 9/1999 Sato 455/574
5,978,207 A 11/1999 Anderson et al. 361/311
5,981,107 A 11/1999 Hamano et al. 429/231.95
5,982,284 A 11/1999 Baldwin et al.
5,995,006 A 11/1999 Walsh 340/572.7
6,001,715 A 12/1999 Manka et al.
6,002,208 A 12/1999 Maishev et al. 315/111.9
6,023,610 A 2/2000 Wood, Jr.
6,025,094 A 2/2000 Visco et al.
6,033,471 A 3/2000 Nakanishi et al. 117/108
6,037,717 A 3/2000 Maishev et al. 315/111.91
6,042,687 A 3/2000 Singh et al. 156/345
6,056,857 A 5/2000 Hunt et al. 204/192.15
6,059,847 A 5/2000 Farahmandi et al. 29/25.03
6,077,621 A * 6/2000 Allen et al. 429/33
6,078,791 A 6/2000 Tuttle et al.
6,086,962 A * 7/2000 Mahoney et al. 427/577
6,094,292 A 7/2000 Goldner et al. 359/265
6,103,412 A 8/2000 Hirano et al. 429/24
6,110,620 A 8/2000 Singh et al. 429/223
6,130,507 A 10/2000 Maishev et al. 315/111.81
6,133,159 A 10/2000 Vaartstra et al. 438/758
6,136,165 A 10/2000 Moslehi 204/298.06
6,139,964 A 10/2000 Sathrum et al. 428/408
6,147,354 A 11/2000 Maishev et al. 250/423 R
6,153,067 A 11/2000 Maishev et al. 204/298.04
6,163,260 A 12/2000 Conwell et al.
6,168,884 B1 1/2001 Neudecker et al.
6,181,237 B1 1/2001 Gehlot
6,181,545 B1 1/2001 Amatucci et al. 361/502

6,203,944 B1 3/2001 Turner et al. 429/218.1
6,222,117 B1 4/2001 Shiozaki 136/256
6,236,061 B1 5/2001 Walpita 257/40
6,238,813 B1 5/2001 Maile et al.
6,264,709 B1 7/2001 Yoon et al. 29/623.5
6,277,523 B1 8/2001 Giron 429/304
6,280,875 B1 8/2001 Kwak et al. 429/162
6,281,795 B1 8/2001 Smith et al.
6,294,722 B1 9/2001 Kondo et al.
6,325,294 B2 12/2001 Tuttle et al.
6,327,909 B1 12/2001 Hung et al. 73/514.16
6,391,664 B1 5/2002 Goruganthu et al.
6,402,795 B1 6/2002 Chu et al.
6,402,796 B1 * 6/2002 Johnson 29/623.5
6,432,577 B1 8/2002 Shul et al. 429/162
6,475,854 B2 11/2002 Narwankar et al. 438/238
6,558,836 B1 5/2003 Whitacre et al. 429/162
6,576,365 B1 6/2003 Meitav et al.
6,576,369 B1 * 6/2003 Moriguchi et al. 429/231.8
6,599,580 B2 7/2003 Muffoletto et al.
6,608,464 B1 8/2003 Lew et al.
6,610,971 B1 8/2003 Crabtree 244/3.1
6,634,232 B1 10/2003 Rettig et al. 73/514.15
6,645,656 B1 * 11/2003 Chen et al. 429/32
6,723,140 B2 4/2004 Chu et al.
6,741,178 B1 5/2004 Tuttle
6,805,998 B2 10/2004 Jenson et al.
6,982,132 B1 * 1/2006 Goldner et al. 429/162
6,989,750 B2 1/2006 Shanks et al.
2001/0014398 A1 * 8/2001 Veerasamy 428/408
2002/0076616 A1 * 6/2002 Lee et al. 429/300
2002/0110733 A1 8/2002 Johnson

FOREIGN PATENT DOCUMENTS

EP 0078404 5/1983
EP 0410627 1/1991
EP 0643544 8/1994
EP 0860888 8/1998
EP 0867752 9/1998
GB 2318127 4/1998
JP 58126679 8/1983
JP 57230095 7/1984
JP 59123236 7/1984
JP 60012679 1/1985
JP 60182961 2/1987
JP 62044960 2/1987
JP 63166151 1/1990
JP 03205757 9/1991
JP 03262697 11/1991
JP 06067018 3/1994
JP 6111828 4/1994
JP 6196178 7/1994
JP 06223805 8/1994
JP 07006933 1/1995
JP 07-050229 2/1995
JP 07057739 3/1995
JP 08017179 1/1996
JP 08293310 5/1996
JP 08236105 9/1996
JP 08287901 11/1996
JP 09035233 2/1997
JP 09211204 8/1997
JP 10021896 1/1998
JP 10021933 1/1998
JP 2000188113 7/2000
WO WO-99/33124 7/1990
WO WO-92/15140 9/1992
WO WO-92/16025 9/1992
WO WO-92/19090 10/1992
WO WO-93/14612 7/1993
WO WO-95/14311 5/1995
WO WO-97/38453 10/1997

WO	WO-97/39491	10/1997
WO	WO-98/13743	4/1998
WO	WO-98/47196	10/1998
WO	WO-99/25908	5/1999

OTHER PUBLICATIONS

- Aramoto, T., et al., "16.0% efficient thin-film CdS/CdTe solar cells", *Jpn. J. Appl. Phys.*, vol. 36, Pt. 1, No. 10, pp. 6304-6305, (1997).
- Birkmire, R.W., et al., "Polycrystalline Thin Film Solar Cells: Present Status and Future Potential", *Annu. Rev. Mater. Sci.*, 27, pp. 625-653, (1997).
- Chu, T.L., et al., "13.4% efficient thin-film CdS/CdTe solar cells", *J. Appl. Phys.*, 70(12), pp. 7608-7612, (Dec. 15, 1991).
- Dudney, N.J., et al., "Nanocrystalline $\text{Li}_x\text{Mn}_{2-y}\text{O}_4$ Cathodes for Solid-State Thin-Film Rechargeable Lithium Batteries", *Journal of the Electrochemical Society*, 146(7), pp. 2455-2464, (1999).
- Jacobson, A.J., "Intercalation Chemistry", In: *Encyclopedia of Inorganic Chemistry*, vol. 3, John Wiley & Sons, pp. 1556-1602, (1994).
- Yoshida, T., "Photovoltaic Properties of Screen-Printed CdTe/CdS Solar Cells on Indium-Tin-Oxide Coated Glass Substrates", *J. Electrochem. Soc.*, 142(9), pp. 3232-3237, (Sep. 1995).
- Dunn, D., et al., "MoS₂ Deposited by ion beam assisted deposition: 2H or random layer structure.", *Naval Research Laboratory*, (1998), pp. 3001-3007.
- Goldner, R., "Ambient temperature synthesis of polycrystalline thin films of lithium cobalt oxide with controlled crystallites orientations", *Electrochemical Soc. Proceedings*, 98, (1999), pp. 268-273.
- Goldner, R., et al., "Ambient Temperature Synthesis of Polycrystalline Thin Films of Lithium Cobalt Oxide with Controlled Crystallites' Orientation", *Mat. Res. Soc. Symp. Proc.*, 548, (1998), pp. 131-136.
- Kyokane, J., et al., "Organic Solid Capacitor with Conducting Thin Films as Electrolyte by Ion-Beam-Assisted Deposition", *Journal of Power Sources*, 60, (1996), pp. 151-155.

- Liu, W., et al., "Deposition, Structural Characterization, and Broadband (1KHz-40GHz) Dielectric Behavior of $\text{Ba}_x\text{Ti}_{2-x}\text{O}_y$ Thin Films", *Mat. Res. Soc. Symp. Proc.*, 310, (1993), pp. 157-162.
- Martin, P., et al., "Modification of the optical and structural properties of dielectric ZrO_2 films by ion-assisted deposition", *Journal of Applied Physics*, 55(1), (1984), pp. 235-241.
- Nomoto, S., et al., "Back-up Performance of Electric Double-Layer Capacitors for Rechargeable Batteries", *Electrochemical Society Proceedings*, vol. 96-25, (1997), 268-279.
- Shodai, T., et al., "Reaction Mechanisms of $\text{Li}_{2.6}\text{Co}_{0.4}$ Anode Material", *Solid State Ionics*, 122, (1999), 85-93.
- Vereda, F., "A study of electronic shorting in IBDA-deposited Lipon films", *Journal of Power Sources*, 89(2), (2000), pp. 201-205.
- Zeitler, M., et al., "In Situ Stress Analysis of Boron Nitride Films Prepared by Ion Beam Assisted Deposition", *Nuclear Instruments and Methods in Physics Research B*, 139, (1998), pp. 327-331.
- Lugscheider, E., et al., "Comparison of the Structure of PVD-Thin Films Deposited With Different Deposition Energies", *Surface and Coatings Technology*, 86-27 (1-3), (Dec. 1, 1996), 177-183.
- McKenzie, D. R., et al., "New Technology for PACVD", *Surface and Coatings Technology*, 82 (3), (1996), 326-333, no month available.
- Doble, Arthur, et al., "High Capacity Cathodes for Lithium-Air Batteries", Yardney Technical Products, Inc./Lithion, Inc. Pawcatuck, CT <<http://www2.electrochem.org/cgi-bin/abs?mtg=206&abs=0496>>.
- Doble, Arthur, et al., "High Capacity Cathodes for Lithium-Air Batteries", Yardney Technical Products, Inc./Lithion, Inc. Pawcatuck, CT Electrochemical Society Conference, (May 20, 2004).
- Doble, Arthur, et al., "Non-aqueous Lithium-Air Batteries with an Advanced Cathode Structure", Yardley Technical Products, Inc. / Lithion, Inc. Pawcatuck, CT 41st Power Sources Conference Proceedings, Philadelphia, PA, (Dec. 10, 2003).

* cited by examiner

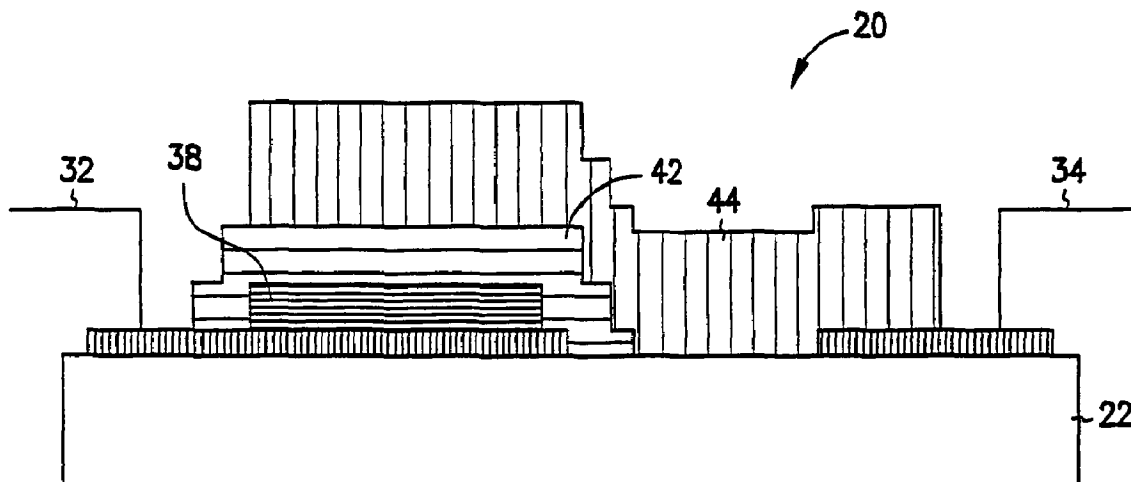


FIG. 1A (Prior Art)

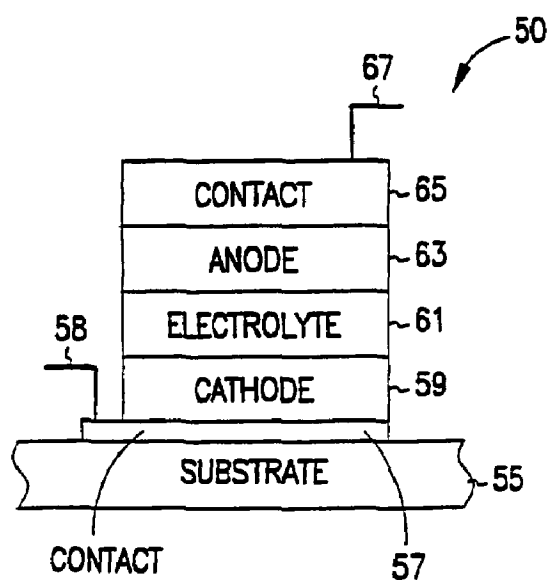


FIG. 1B

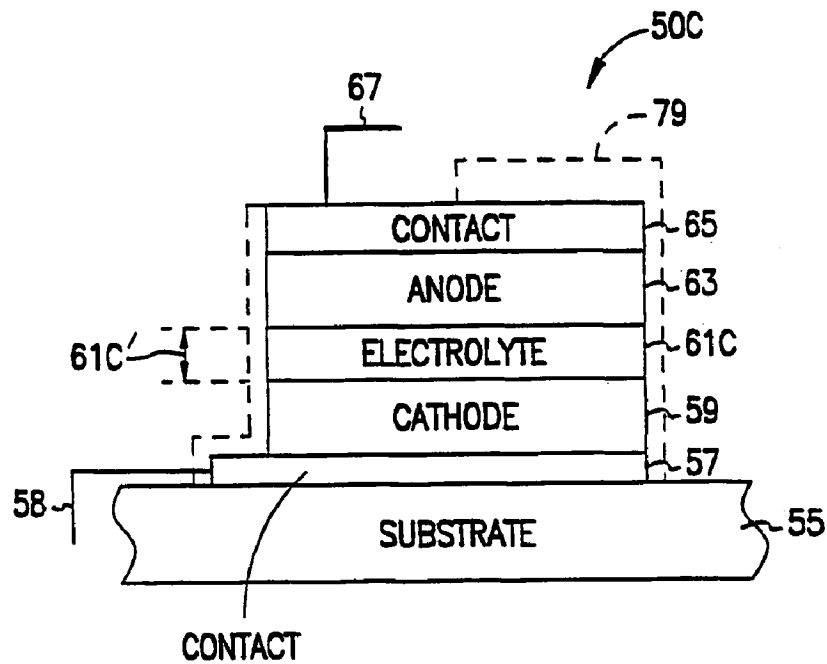


FIG. 1C

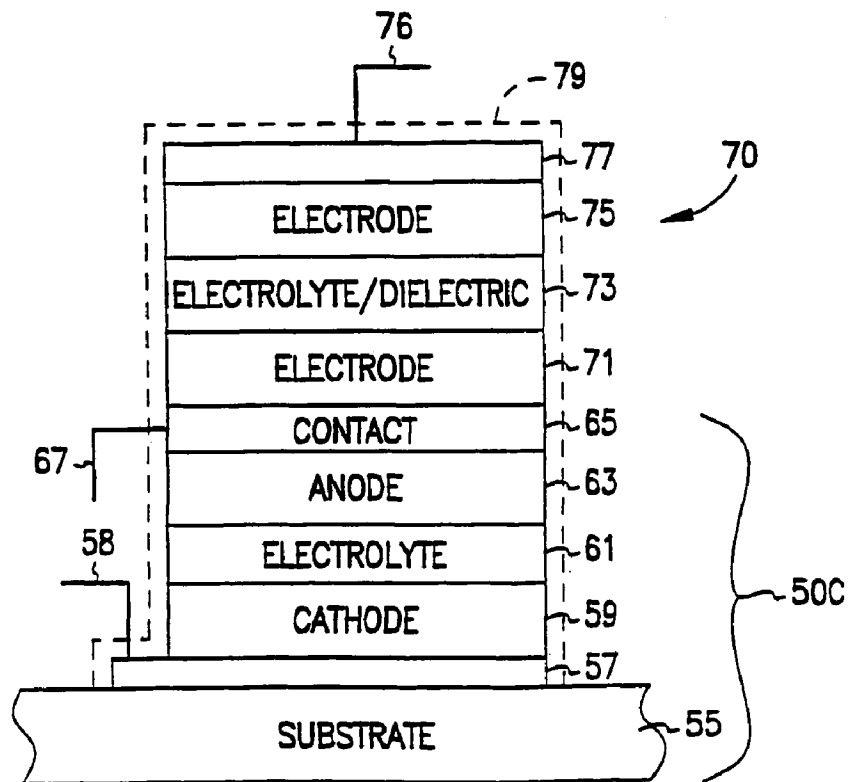


FIG. 1D

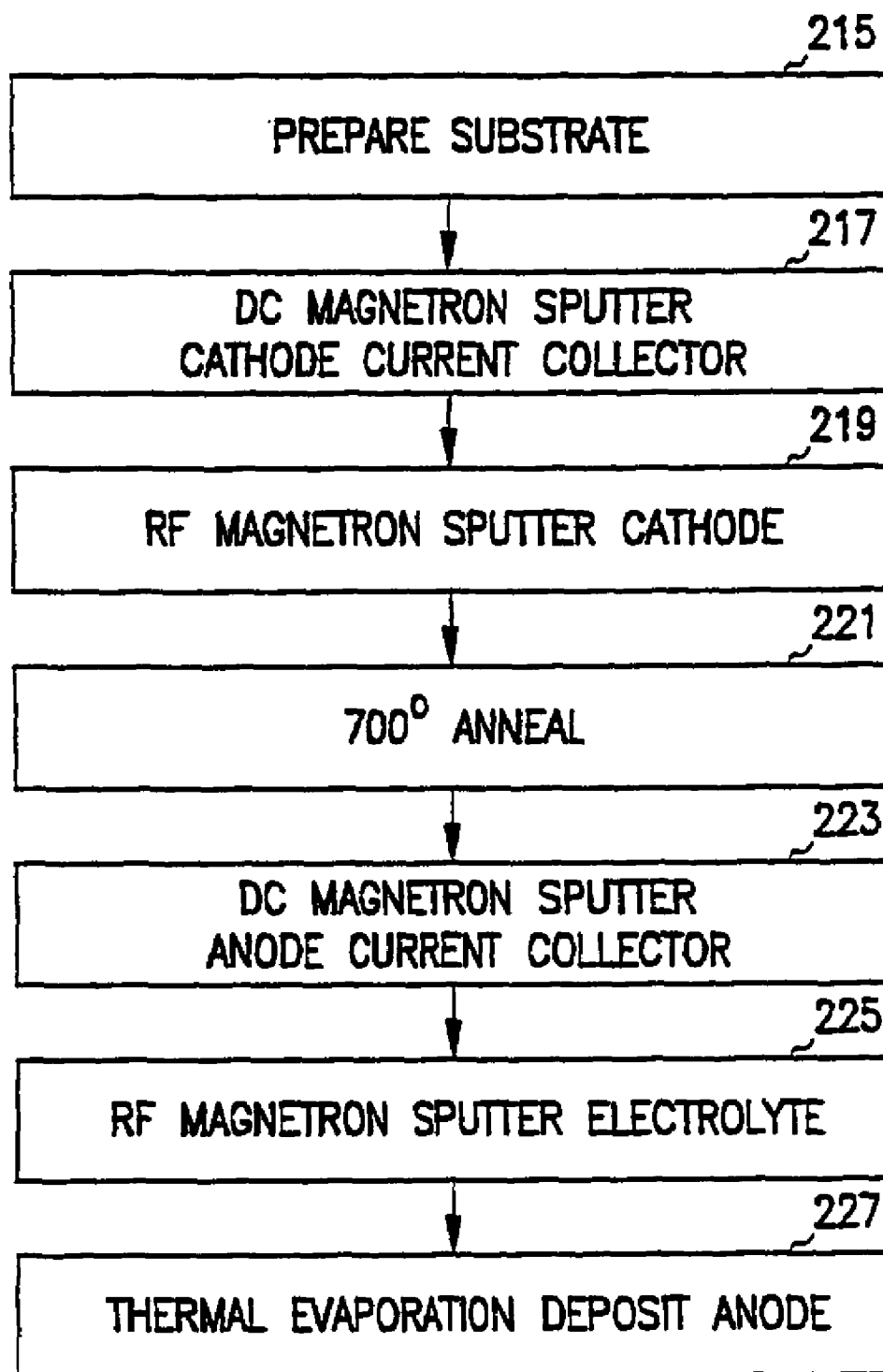


FIG. 2A (Prior Art)

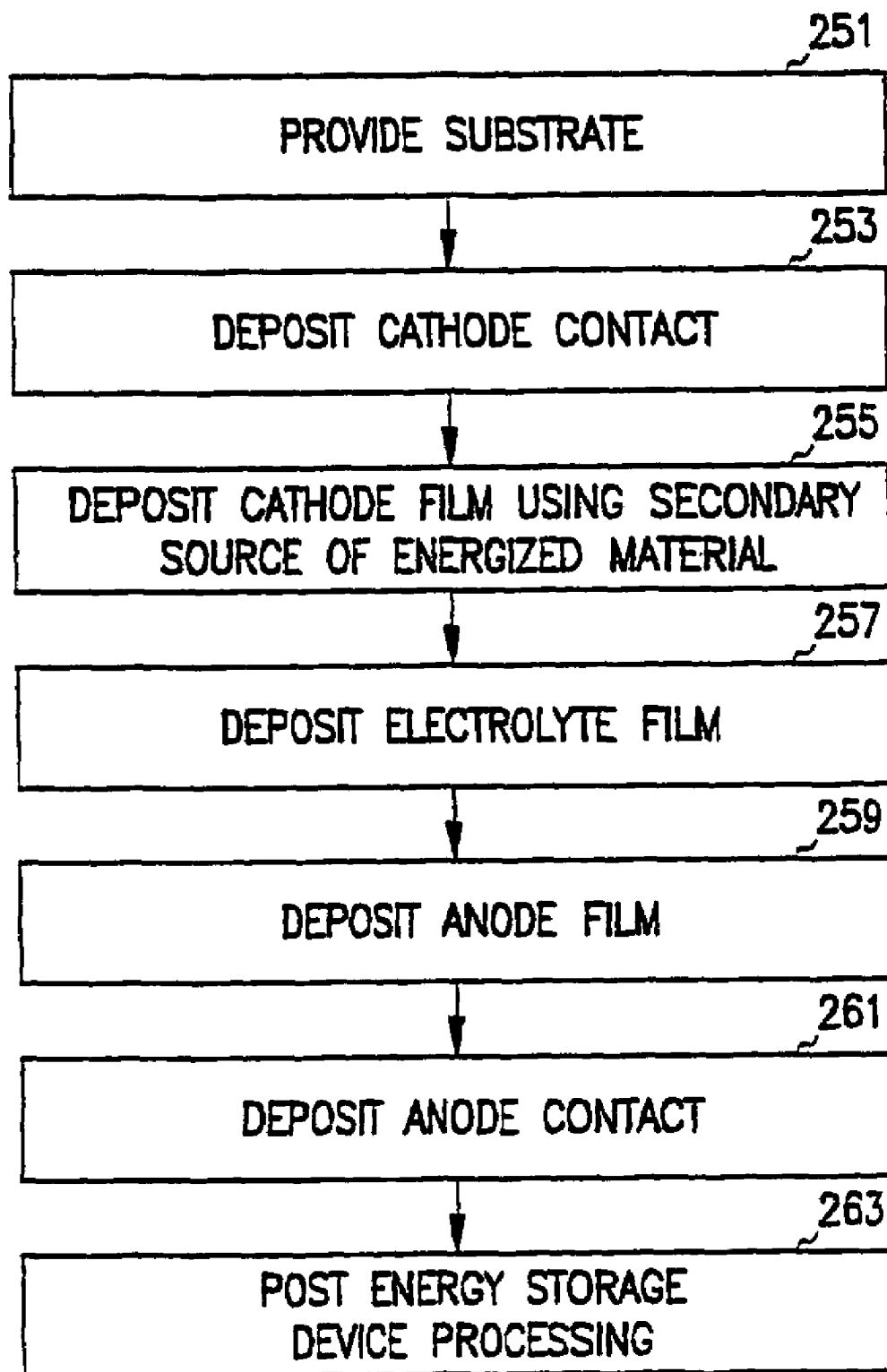


FIG. 2B

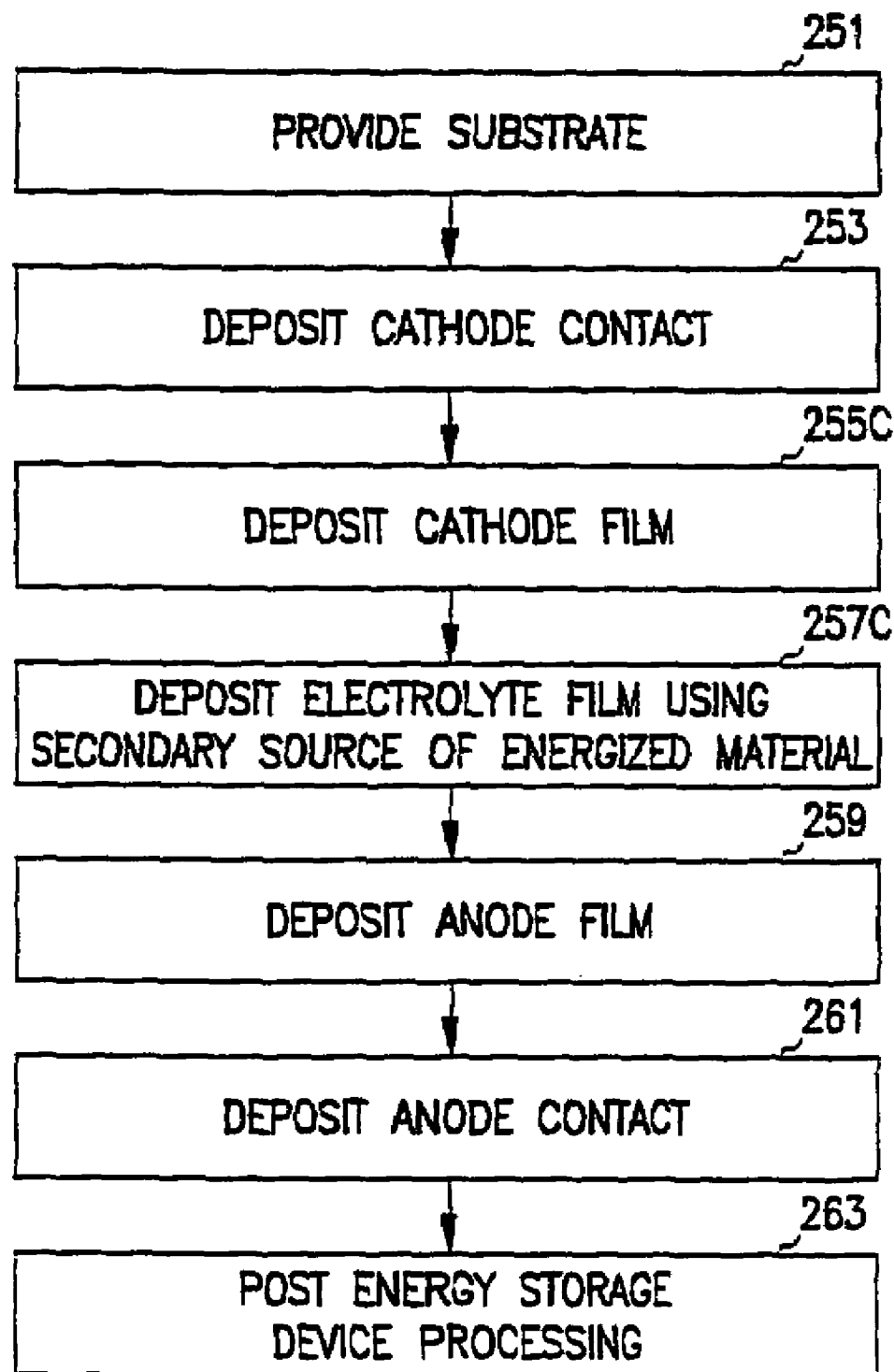


FIG. 2C

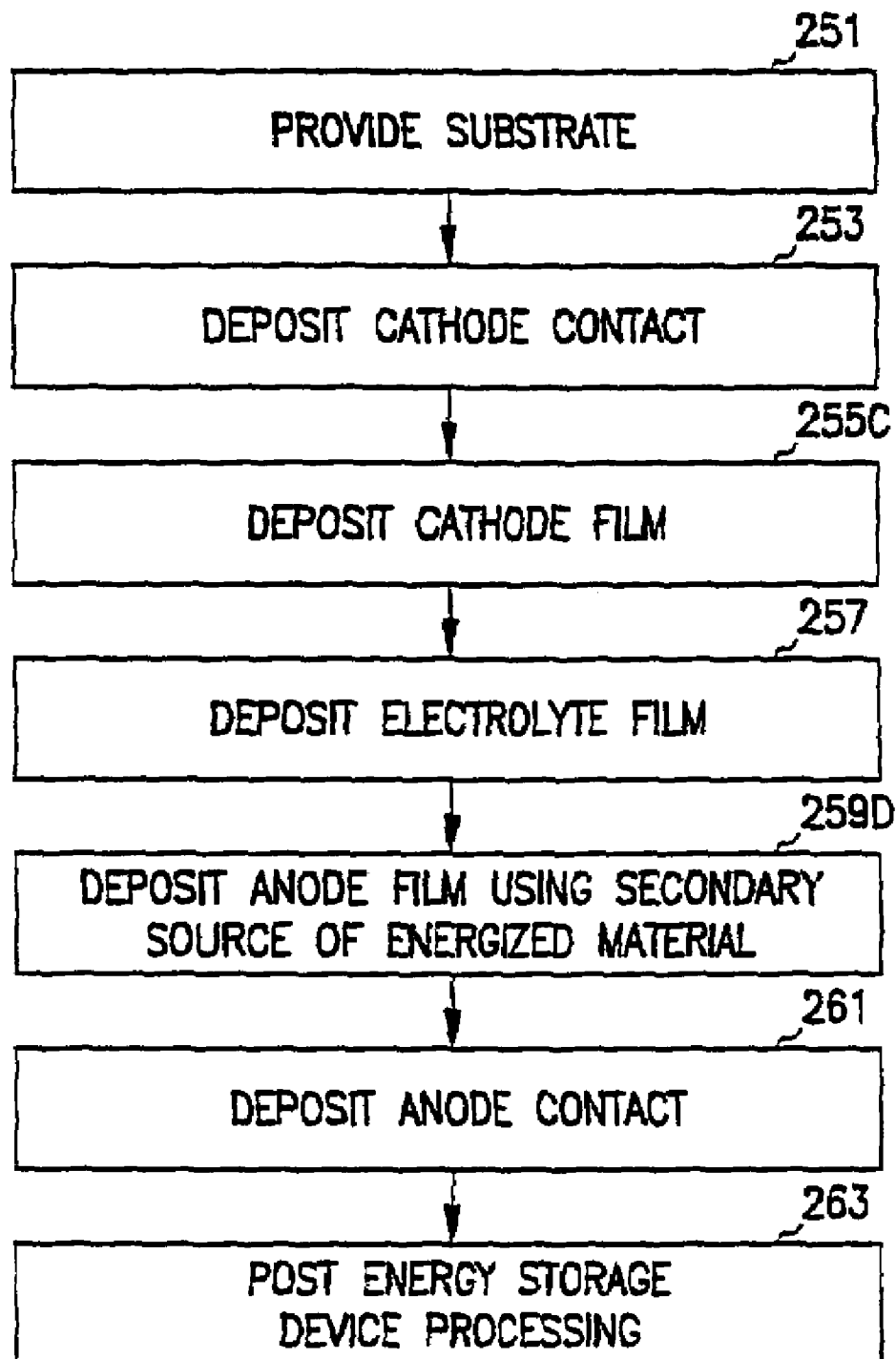


FIG. 2D

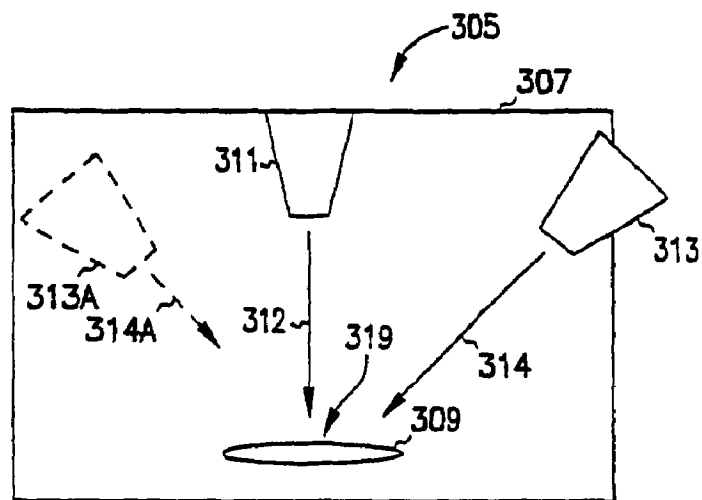


FIG. 3A

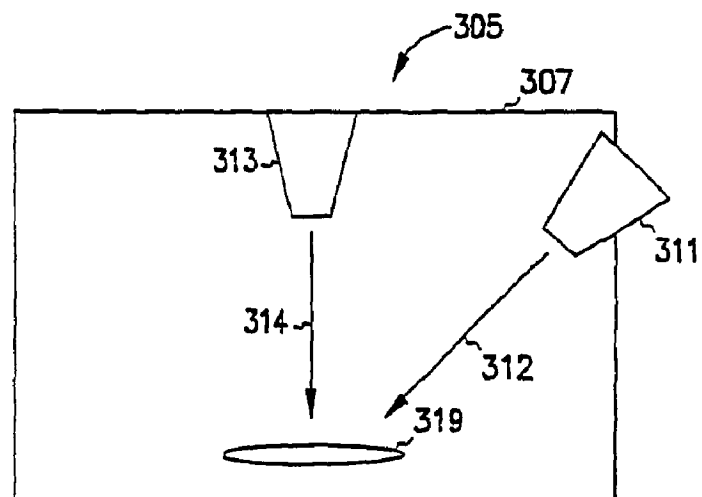


FIG. 3B

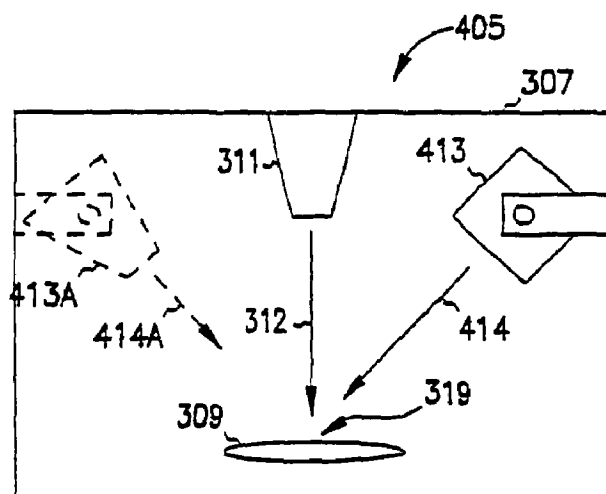


FIG. 4

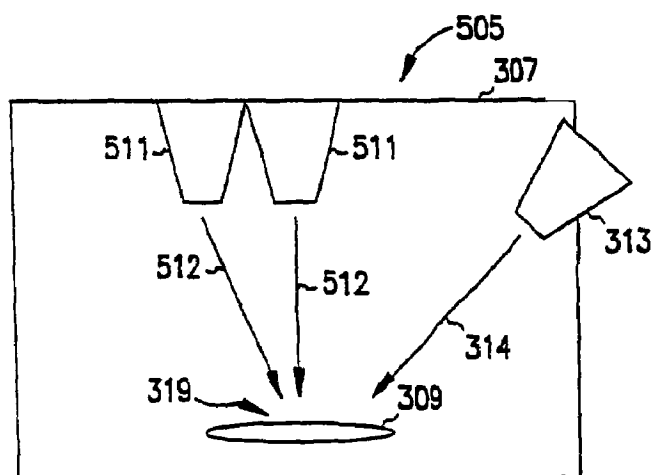


FIG. 5A

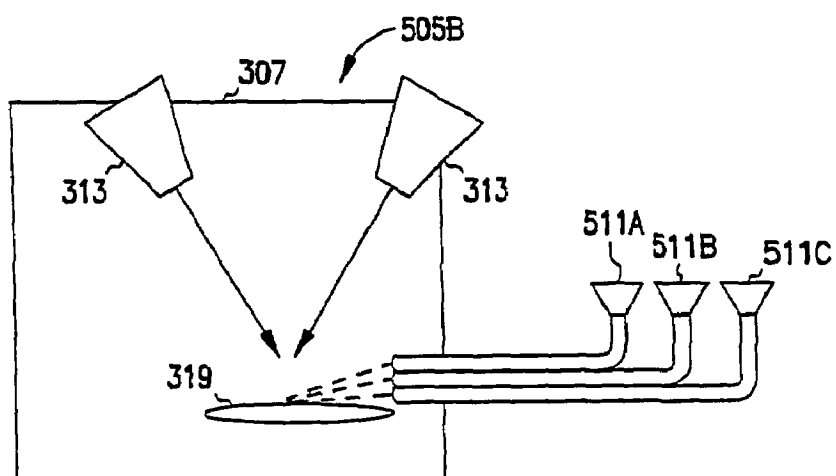


FIG. 5B

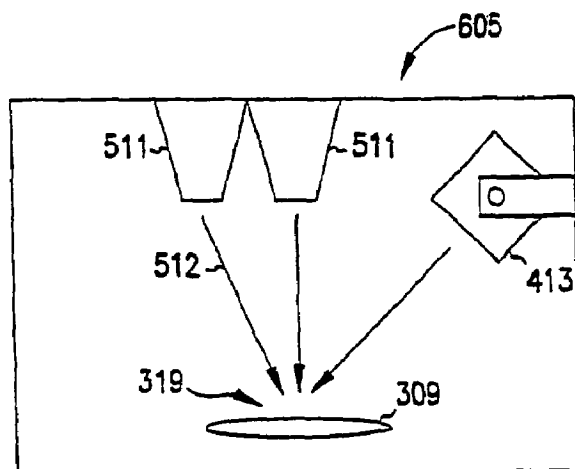


FIG. 6

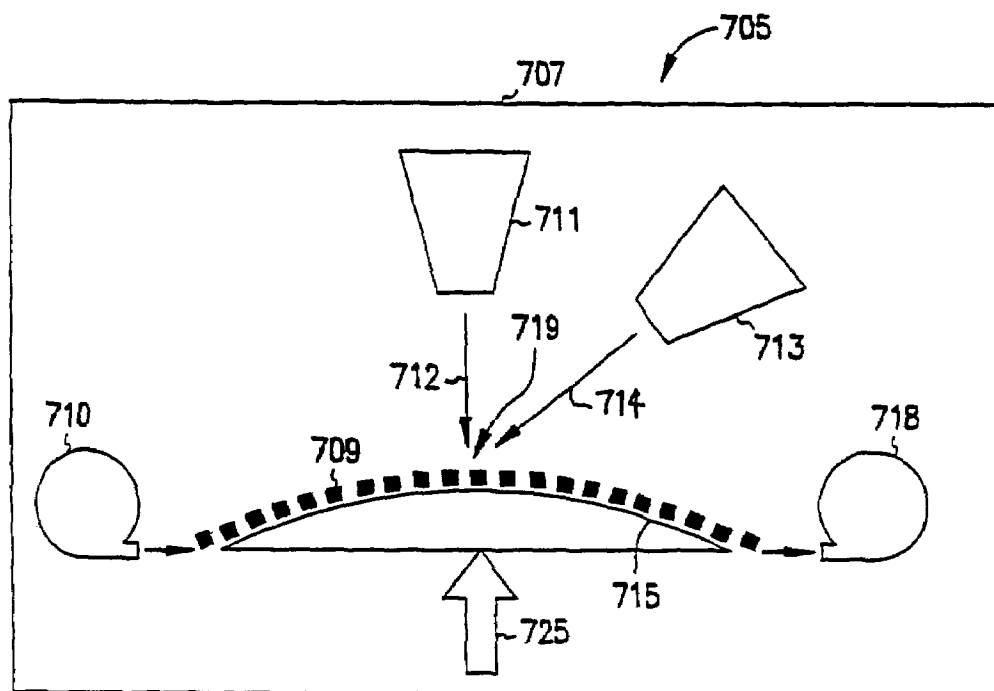


FIG. 7

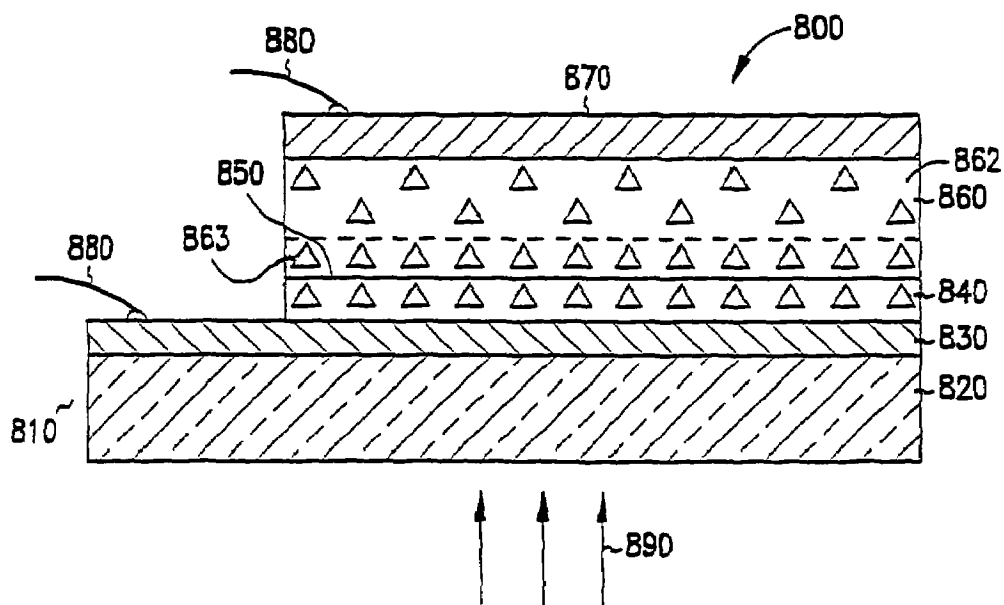


FIG. 8

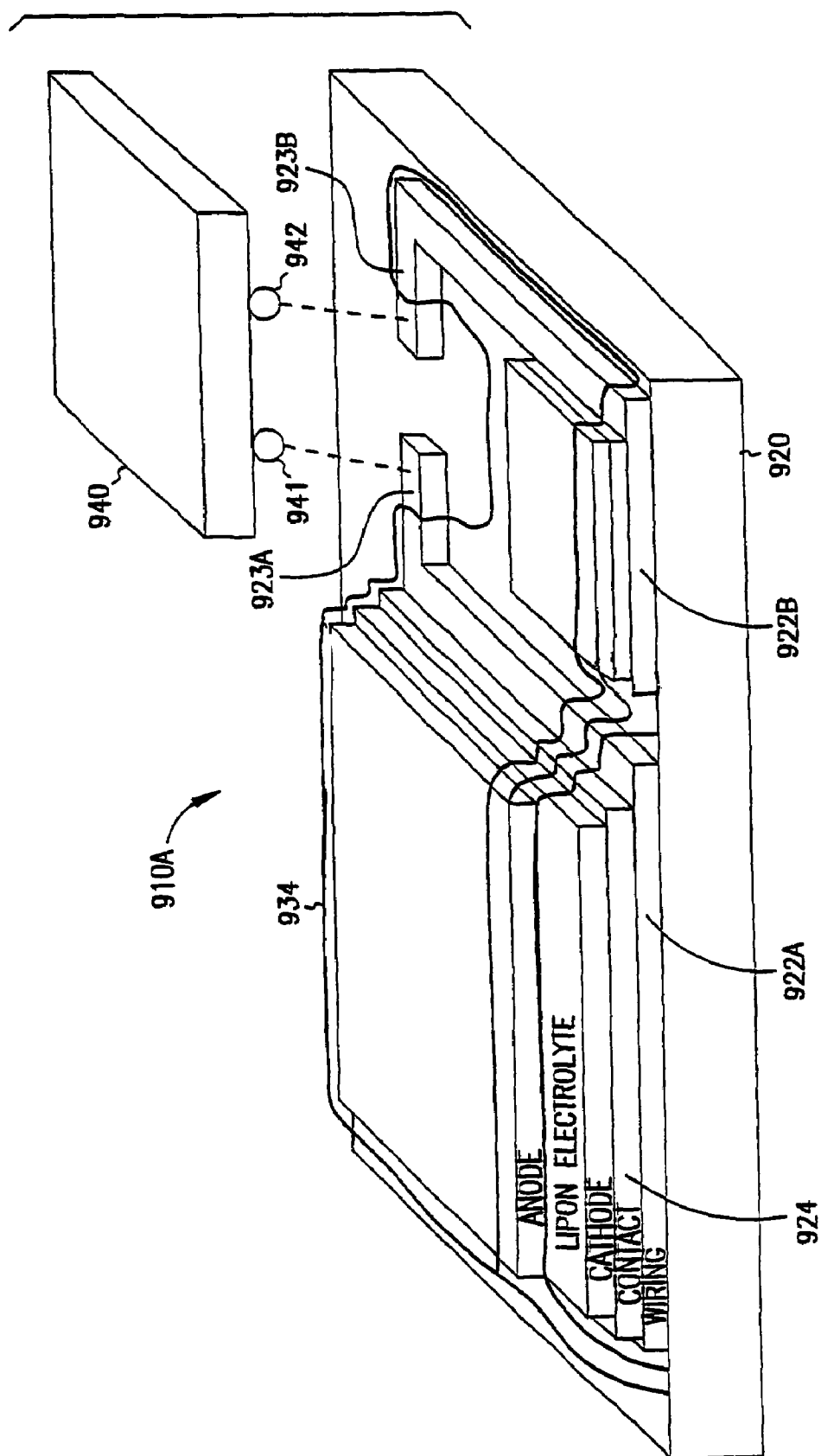


FIG. 9A

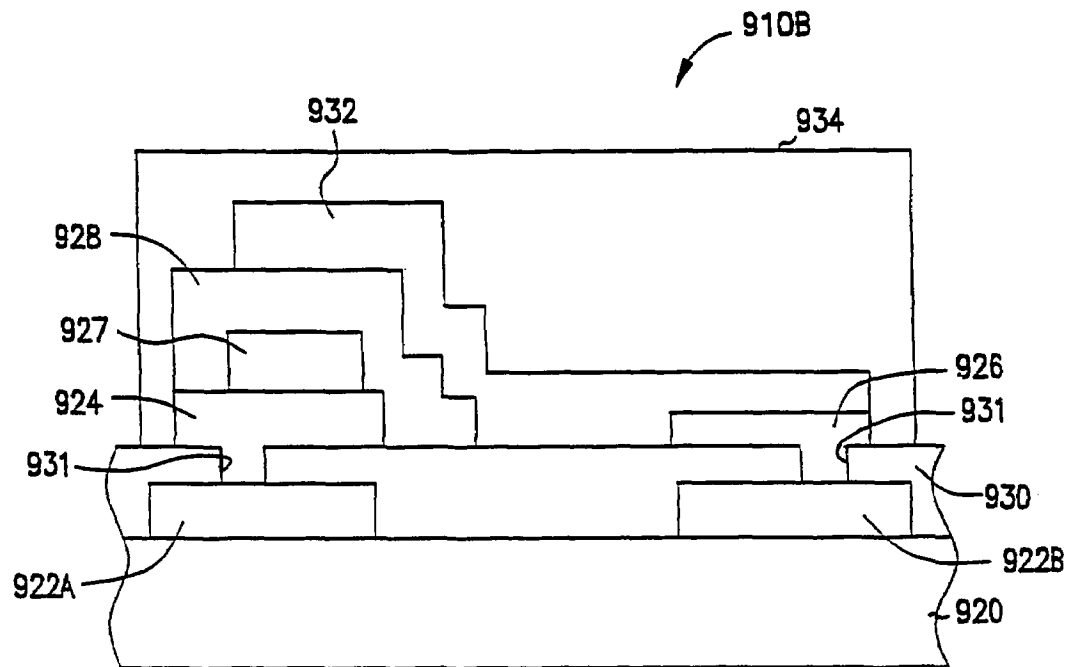


FIG. 9B

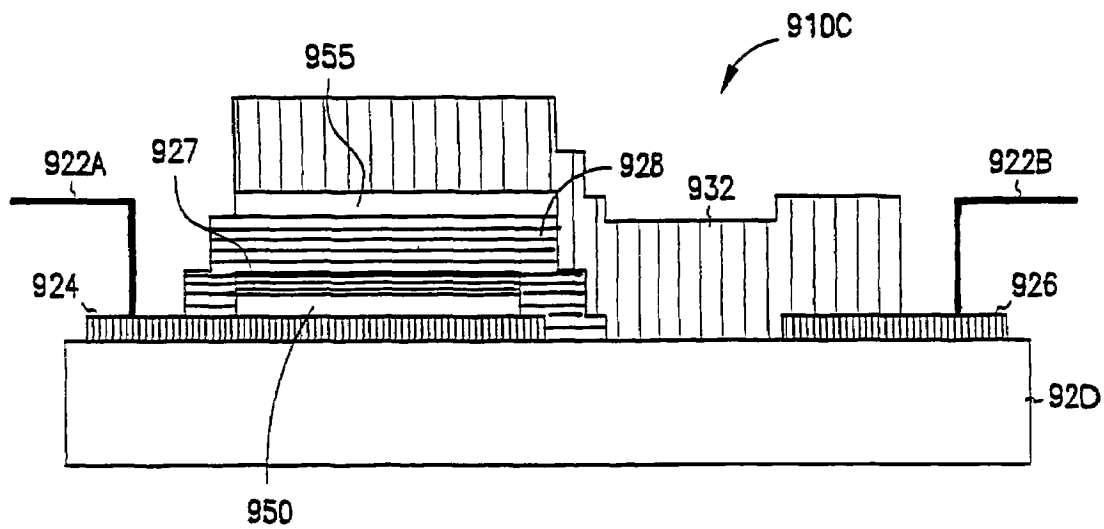


FIG. 9C

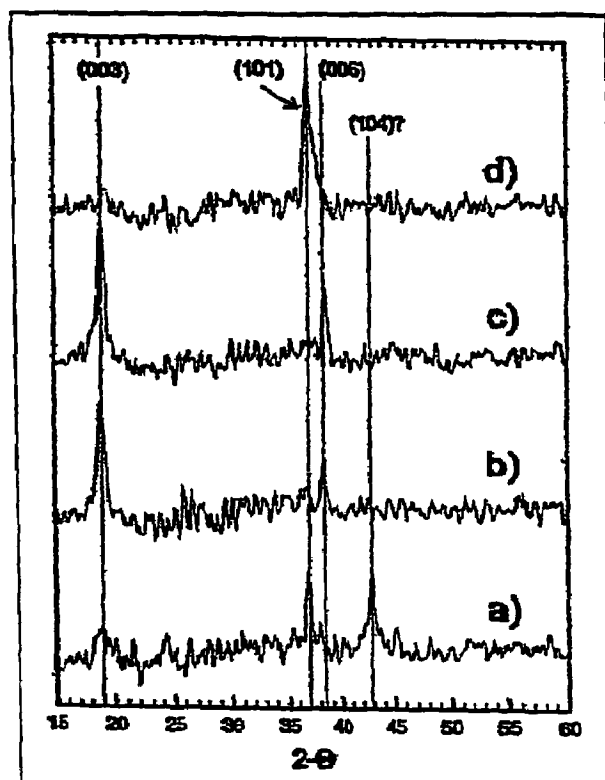


FIG. 10

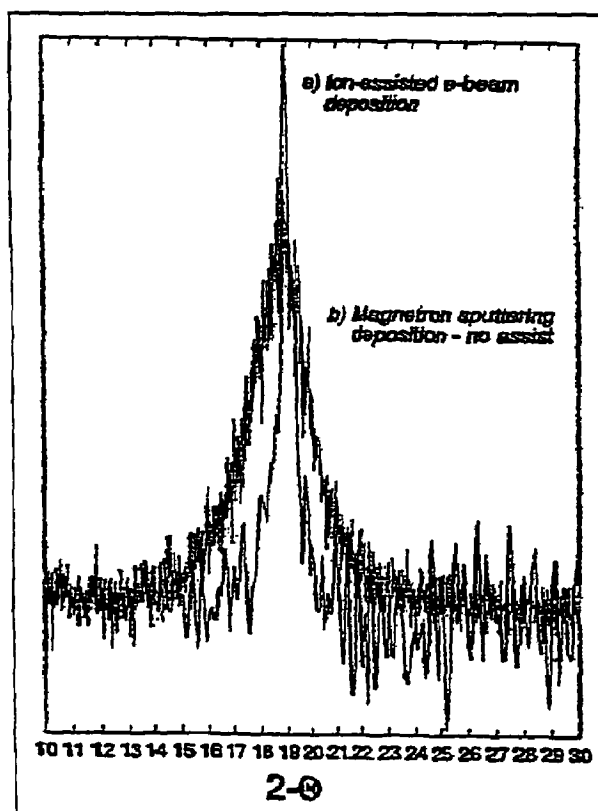


FIG. 11

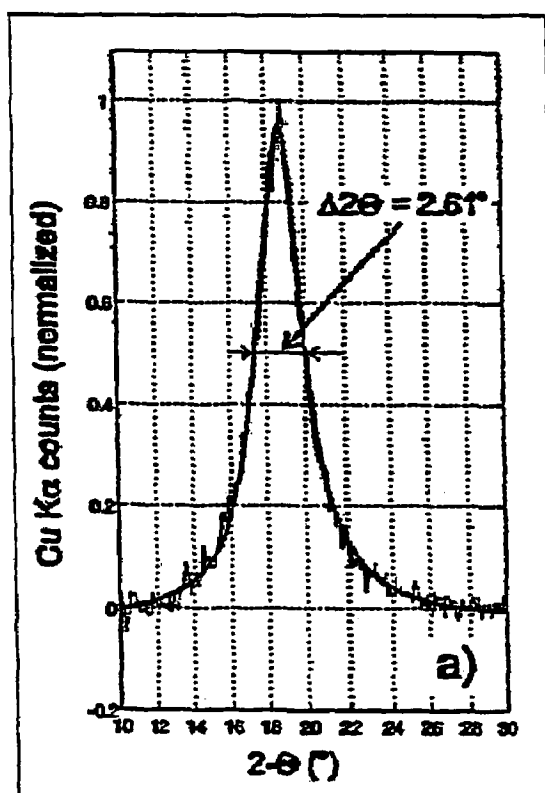


FIG. 12A

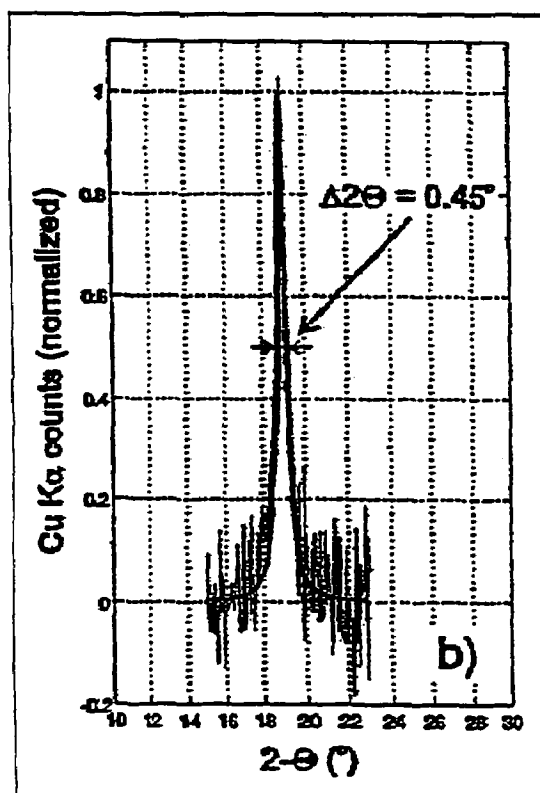


FIG. 12B

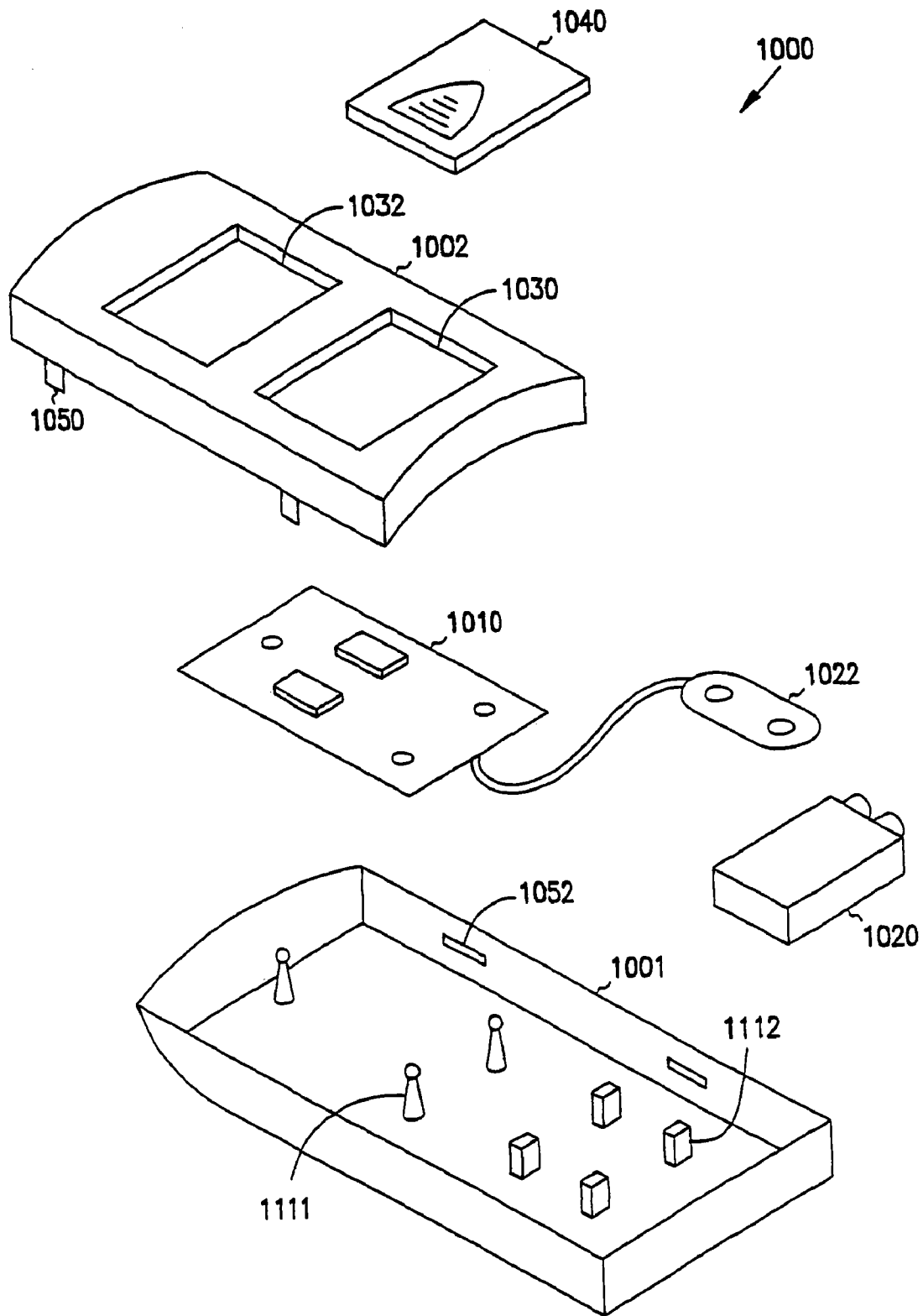


FIG. 13

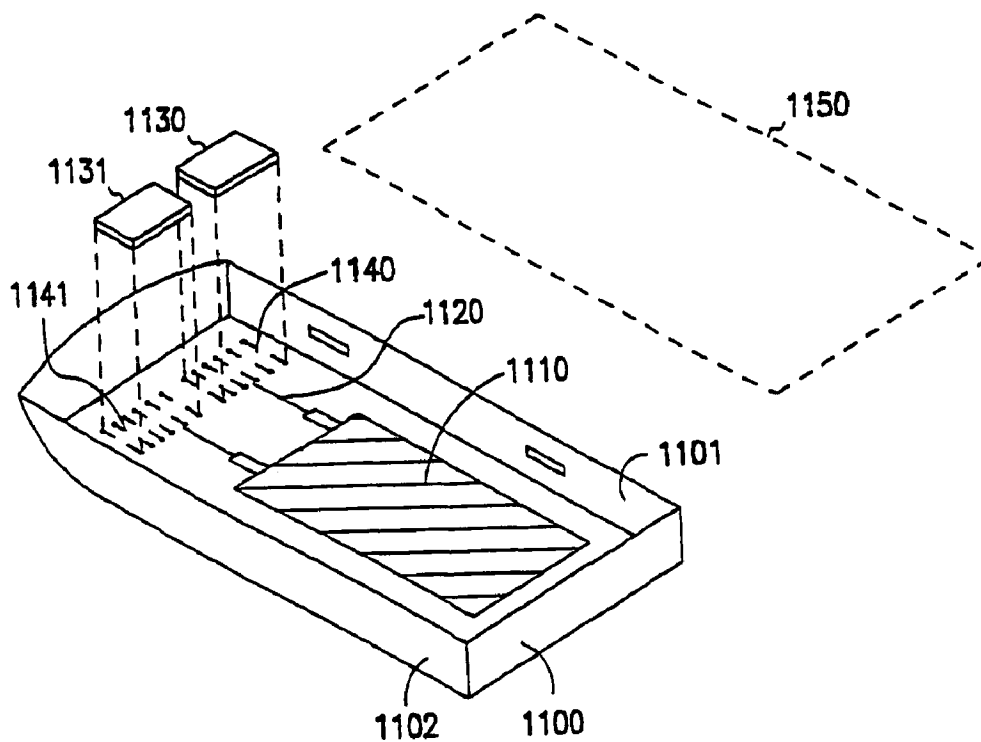


FIG. 14A

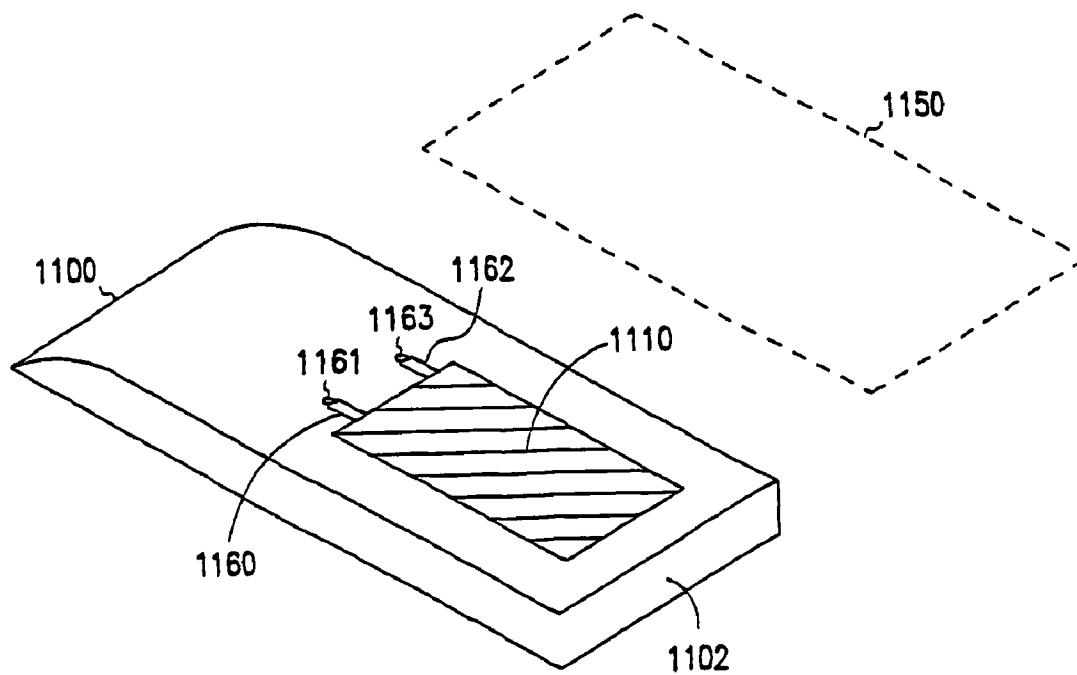


FIG. 14B

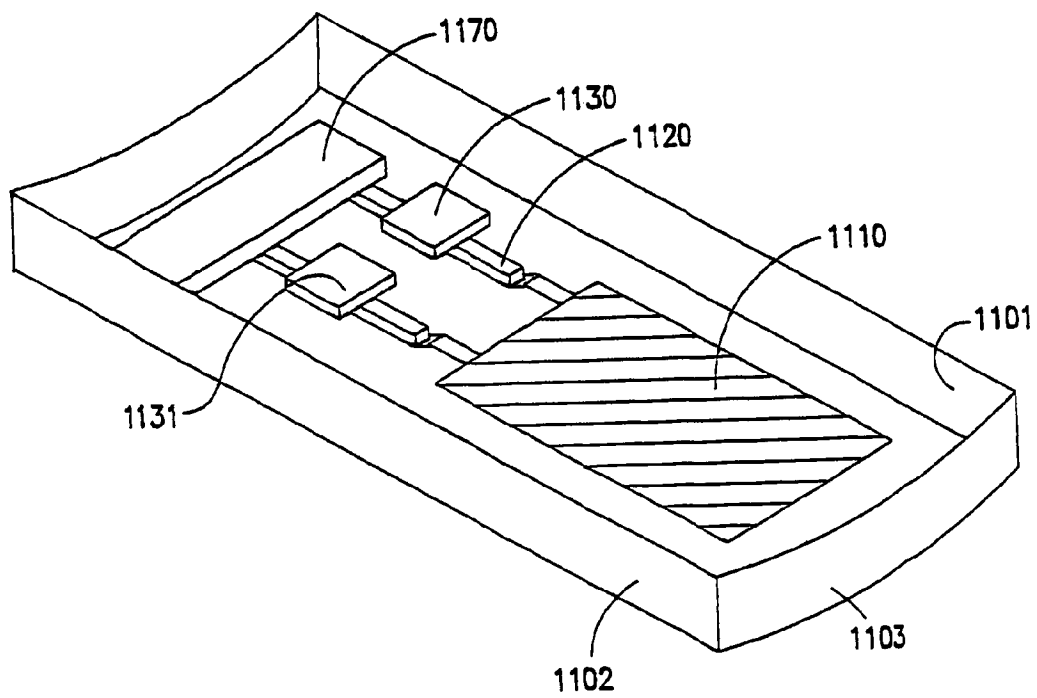
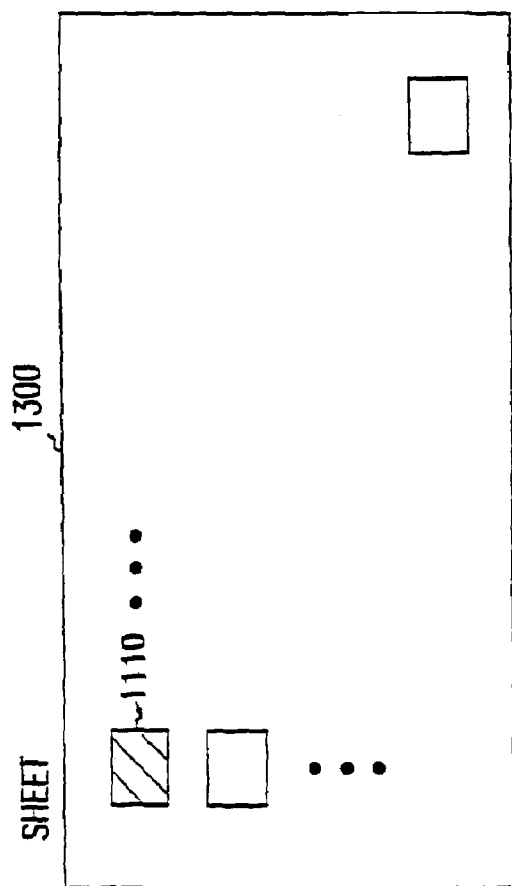
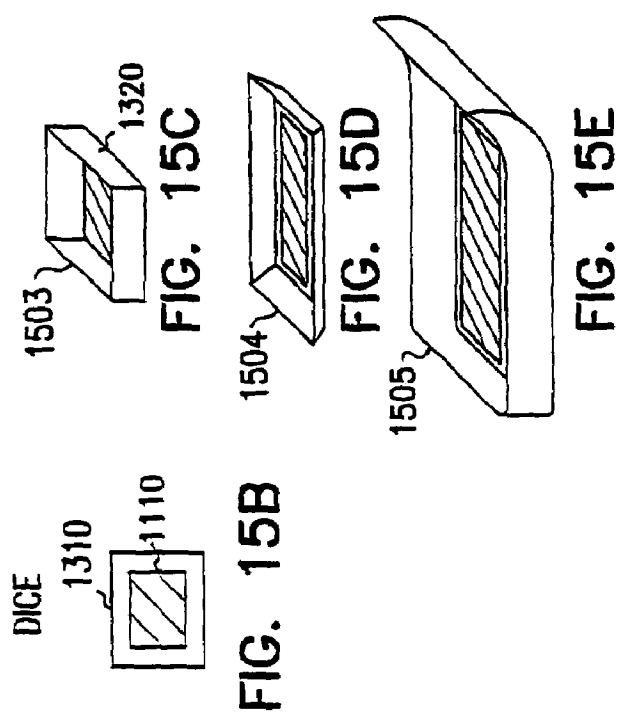


FIG. 14C



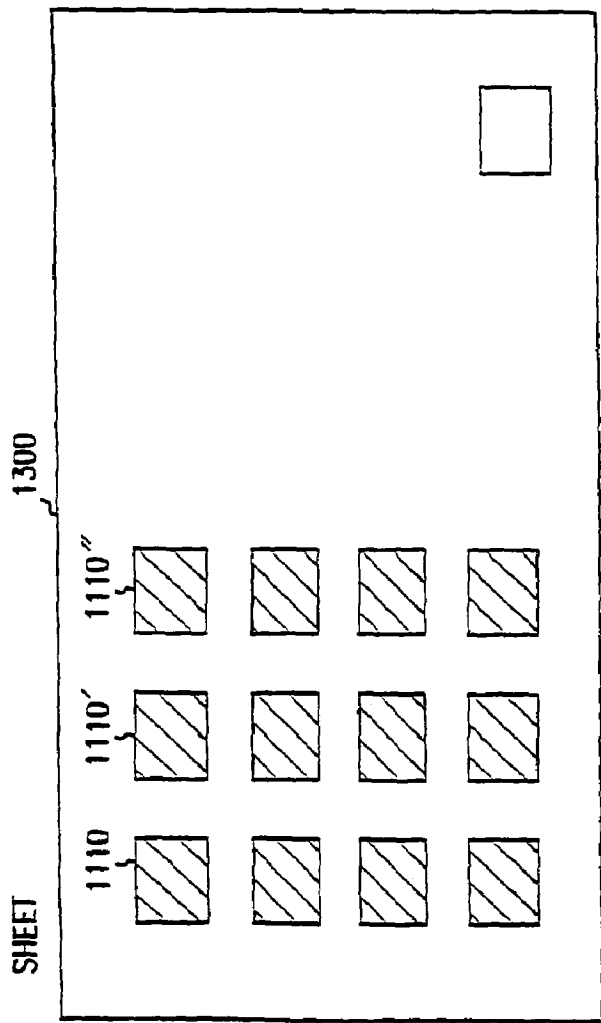


FIG. 15F

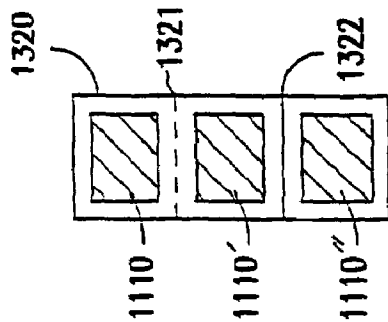


FIG. 15G

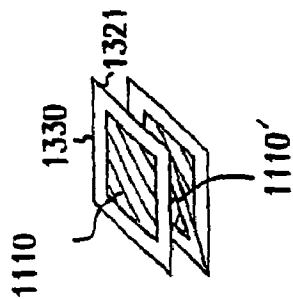


FIG. 15H

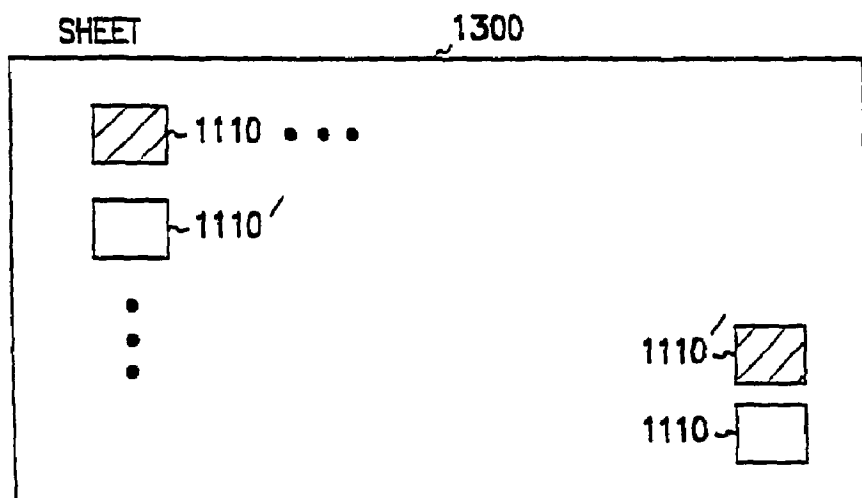


FIG. 15I

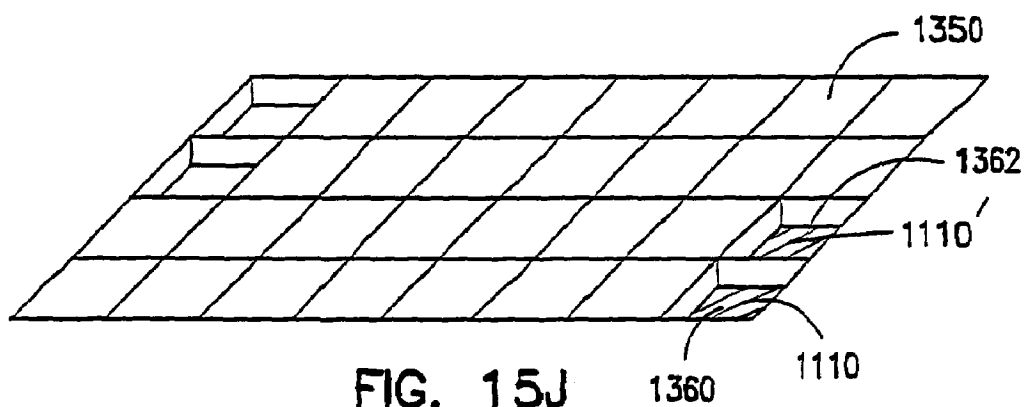


FIG. 15J

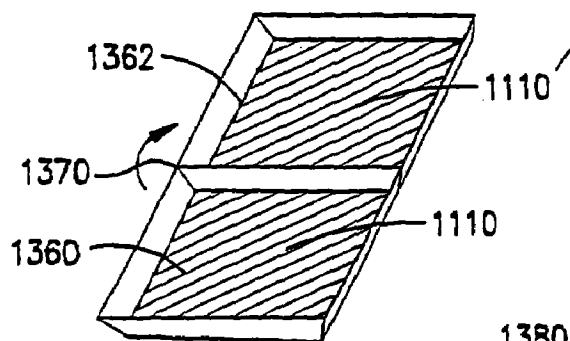


FIG. 15K

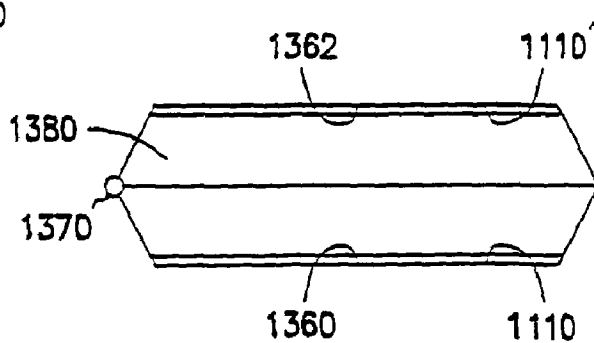
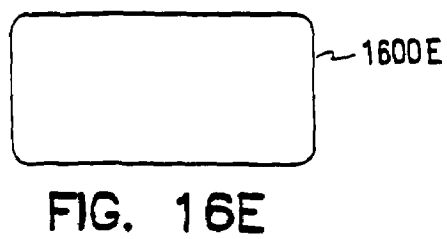
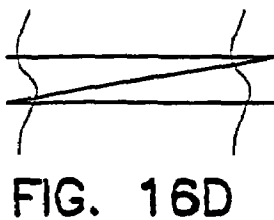
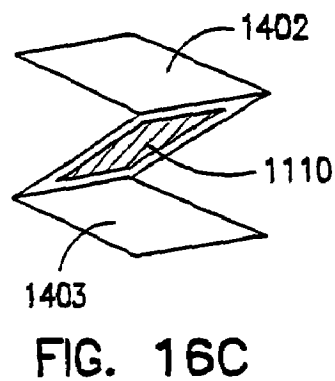
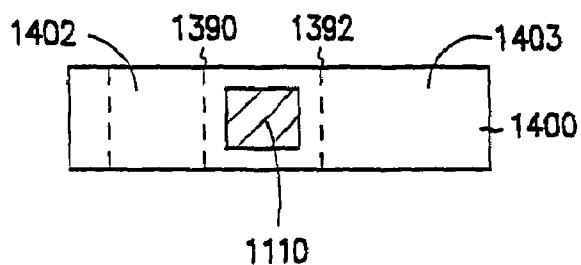
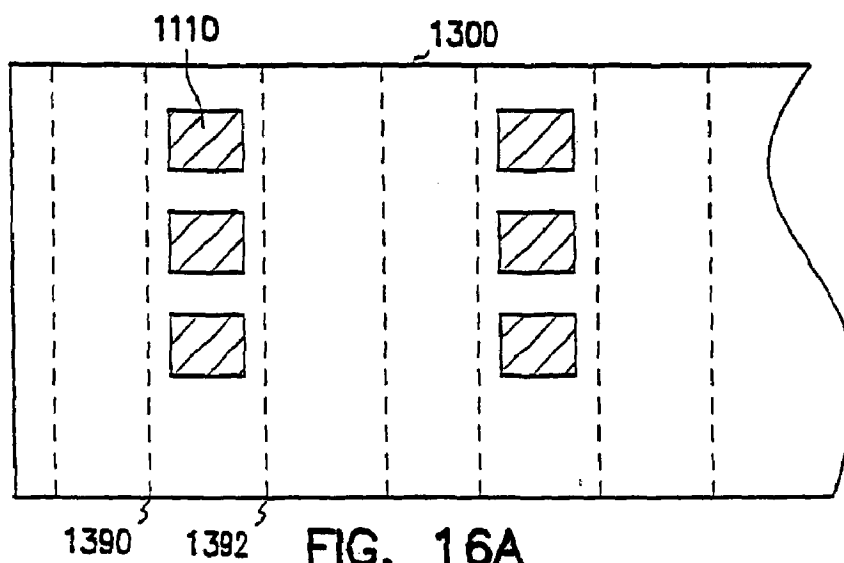


FIG. 15L



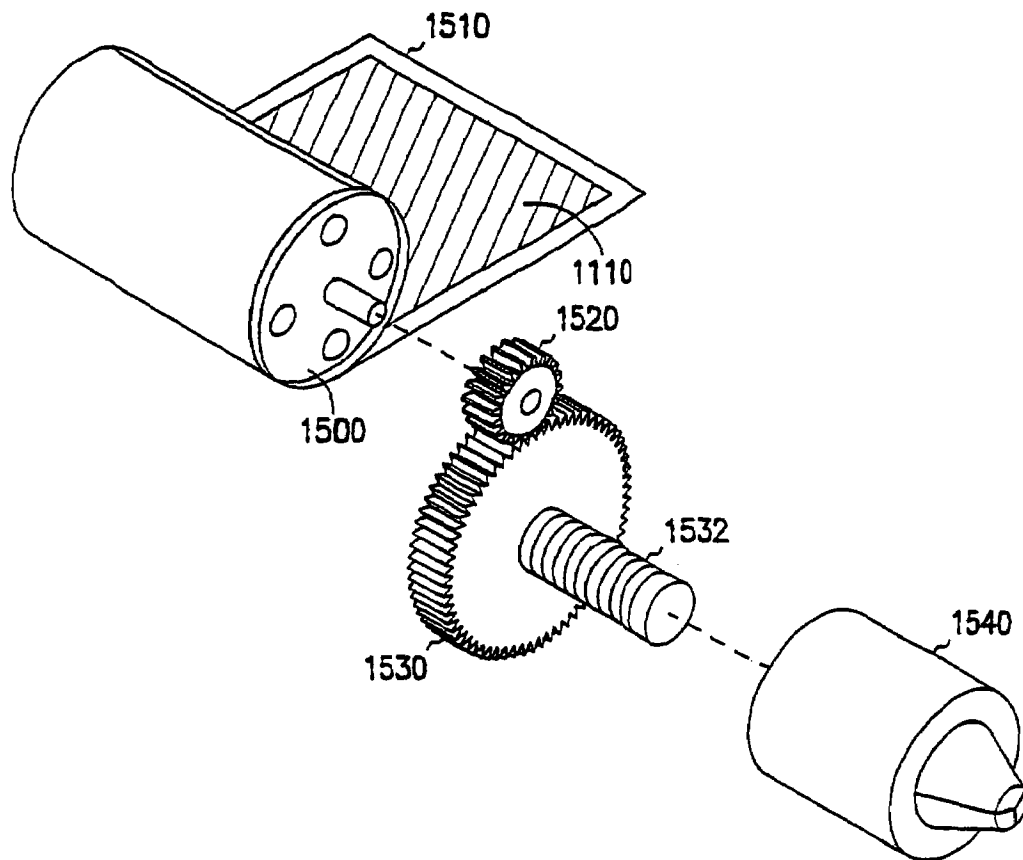


FIG. 17

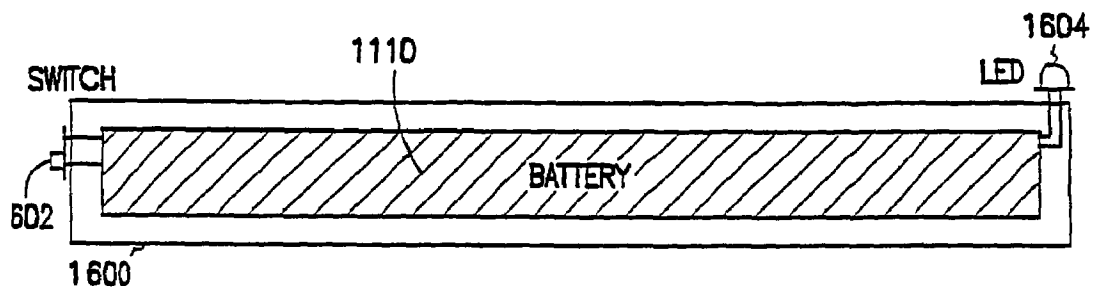


FIG. 18A

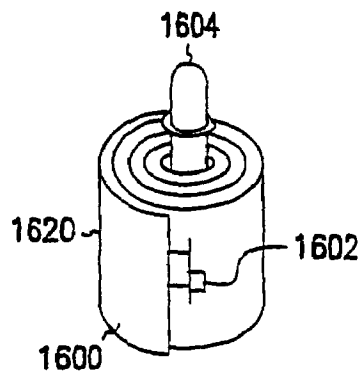


FIG. 18B

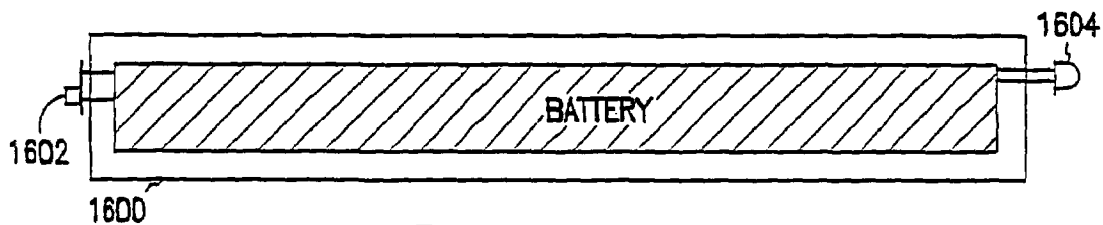


FIG. 18C

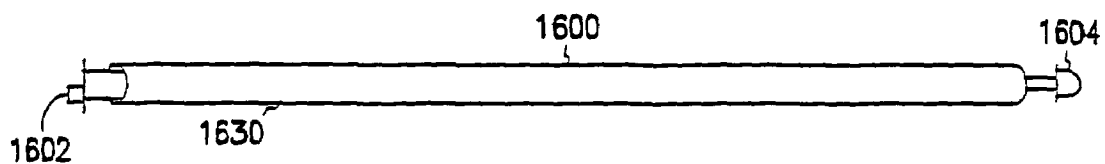


FIG. 18D

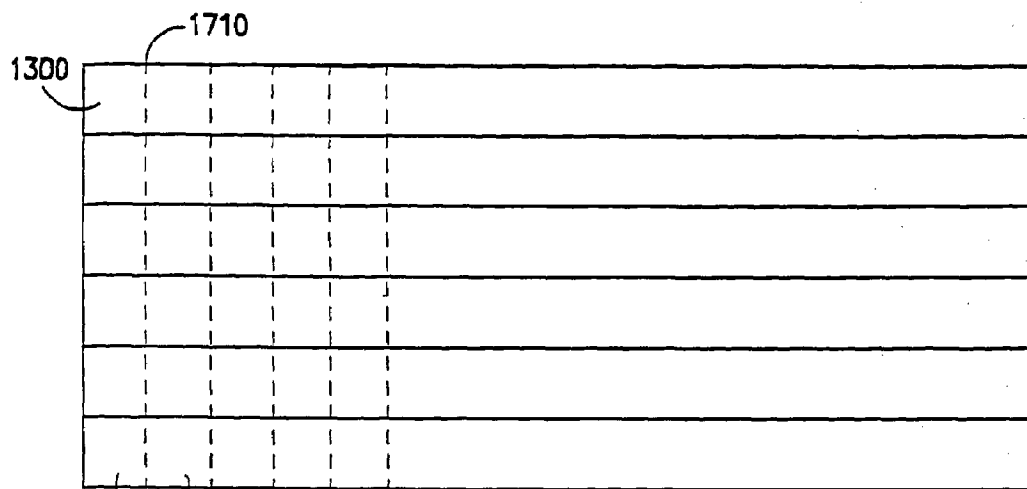


FIG. 19A

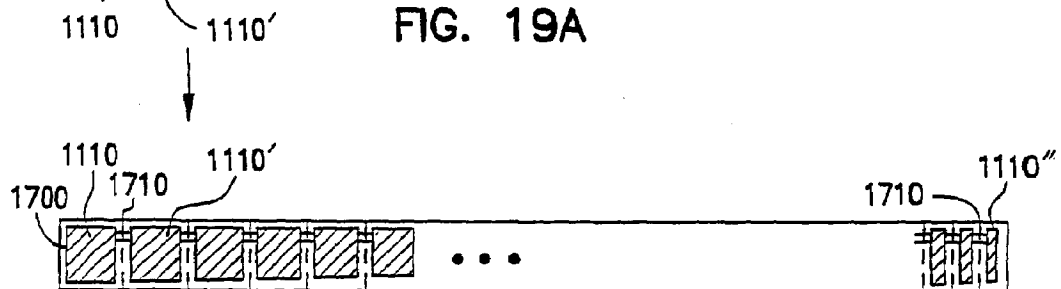


FIG. 19B

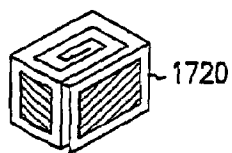


FIG. 19C

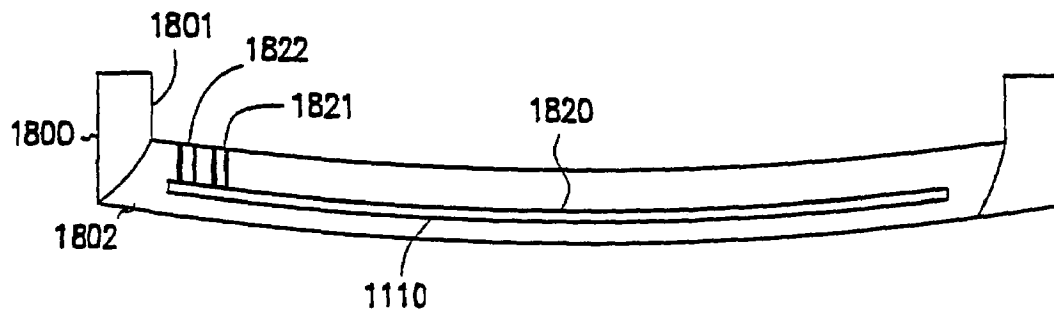


FIG. 20

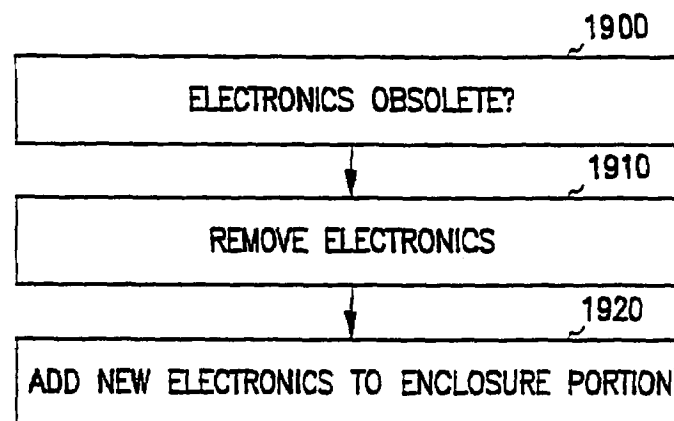


FIG. 21A

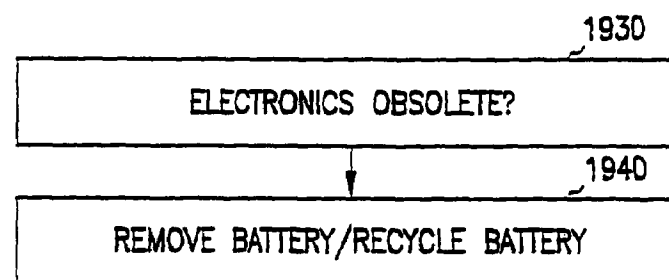


FIG. 21B

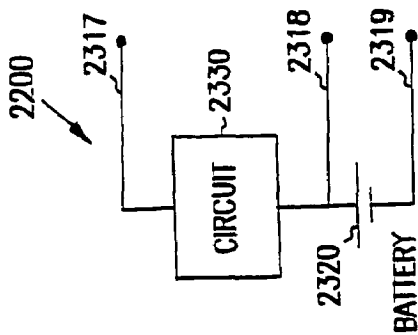


FIG. 22A

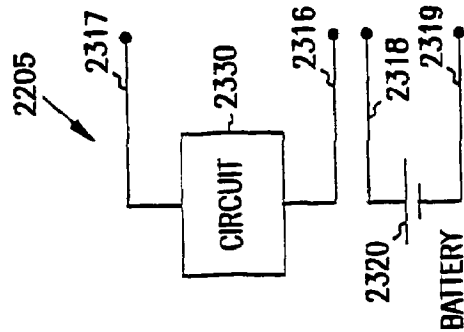


FIG. 22D

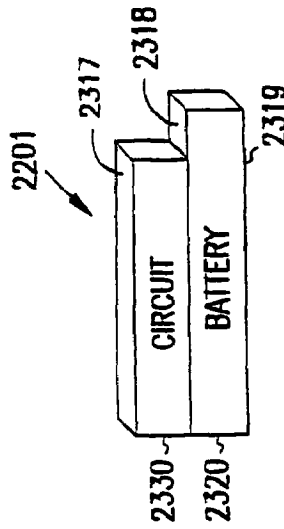


FIG. 22B

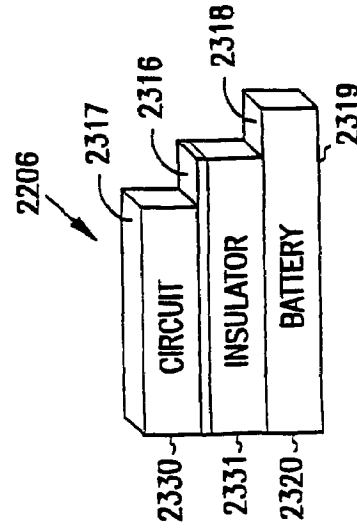


FIG. 22E

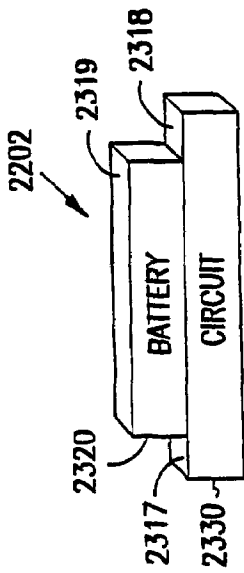


FIG. 22C

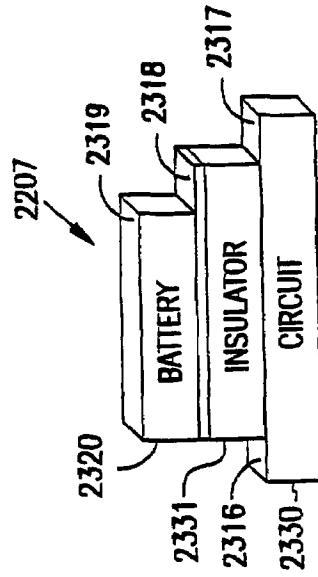


FIG. 22F

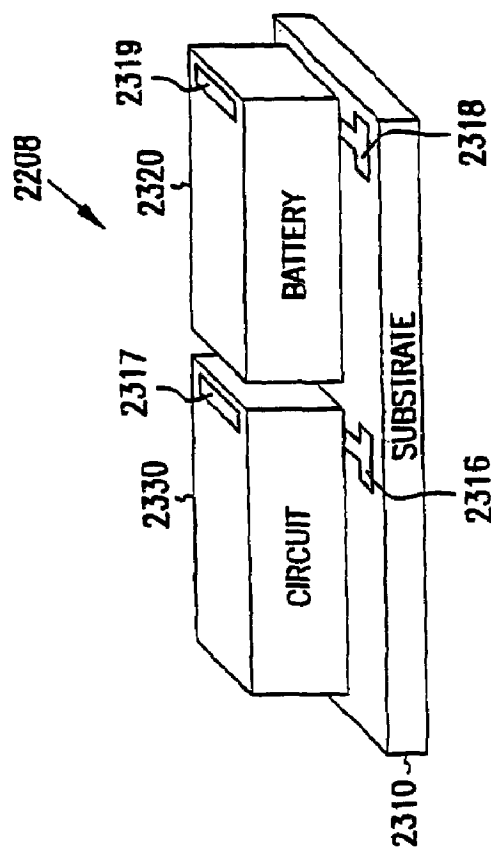


FIG. 22H

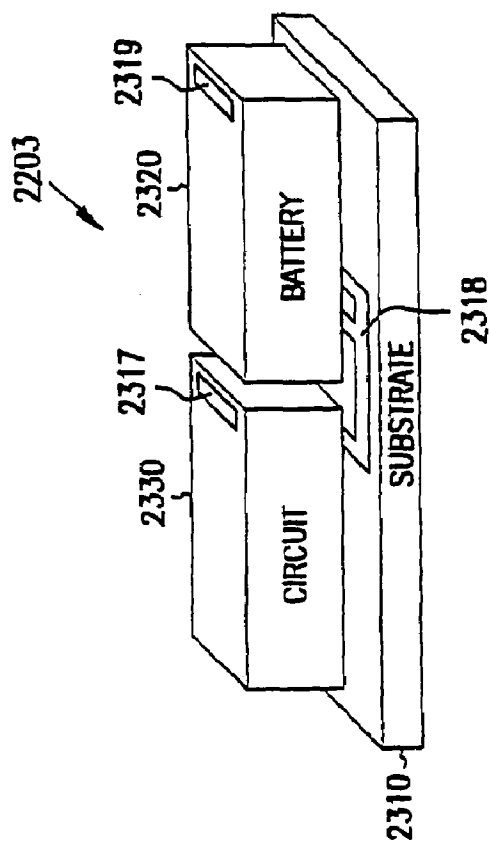


FIG. 22G

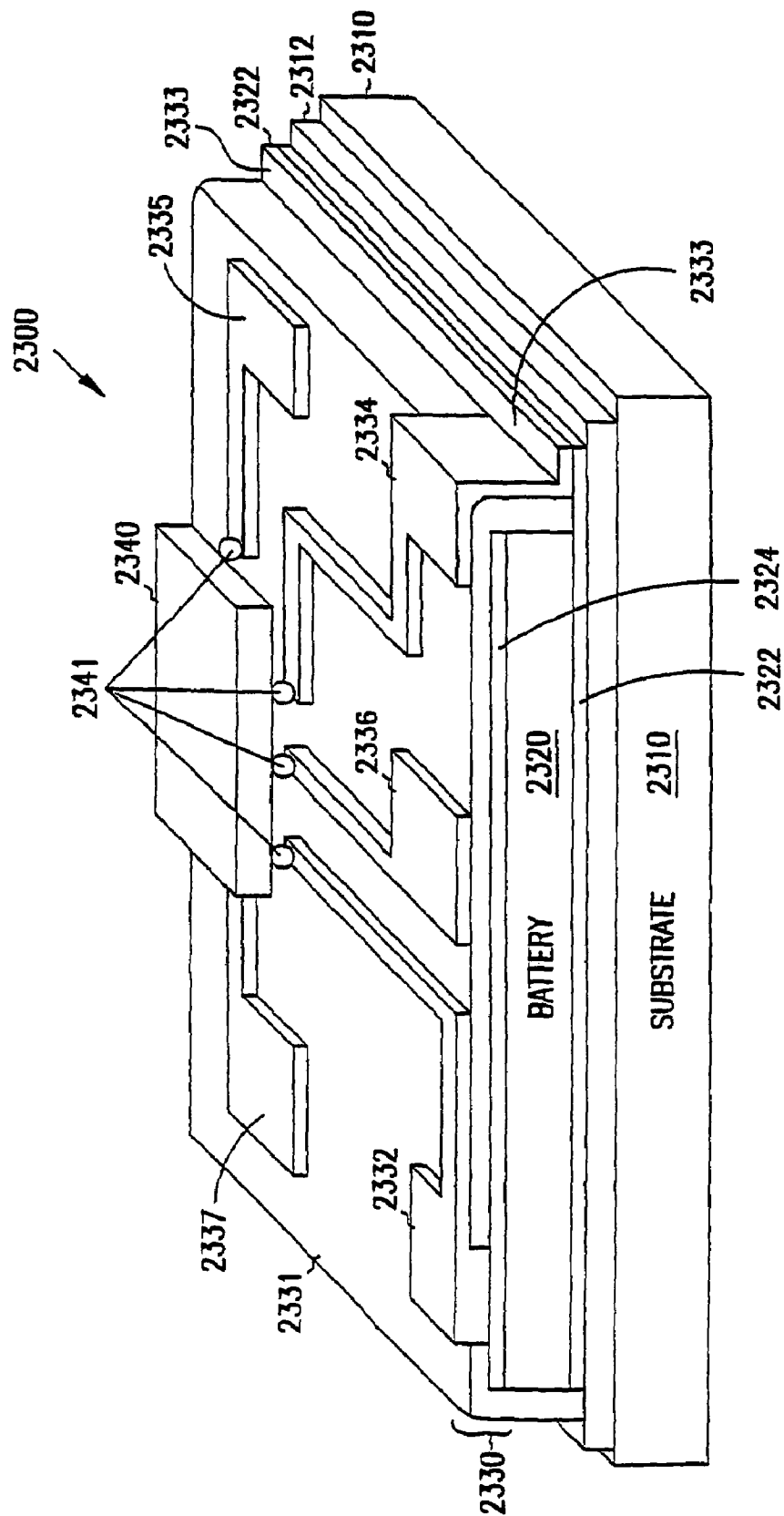


FIG. 23

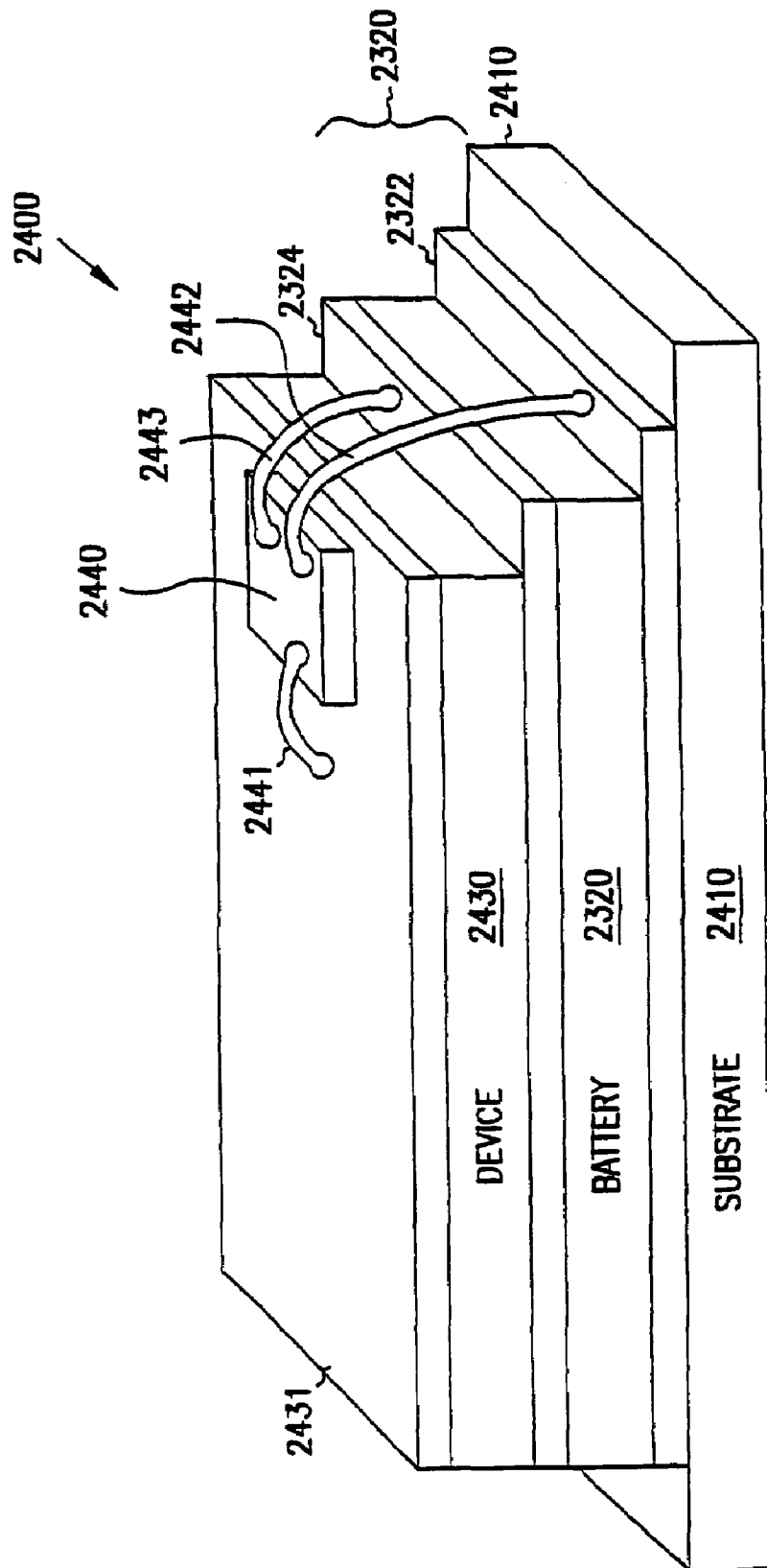


FIG. 24A

SOLID STATE
LITHIUM BATTERY
DEPOSITION

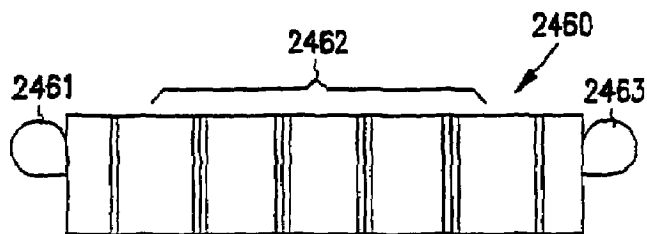


FIG. 24B

ENERGY STORAGE
MATERIAL DEPOSITED
ON TOP OF SHEET
USING SHADOW
MASKS

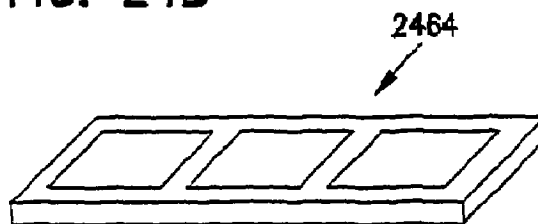


FIG. 24C

DIRECT ENERGY
CONVERSION MATERIAL
DEPOSITION

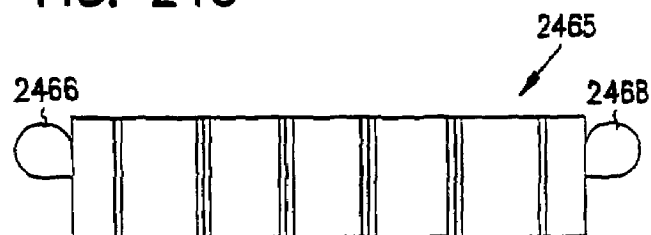


FIG. 24D

DIRECT ENERGY
CONVERSION MATERIAL
DEPOSITED ON TOP
OF BATTERY USING
SHADOW MASKS

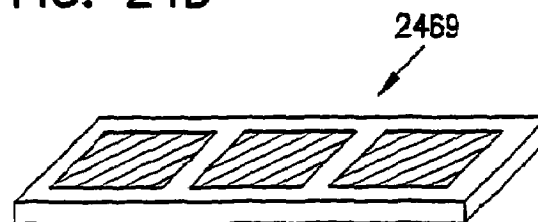


FIG. 24E

FABRIC CUT
INTO DESIRED
UNIT SIZE

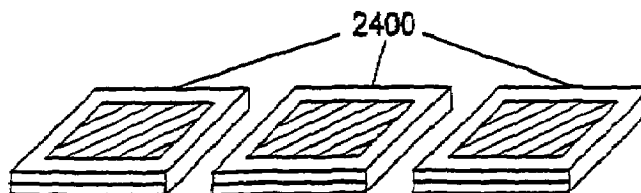


FIG. 24F

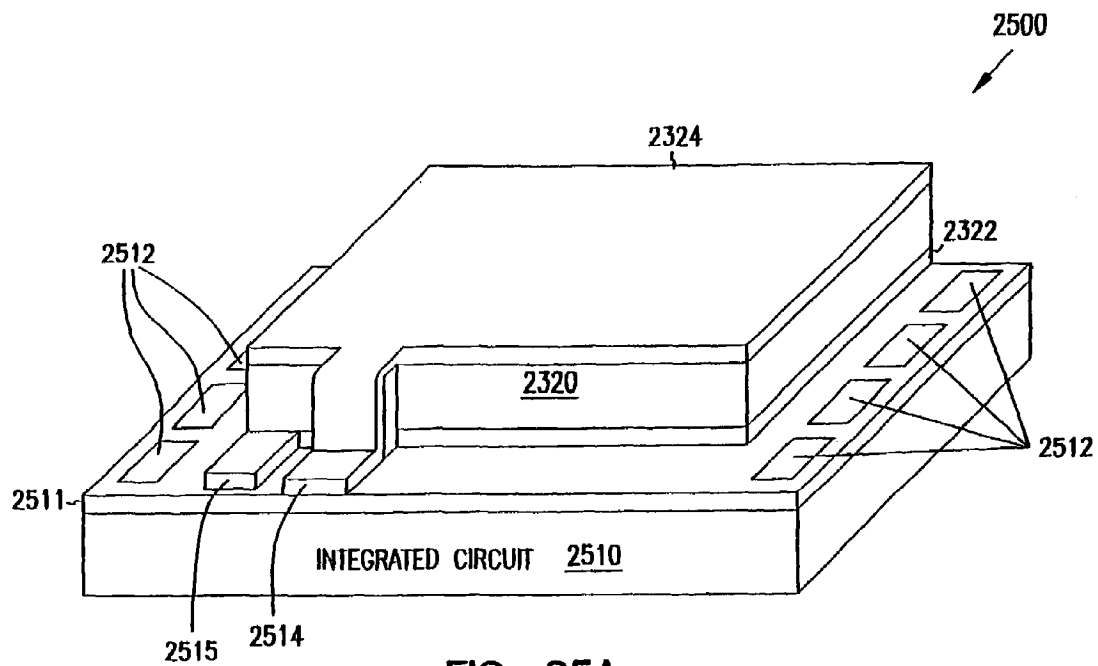


FIG. 25A

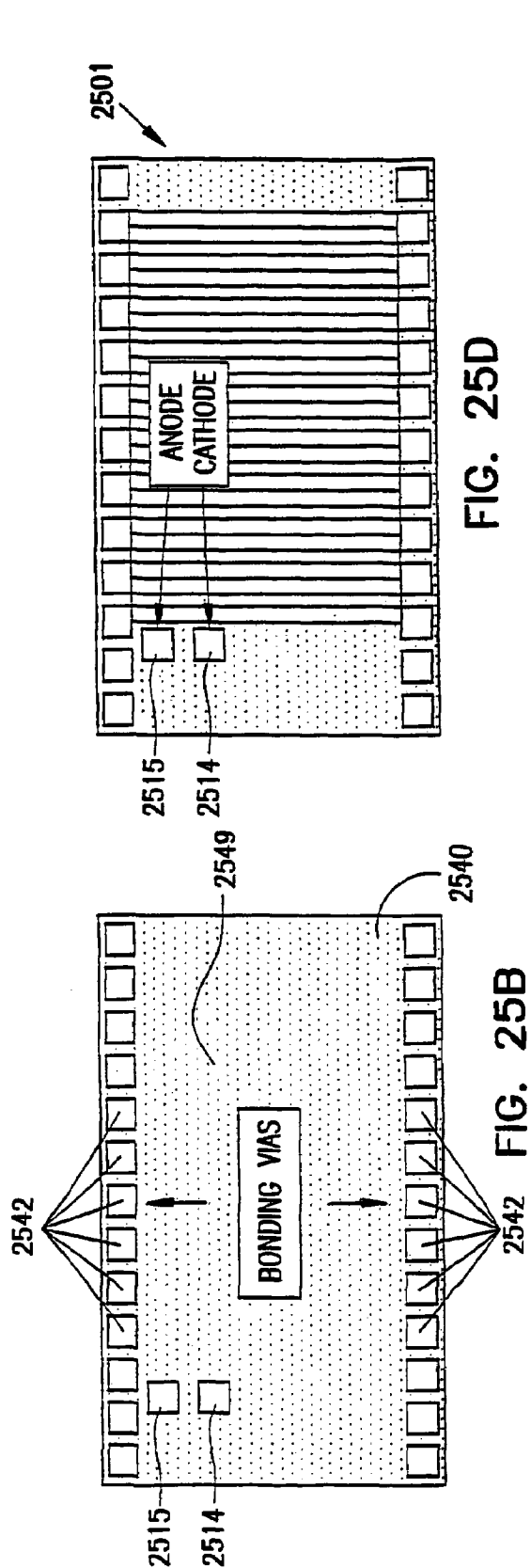


FIG. 25D

FIG. 25B

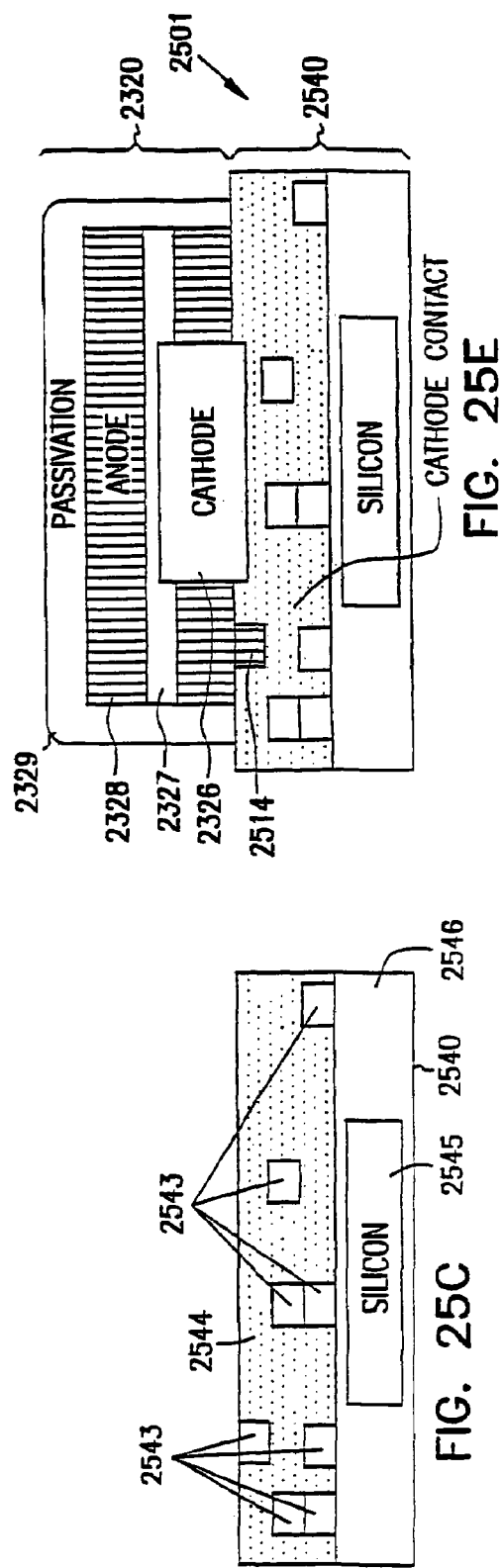


FIG. 25E

FIG. 25C

DIRECT ENERGY
MATERIAL DEPOSITION

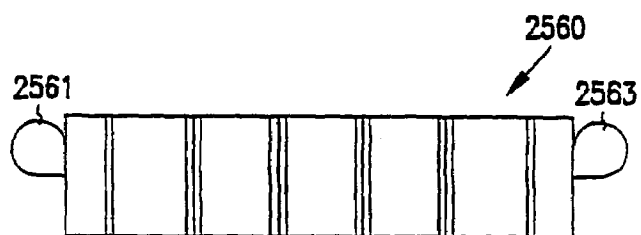


FIG. 25F

DIRECT ENERGY
MATERIAL DEPOSITED
ON TOP OF SHEET

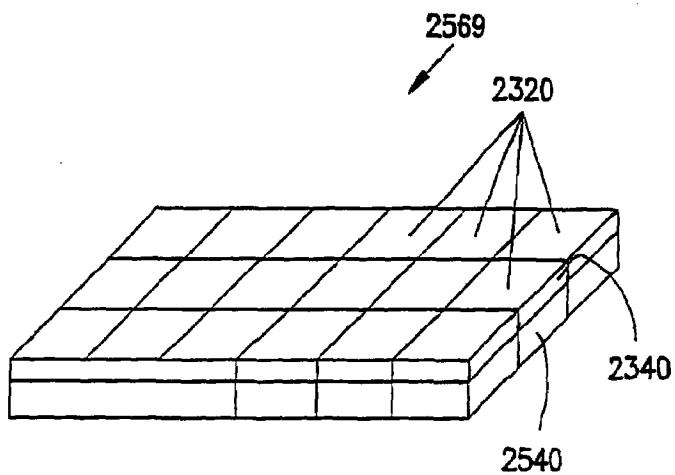


FIG. 25G

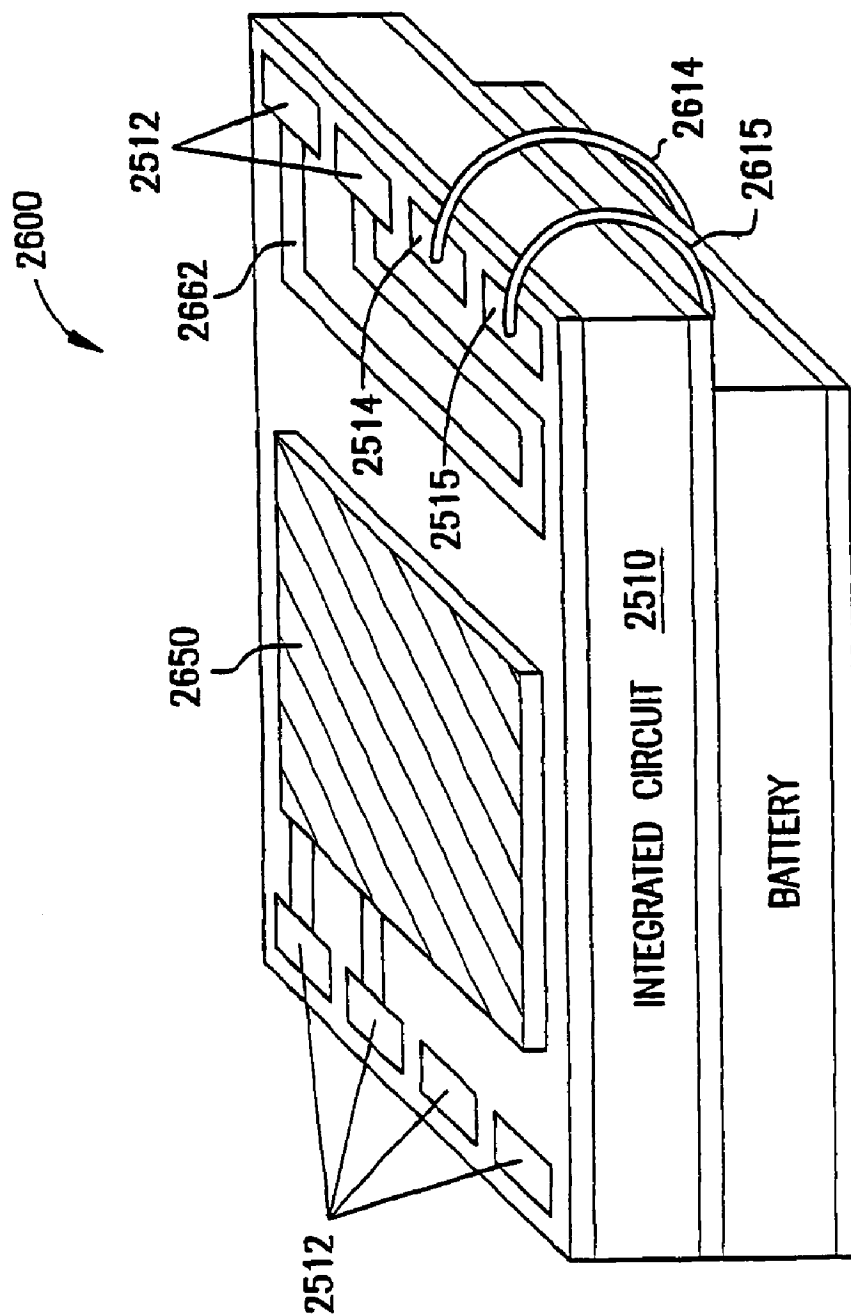


FIG. 26A

SOLID STATE
LITHIUM BATTERY
DEPOSITION

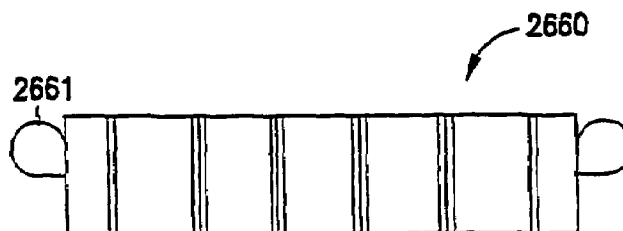


FIG. 26B

ENERGY STORAGE
MATERIAL DEPOSITED
ON BACK OF SHEET

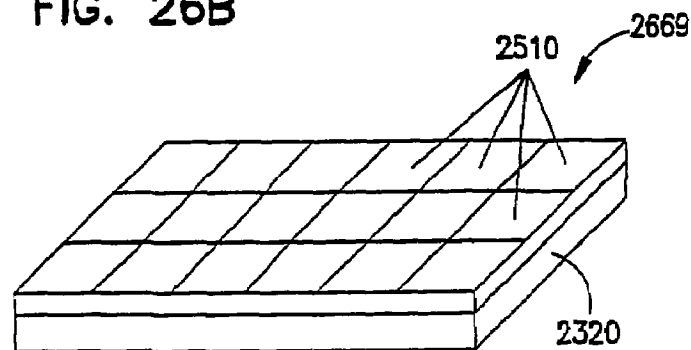


FIG. 26C

FABRIC CUT
INTO DESIRED
UNIT SIZE

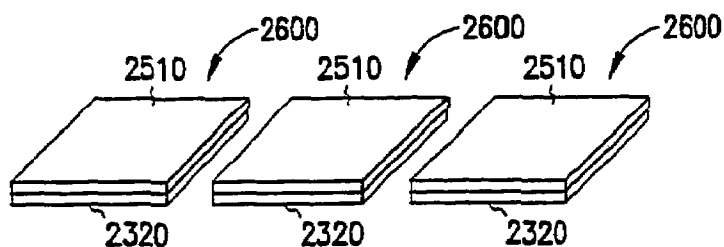


FIG. 26D

ENERGY CONVERSION
MATERIAL WIRED
TO ENERGY
STORAGE MATERIAL

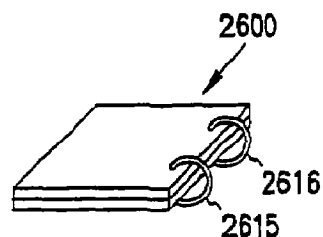


FIG. 26E

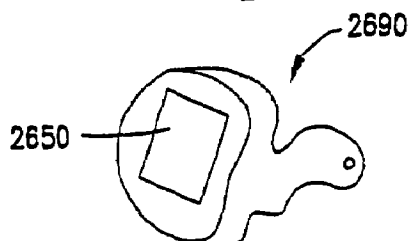


FIG. 26F

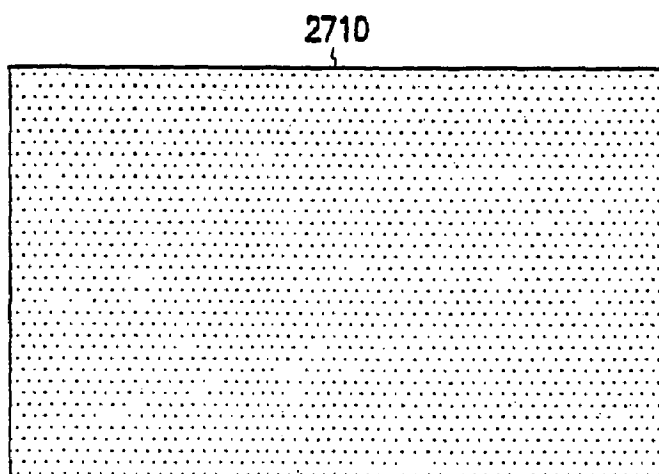


FIG. 27A



FIG. 27F

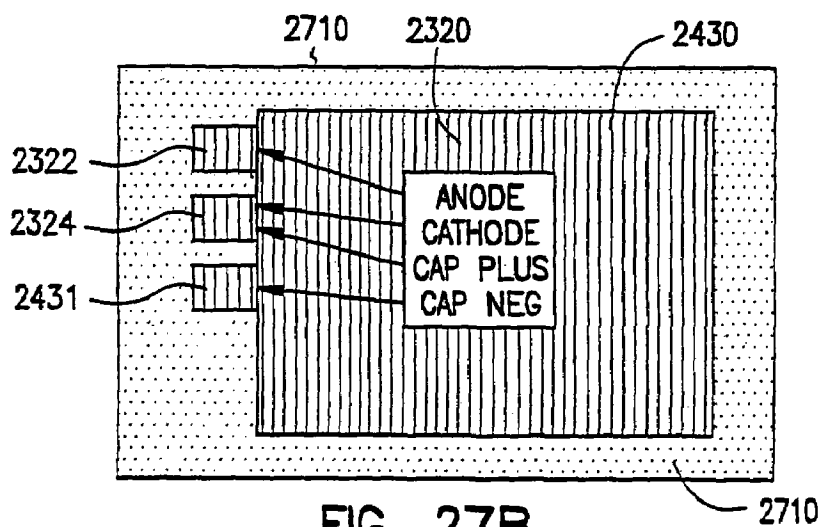


FIG. 27B

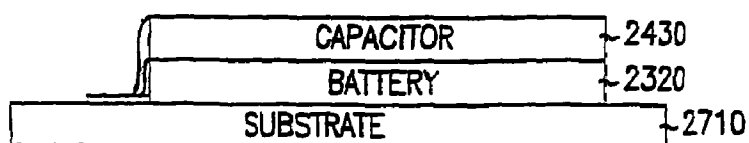
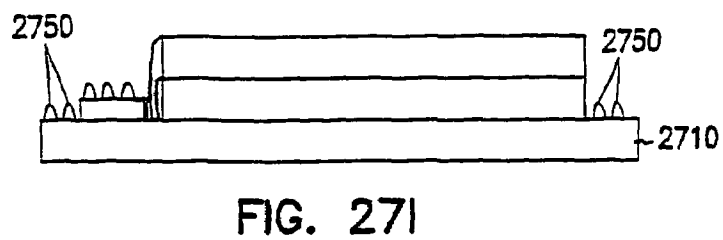
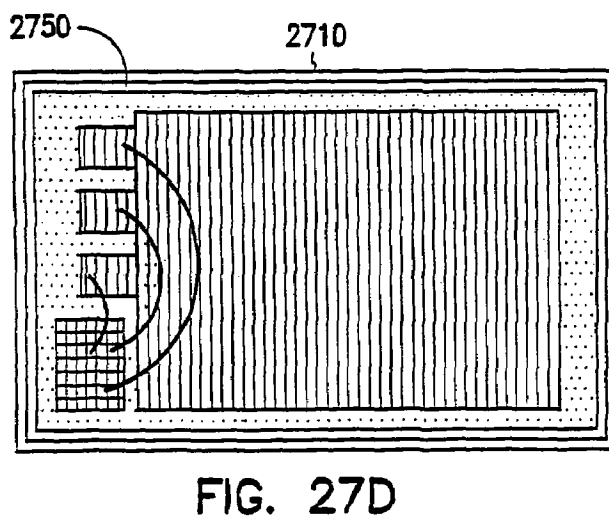
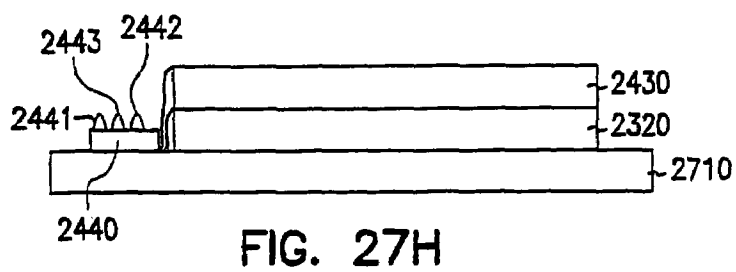
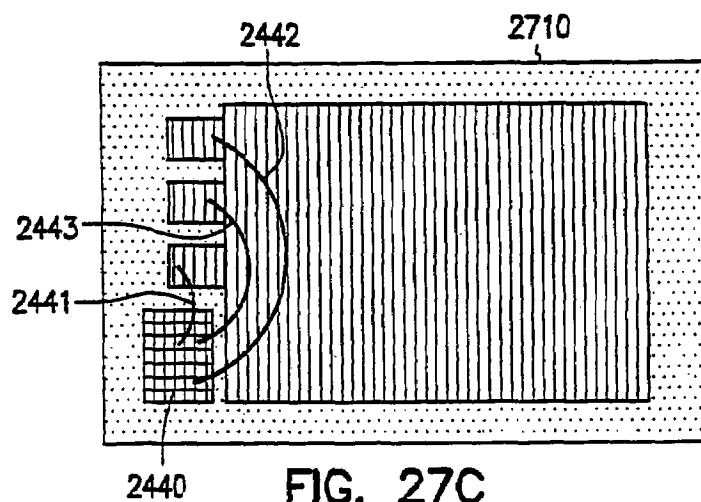
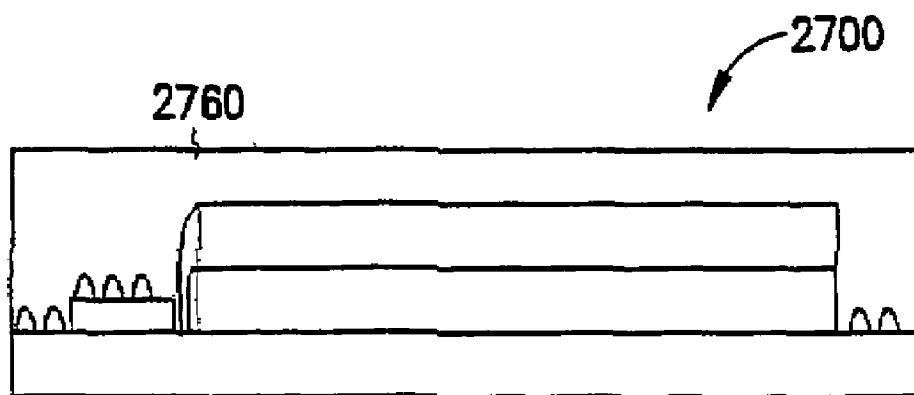
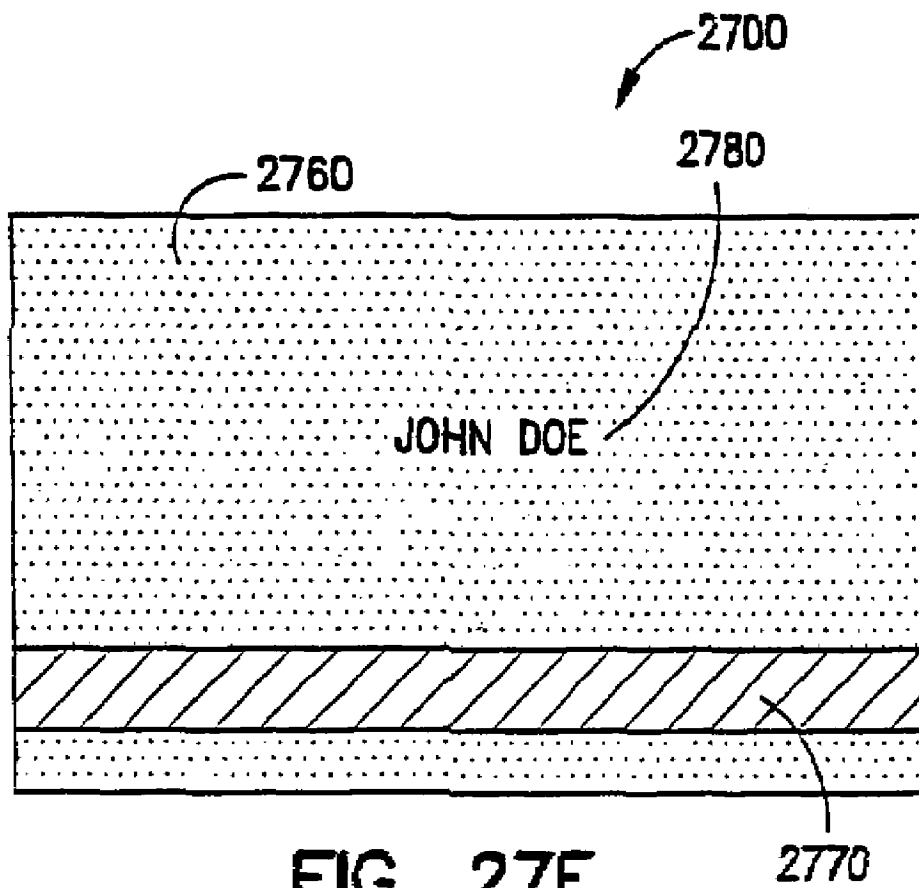


FIG. 27G





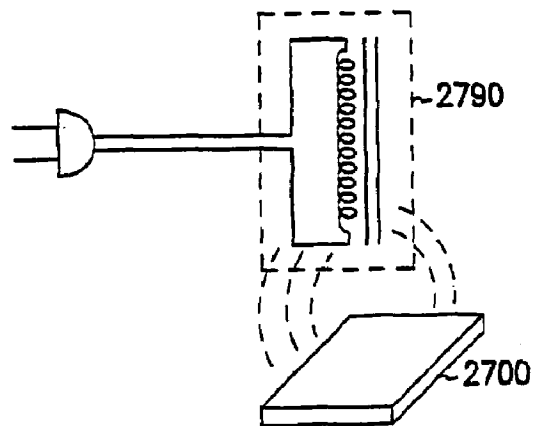


FIG. 27K

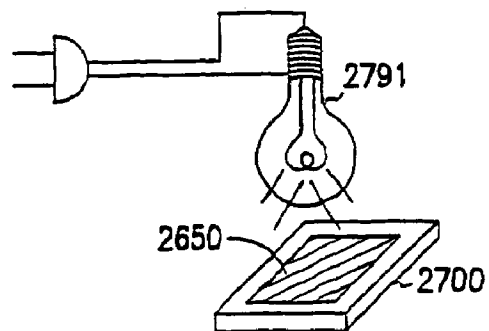


FIG. 27L

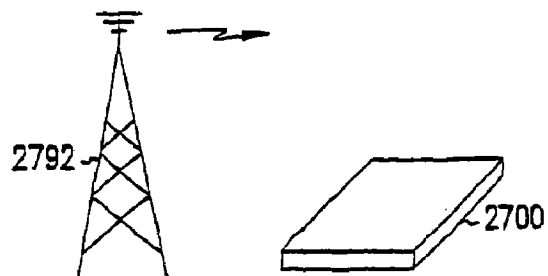


FIG. 27M

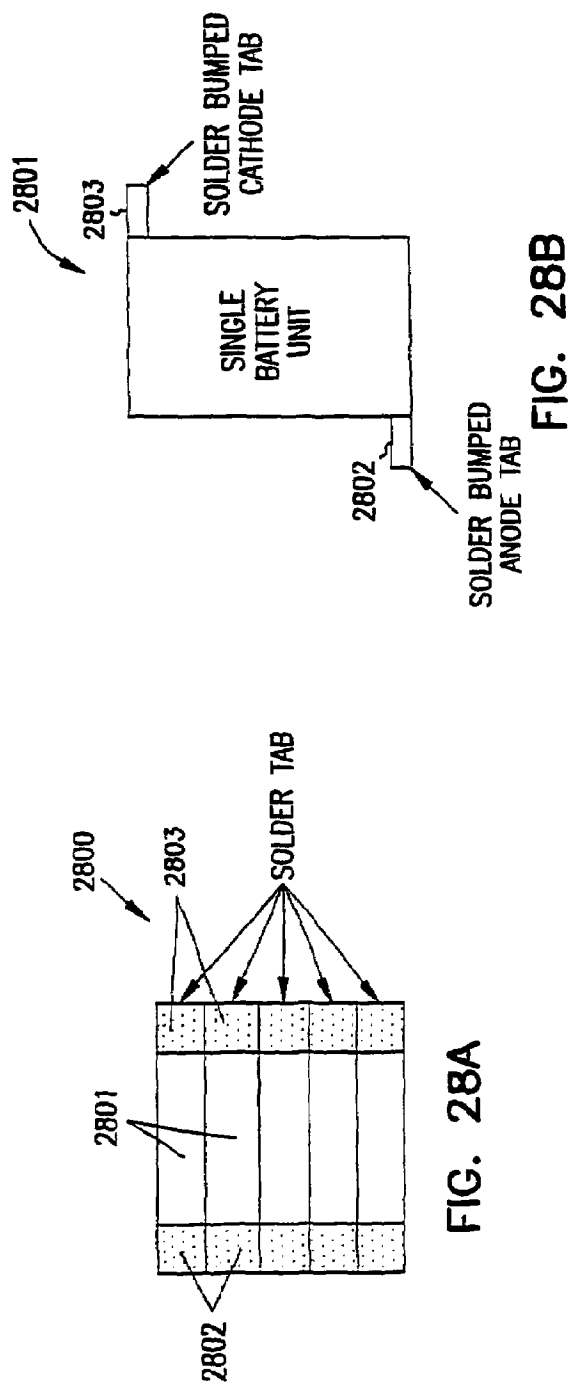


FIG. 28B

FIG. 28A

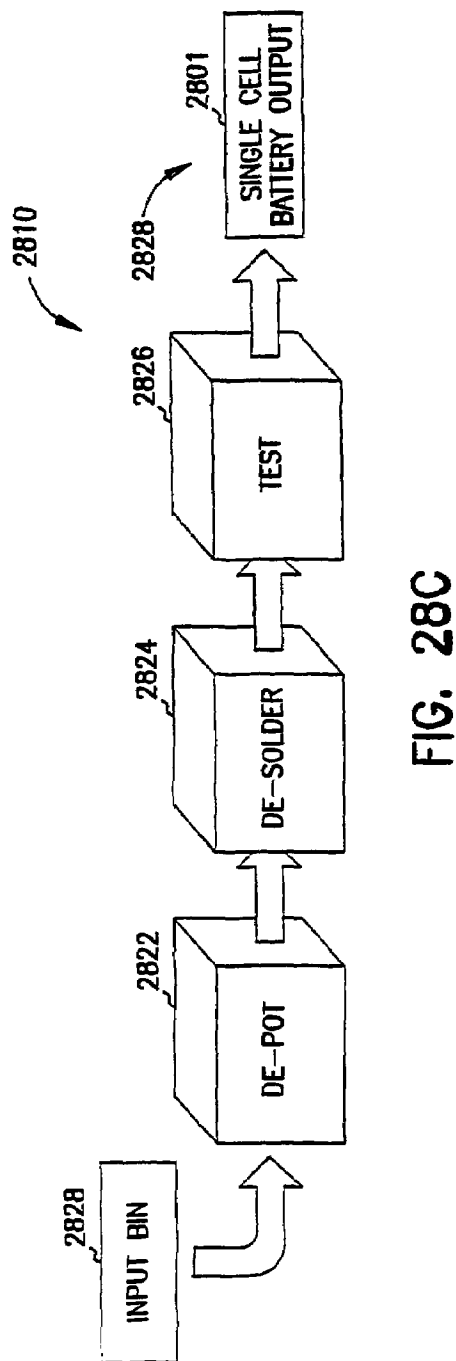
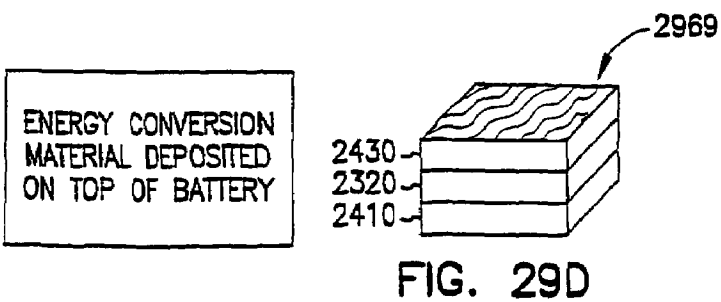
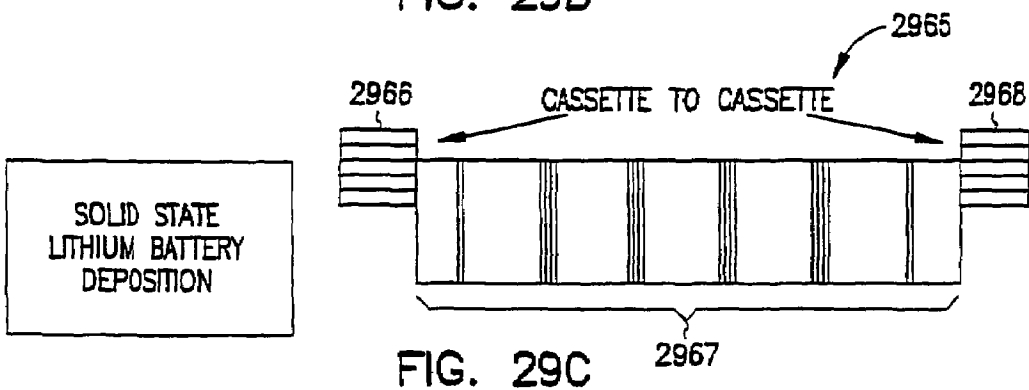
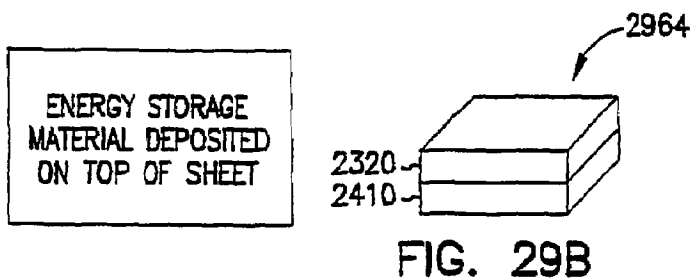
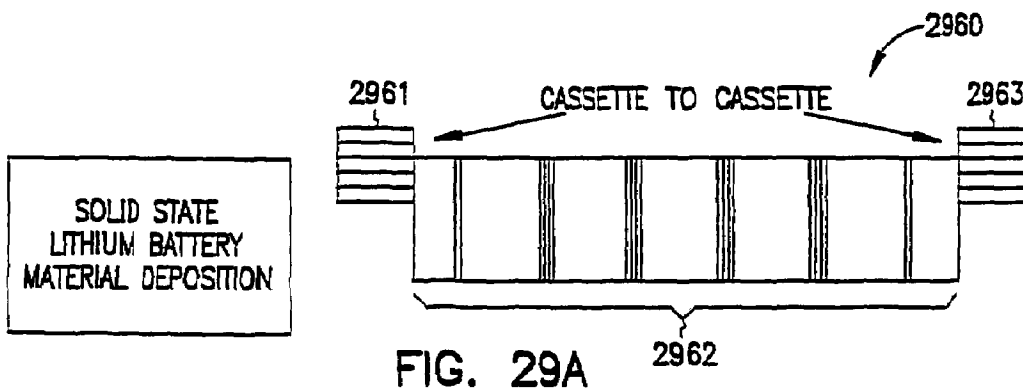


FIG. 28C



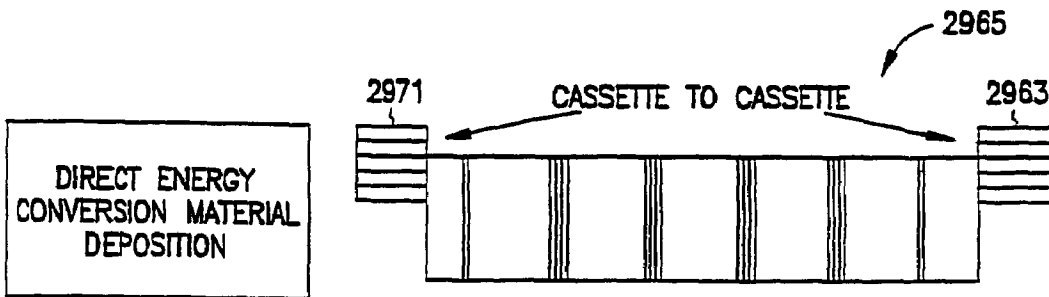


FIG. 29E

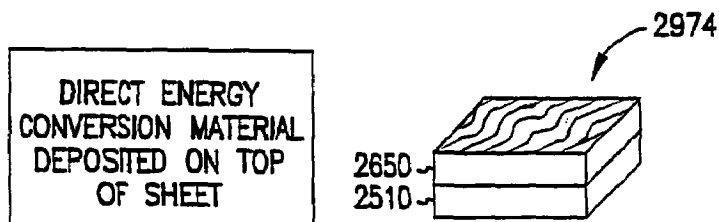


FIG. 29F

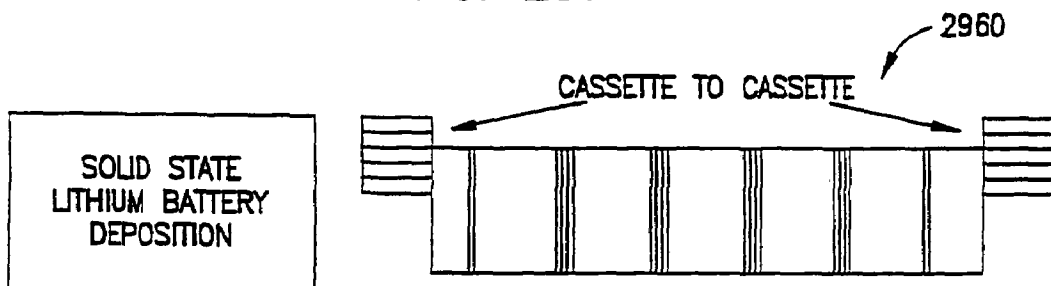


FIG. 29G

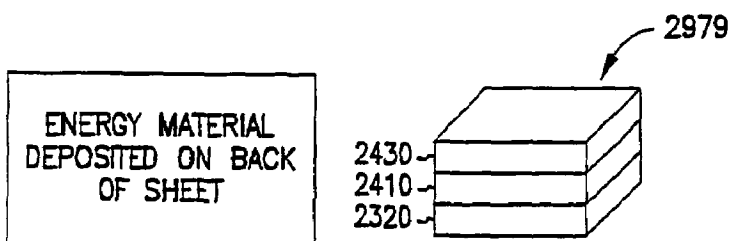


FIG. 29H

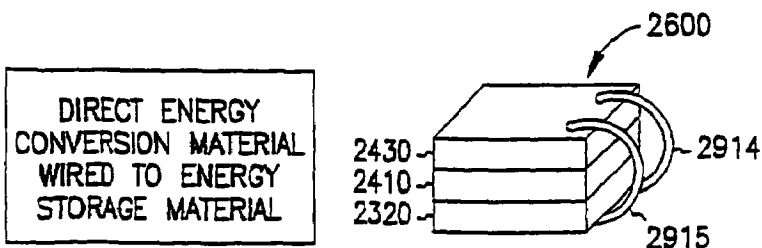


FIG. 29I

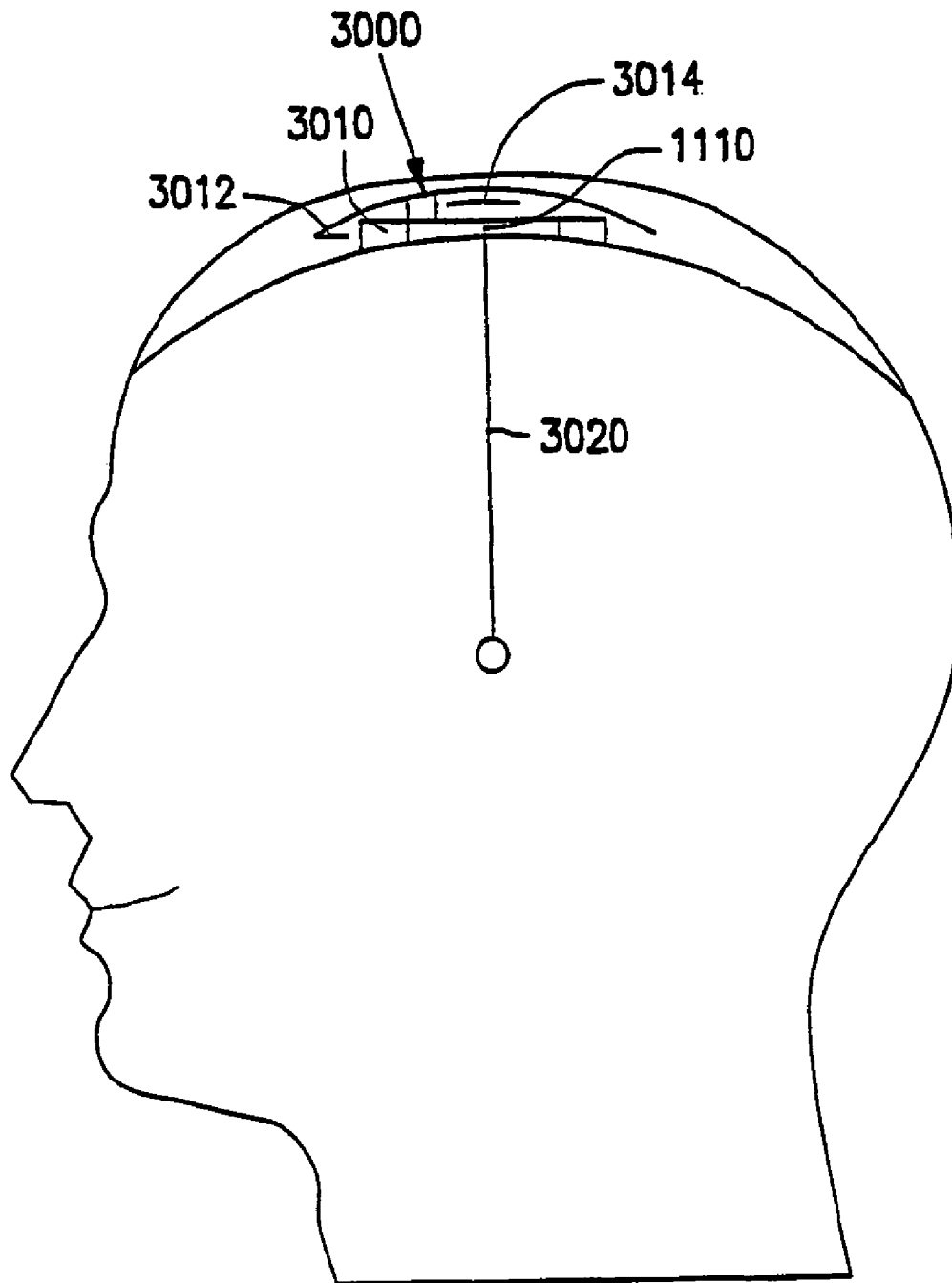


FIG. 30

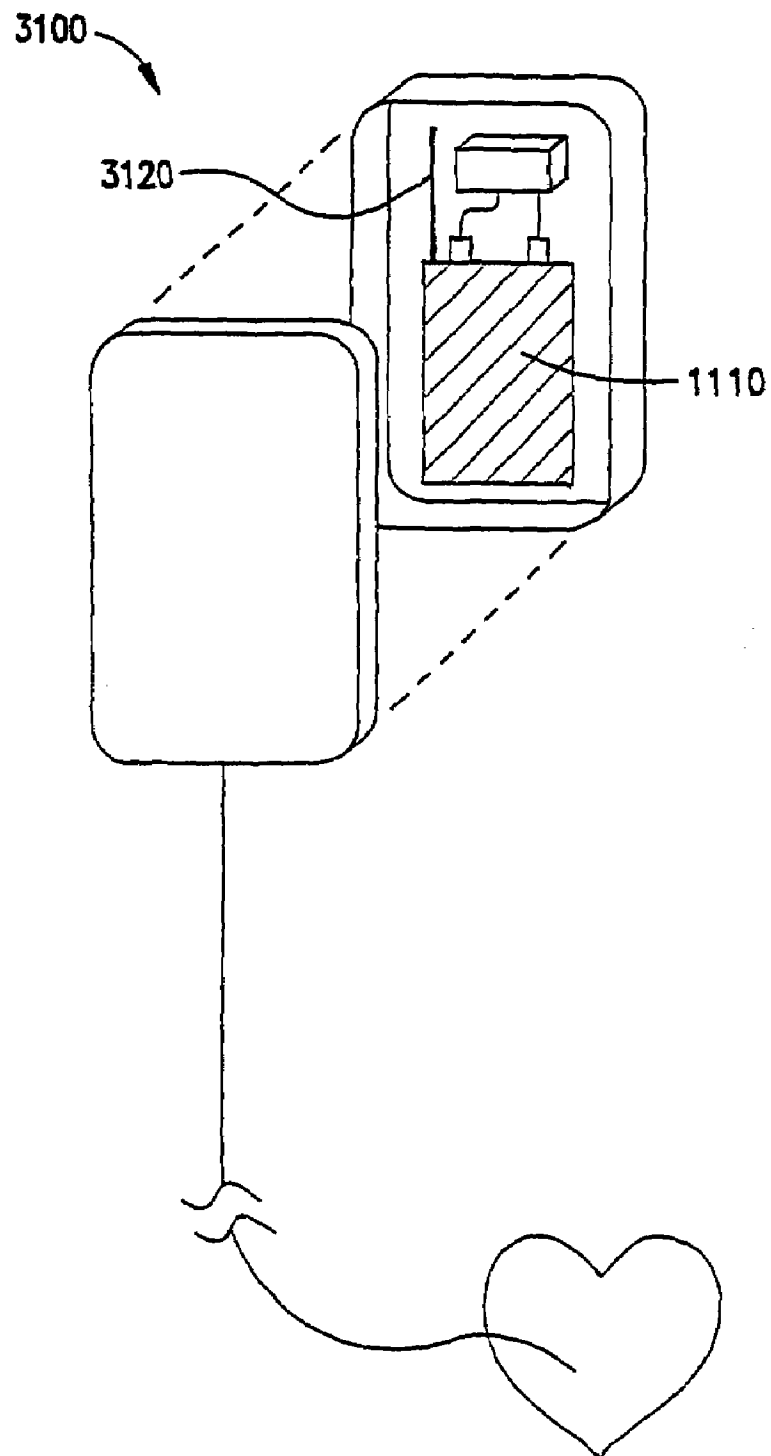


FIG. 31A

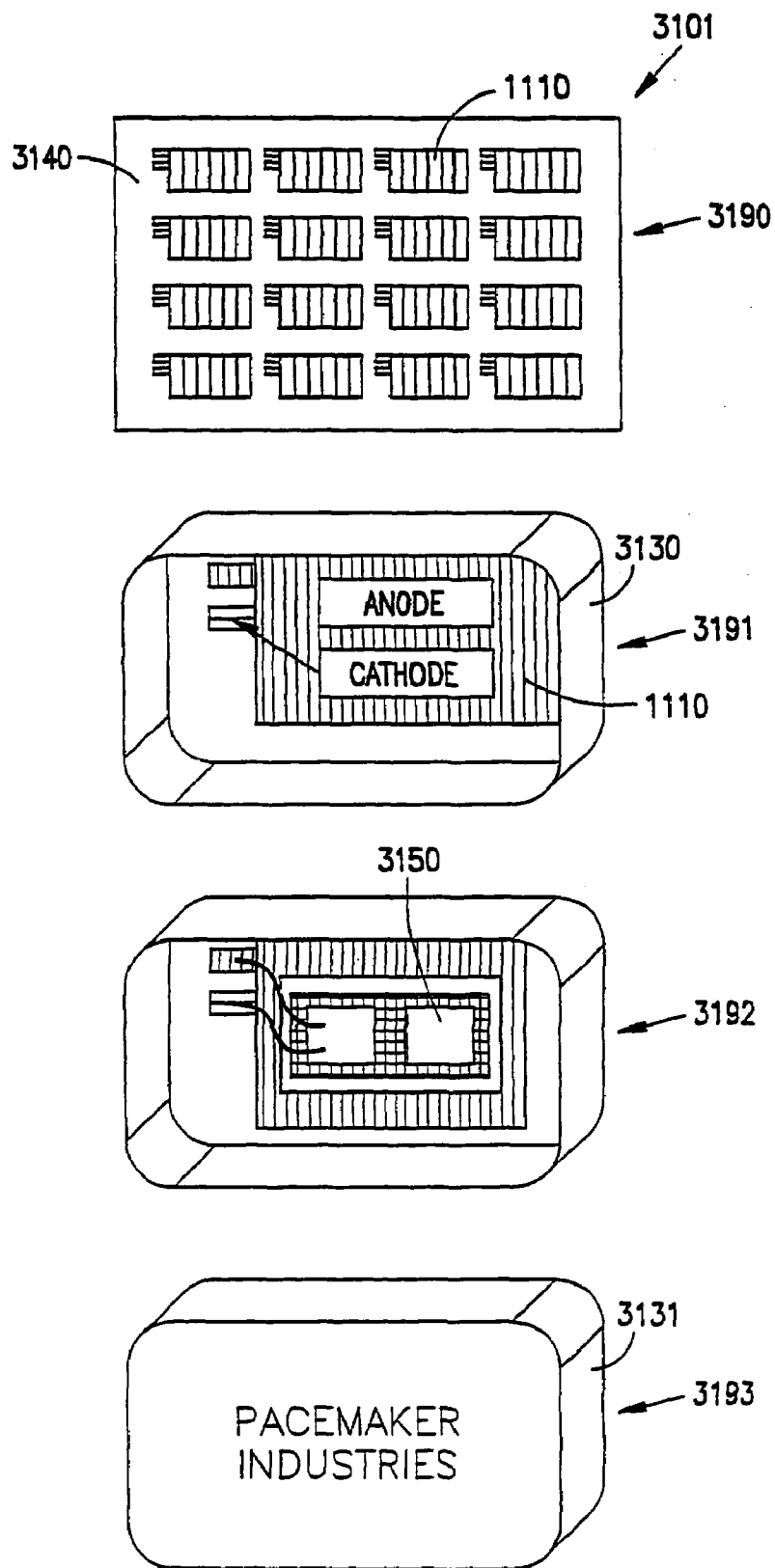


FIG. 31B

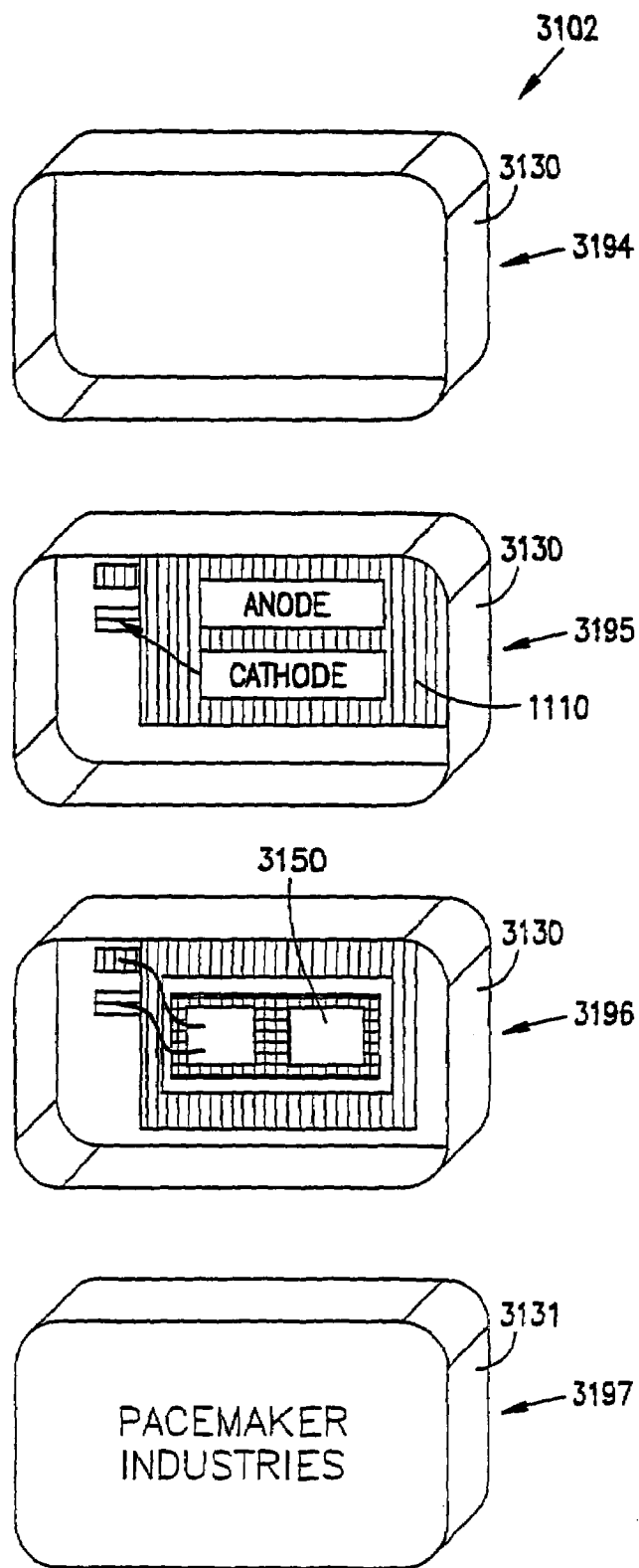


FIG. 31C

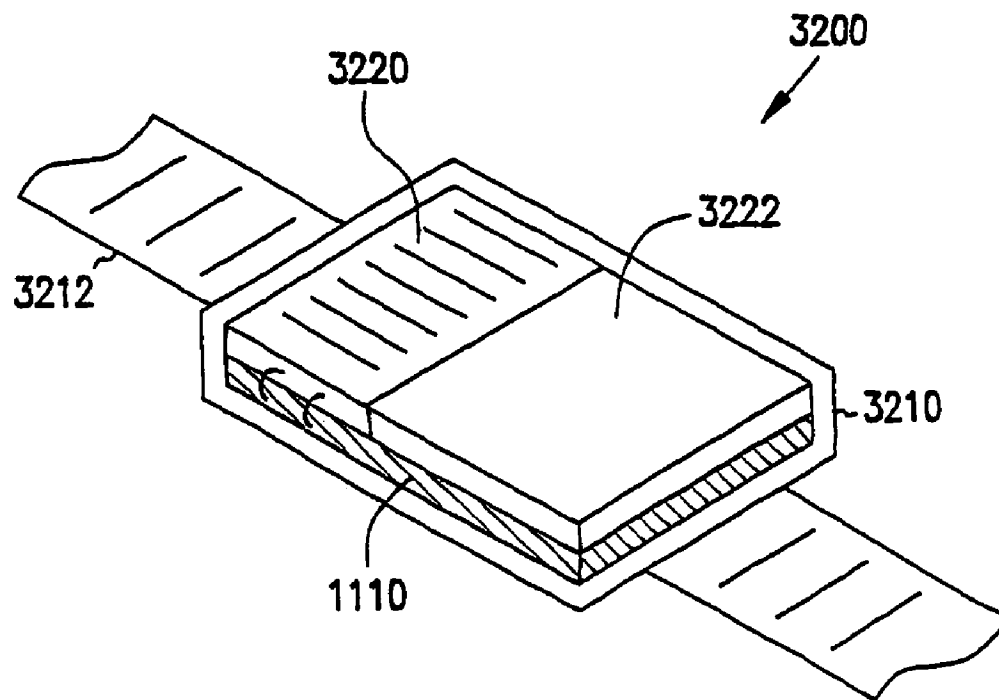


FIG. 32A

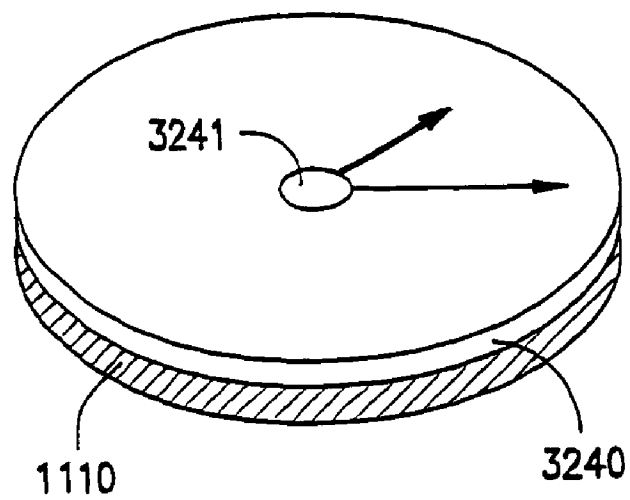


FIG. 32B

1

THIN-FILM BATTERY HAVING ULTRA-THIN ELECTROLYTE AND ASSOCIATED METHOD

CROSS-REFERENCES TO RELATED INVENTIONS

This invention claims priority to the following three provisional U.S. patent applications: filed: Mar. 24, 2000, Ser. No. 60/191,774, titled "Comprehensive Patent for the Fabrication of a High Volume, Low Cost Energy Products Such as Solid State Lithium Ion Rechargeable Battery, Supercapacitors and Fuel Cells," filed: Aug. 14, 2000, Ser. No. 60/225,134, titled "Apparatus and Method for Rechargeable Batteries and for Making and Using Batteries" and filed: Oct. 6, 2000, Ser. No. 60/238,673, Titled "Battery Having Ultrathin Electrolyte," each of which is incorporated by reference.

This invention also is related to patent applications for the following six attorney dockets each filed on even date herewith: 1327.003us1 titled "Low-Temperature Fabrication of Thin-Film Energy-Storage Devices," 1327.007us1 titled "Integrated Capacitor-Like Battery and Associated Method," 1327.008us1 titled "Method and Apparatus for Integrated-Battery Devices," 1327.009us1 titled "Continuous Processing of Thin-Film Batteries and Like Devices," 1327.010us1 titled "Device Enclosures and Devices with Integrated Battery," and 1327.011us1 titled "Battery-Operated Wireless-Communication Apparatus and Method," each of which is incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to solid-state energy-storage devices, and, more particularly, to electrolyte films in such devices. This invention also relates to methods and systems for fabricating solid-state energy-storage devices and the resulting devices such as batteries and supercapacitors. The present invention further relates to solid-state energy-conversion devices, such as photovoltaics and fuel cells, and associated methods.

BACKGROUND OF THE INVENTION

Electronics have been incorporated into many portable devices such as computers, mobile phones, tracking systems, scanners, etc. One drawback to portable devices is the need to include the power supply with the device. Portable devices typically use batteries as power supplies. Batteries must have sufficient capacity to power the device for at least the length of time the device is in use. Sufficient battery capacity can result in a power supply that is quite heavy or large compared to the rest of the device. Accordingly, smaller and lighter batteries (i.e., power supplies) with sufficient energy storage are desired. Other energy storage devices, such as supercapacitors, and energy conversion devices, such as photovoltaics and fuel cells, are alternatives to batteries for use as power supplies in portable electronics and non-portable electrical applications.

Another drawback of conventional batteries is the fact that some are fabricated from potentially toxic materials that may leak and be subject to governmental regulation. Accordingly, it is desired to provide an electrical power source that is safe, solid-state and rechargeable over many charge/discharge life cycles.

One type of an energy-storage device is a solid-state, thin-film battery. Examples of thin-film batteries are

2

described in U.S. Pat. Nos. 5,314,765; 5,338,625; 5,445,126; 5,445,906; 5,512,147; 5,561,004; 5,567,210; 5,569,520; 5,597,660; 5,612,152; 5,654,084; and 5,705,293, each of which is herein incorporated by reference. U.S. Pat. No. 5,338,625 describes a thin-film battery, especially a thin-film microbattery, and a method for making same having application as a backup or first integrated power source for electronic devices. U.S. Pat. No. 5,445,906 describes a method and system for manufacturing a thin-film battery structure formed with the method that utilizes a plurality of deposition stations at which thin battery component films are built up in sequence upon a web-like substrate as the substrate is automatically moved through the stations.

FIG. 1A shows a prior art thin-film battery **20** formed on substrate **22**. The battery includes a cathode current collector **32** and an anode current collector **34** formed on the substrate **22**. A cathode layer **38** is formed on the cathode current collector **32**. An electrolyte layer **42** is formed on the cathode layer **38**. An anode layer **44** is formed on the electrolyte layer **42**, the substrate **22** and the anode current collector **34**. The current collectors **32** and **34** are connected to external circuitry to provide electrical power to the same. In a discharge operation, ions in the anode layer **44** travel through the electrolyte layer **42** and are stored in the cathode layer **38**. Thereby, creating current flowing from the anode current collector **34** to the cathode current collector **32**. In a charge operation, an external electrical charge is applied to the current collectors **32** and **34**. Thereby, ions in the cathode layer **38** are forced to travel through the electrolyte layer **42** and are stored in the anode layer **44**.

FIG. 2A shows a prior art method for fabricating the thin-film battery **20**. First, the substrate is prepared for deposition of the thin-film battery (step **215**). The cathode current collector is deposited on the substrate using DC-magnetron sputtering (step **217**). The cathode is deposited on the cathode current collector by RF-magnetron sputtering (step **219**). In this method, the magnetron source provides sputtered material having energy of about 1–3 eV, which is insufficient to crystallize the cathode material to form desirable crystal structures that encourage ion movement into and out of the cathode material. The cathode must be annealed to produce a crystalline lattice structure in the cathode, which is necessary to produce an energy-storage device that has the required electrical performance characteristics. In some embodiments, a desired electrical characteristic of a battery is a discharge curve that has a relatively constant voltage (small delta) over a range of capacity and then the voltage decreases rapidly as remaining capacity is exhausted (large delta). Accordingly, the stack of the substrate, cathode current collector and the cathode are annealed at a temperature of 700 degrees Celsius (step **221** of FIG. 2A). The anneal step **221** complicates and adds cost to the fabrication of this type of solid-state battery. Further, the anneal step **221** precludes the use of any material as the substrate or other part of the battery thus formed that is unable to withstand the high anneal temperature. The anode current collector is deposited on the substrate by DC-magnetron sputtering (step **223**). The electrolyte layer is deposited by RF-magnetron sputtering (step **225**). The anode is deposited by thermal evaporation (step **227**).

U.S. Pat. No. 5,597,660 describes a thin-film battery and method for making such a battery. The battery includes an electrolyte amorphous lithium phosphorus oxynitride (Li-PON) which is electrochemically stable and does not react with the lithium anode and a vanadium oxide cathode.

One major factor limiting the efficiency of batteries is the internal resistance. A source of internal resistance is resis-

tance created by the electrolyte film, which impedes the movement of ions from one electrode to the other electrode.

Accordingly, there is a need for solid-state energy-storage devices, e.g., thin-film batteries and capacitors, that can be rapidly fabricated and that have acceptable electrical properties for use in a variety of electrical devices. More specifically, there is a need for a fabrication method and system that does not require a high-temperature anneal to form a solid-state energy-storage device.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a cross-sectional view of a conventional lithium-ion battery.

FIG. 1B is a cross-sectional view of an energy-storage device according to the present invention.

FIG. 1C is a cross-sectional view of an energy-storage device according to the present invention.

FIG. 1D is a cross-sectional view of an energy-storage device and a supercapacitor according to the present invention.

FIG. 2A is a flowchart of a conventional method for manufacturing the lithium-ion battery of FIG. 1A.

FIG. 2B is a flowchart of one embodiment of a fabrication process according to the teachings of the present invention.

FIG. 2C is a flowchart of one embodiment of a fabrication process according to the teachings of the present invention.

FIG. 2D is a flowchart of one embodiment of a fabrication process according to the teachings of the present invention.

FIG. 3A is a diagram of a device for fabricating a thin-film battery according to the teachings of the present invention.

FIG. 3B is a diagram of a device for fabricating a thin-film battery according to the teachings of the present invention.

FIG. 4 is a diagram of another embodiment of a device for fabricating a thin-film battery according to the teachings of the present invention.

FIG. 5A is a diagram of another embodiment of a device for fabricating a thin-film battery according to the teachings of the present invention.

FIG. 5B is a diagram of another embodiment of a device for fabricating a thin-film battery according to the teachings of the present invention.

FIG. 6 is a diagram of another embodiment of a device for fabricating a thin-film battery according to the teachings of the present invention.

FIG. 7 is a diagram of another embodiment of a device for fabricating a thin-film battery according to the teachings of the present invention.

FIG. 8 is a cross-sectional view of a photovoltaic cell according to the teachings of the present invention.

FIG. 9A is a perspective view of a thin-film energy-storage device according to the teachings of the present invention.

FIG. 9B is a view of another embodiment of a thin-film energy-storage device according to the teachings of the present invention.

FIG. 9C is a view of another embodiment of a thin-film energy-storage device according to the teachings of the present invention.

FIG. 10 shows X-ray diffraction spectra of cathode films for thin-film batteries.

FIG. 11 shows X-ray diffraction spectra of both a conventional cathode layer and a cathode film according to the teachings of the present invention.

FIG. 12A shows X-ray diffraction spectra for a conventional magnetron sputtered cathode layer.

FIG. 12B shows X-ray diffraction spectra for a thin film for an energy-storage device according to the present disclosure.

FIG. 13 is an exploded perspective view of an electronic device with a separate printed circuit board and battery.

FIG. 14A is an exploded perspective view of a portion of an enclosure for an electronic device according to one embodiment of this invention.

FIG. 14B is an exploded perspective view of a portion of an enclosure for an electronic device according to another embodiment of this invention.

FIG. 14C is an exploded perspective view of a portion of an enclosure for an electronic device according to yet another embodiment of this invention.

FIG. 15A is a plan view of a sheet including a plurality of battery cells.

FIG. 15B is a plan view of a diced battery cell before forming.

FIG. 15C is a perspective view of a battery cell after forming.

FIG. 15D is a perspective view of a battery cell after forming.

FIG. 15E is a perspective view of a battery cell after forming.

FIG. 15F is a plan view of a sheet including a plurality of battery cells.

FIG. 15G is a plan view of a plurality of diced battery cells before forming.

FIG. 15H is a perspective view of a fan folded plurality of diced battery cells before forming.

FIG. 15I is a plan view of a sheet including a plurality of battery cells.

FIG. 15J is a perspective view of a sheet including a plurality of battery cells formed on the sheet according to this invention.

FIG. 15K is a perspective view of a sheet including two battery cells formed into a case from the sheet shown in FIG. 15J according to this invention.

FIG. 15L is a side view of an electronic device enclosure formed from a sheet.

FIG. 16A is a plan view of a sheet including a plurality of battery cells.

FIG. 16B is a plan view of a diced battery cell before forming.

FIG. 16C is a perspective view of a fan folded diced battery cell before forming.

FIG. 16D shows a fan folded cord being truncated.

FIG. 16E shows a finished cord.

FIG. 17 is an exploded perspective view of a sheet including at least one battery cell rolled around an electrical motor in accordance with this invention.

FIG. 18A is a plan view of a diced battery cell and LED before forming.

FIG. 18B is a perspective view of a diced battery cell and LED after forming.

FIG. 18C is a plan view of a diced battery cell and LED before forming.

FIG. 18D is a perspective view of a diced battery cell and LED after forming.

FIG. 19A is a plan view of a sheet including a plurality of battery cells according to another embodiment of this invention.

FIG. 19B is a plan view of a plurality of diced battery cells before forming.

FIG. 19C is a perspective view of a formed battery including a plurality of cells.

FIG. 20 is a cutaway side view of a sheet including a plurality of battery cells, which are embedded in an enclosure portion.

FIG. 21A is a flow chart for a first recycling method using the inventive battery and enclosure.

FIG. 21B is a flow chart for a first recycling method using the inventive battery and enclosure.

FIG. 22A shows a schematic circuit of an embodiment of an integrated battery and circuit sharing a common terminal.

FIG. 22B shows a block diagram perspective view of an integrated device implementing the circuit of FIG. 22A having the circuit built on the battery.

FIG. 22C shows a block diagram perspective view of an integrated device implementing the circuit of FIG. 22A having the battery built on the circuit.

FIG. 22D shows a schematic circuit of an embodiment 2202 of an integrated battery and circuit each having separate terminals.

FIG. 22E shows a block diagram perspective view of an integrated device implementing the circuit of FIG. 22D having the circuit built on the battery.

FIG. 22F shows a block diagram perspective view of an integrated device implementing the circuit of FIG. 22D having the battery built on the circuit.

FIG. 22G shows a block diagram perspective view of an integrated device implementing the circuit of FIG. 22A having the battery and the circuit built side-by-side on a substrate.

FIG. 22H shows a block diagram perspective view of an integrated device implementing the circuit of FIG. 22D having the battery and the circuit built side-by-side on a substrate.

FIG. 23 shows a perspective view of an embodiment 2300 of the present invention having a battery overlaid with circuitry.

FIG. 24A shows a perspective view of an embodiment 2400 of the present invention having a battery overlaid with an integrated device.

FIG. 24B shows a block diagram of a layer-deposition system 2460.

FIG. 24C shows a perspective view of a partially processed sheet 2464.

FIG. 24D shows a block diagram of a layer-deposition system 2465.

FIG. 24E shows a perspective view of a processed sheet 2469.

FIG. 24F shows a perspective view of a diced final device 2400.

FIG. 25A shows a perspective view of an embodiment 2500 of the present invention having an integrated circuit overlaid with a battery.

FIG. 25B shows a plan view of IC 2540.

FIG. 25C shows an elevational view of IC 2540.

FIG. 25D shows a plan view integrated battery-IC 2501.

FIG. 25E shows an elevational view of integrated battery-IC 2501.

FIG. 25F shows a block diagram of a layer-deposition system 2560.

FIG. 25G shows a perspective view of a processed sheet 2569.

FIG. 26A shows a perspective view of an embodiment 2600 of the present invention having an integrated circuit overlaid on its back with a battery.

FIG. 26B shows a block diagram of a layer-deposition system 2660.

FIG. 26C shows a perspective view of a processed sheet 2669.

FIG. 26D shows a perspective view of diced final devices 2600.

FIG. 26E shows a perspective view of wired diced final device 2600.

FIG. 26F shows a perspective view of a hearing aid 2690 incorporating a wired diced final device 2600.

FIG. 27A shows a plan view of a starting substrate of an embodiment that will have an integrated battery and device sharing a common terminal.

FIG. 27B shows a plan view of the substrate of FIG. 27A after deposition of the integrated battery and device sharing a common terminal.

FIG. 27C shows a plan view of the substrate of FIG. 27B after placing and wiring a separately fabricated chip connected to the integrated battery and device sharing a common terminal.

FIG. 27D shows a plan view of the substrate of FIG. 27C after placing and wiring a loop antenna.

FIG. 27E shows a plan view of the substrate of FIG. 27D after a top encapsulation layer has been deposited.

FIG. 27F shows an elevation view of the starting substrate of FIG. 27A.

FIG. 27G shows an elevation view of the partially built device of FIG. 27B.

FIG. 27H shows an elevation view of the partially built device of FIG. 27C.

FIG. 27I shows an elevation view of the partially built device of FIG. 27D.

FIG. 27J shows an elevation view of the device of FIG. 27E.

FIG. 27K shows a perspective view of the device of FIG. 27E at a magnetic-recharging station.

FIG. 27L shows a perspective view of the device of FIG. 27E at a light-recharging station.

FIG. 27M shows a schematic of the device of FIG. 27E at a radio-wave-recharging station.

FIG. 28A shows an elevation view of a battery 2800 having stacked cells.

FIG. 28B shows a plan view of a single battery cell after recycling.

FIG. 28C shows a process 2810 used for recycling.

FIG. 29A shows a block diagram of a layer-deposition system 2960.

FIG. 29B shows a perspective view of a partially processed wafer 2964.

FIG. 29C shows a block diagram of a layer-deposition system 2965.

FIG. 29D shows a perspective view of a processed wafer 2969.

FIG. 29E shows a block diagram of a layer-deposition system 2965.

FIG. 29F shows a perspective view of a partially processed wafer 2974.

FIG. 29G shows a block diagram of a layer-deposition system 2960.

FIG. 29H shows a perspective view of a processed wafer 2979.

FIG. 29I shows a perspective view of wired diced final device 2600.

FIG. 30 is a perspective view of an implantable device according to this invention.

FIG. 31A is an exploded perspective view of a pacemaker according to this invention.

FIG. 31B is an exploded perspective view of one pacemaker as it is being formed.

FIG. 31C is an exploded perspective view of another pacemaker as it is being formed.

FIG. 32A is a perspective view of a first embodiment of a watch of the invention.

FIG. 32B is a perspective view of a second embodiment of a watch.

In the drawings, like numerals describe substantially similar components throughout the several views. Signals and connections may be referred to by the same reference number, and the meaning will be clear from the context of the description.

DETAILED DESCRIPTION

In the following detailed description of the preferred embodiments, reference is made to the accompanying drawings that form a part hereof, and in which are shown, by way of illustration, specific embodiments in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the present invention.

It is to be understood that in different embodiments of the invention, each battery in the Figures or the description can be implemented using one or more cells, and if a plurality of cells is implemented, the cells can be wired in parallel or in series. Thus, where a battery or more than one cell is shown or described, other embodiments use a single cell, and where a single cell is shown or described, other embodiments use a battery or more than one cell. Further, the references to relative terms such as top, bottom, upper, lower, etc. refer to an example orientation such as used in the Figures, and not necessarily an orientation used during fabrication or use.

The terms wafer and substrate as used herein include any structure having an exposed surface onto which a film or layer is deposited, for example, to form an integrated circuit (IC) structure or an energy-storage device. The term substrate is understood to include semiconductor wafers, plastic film, metal foil, and other structures on which an energy-storage device may be fabricated according to the teachings of the present disclosure. The term substrate is also used to refer to structures during processing that include other layers that have been fabricated thereupon. Both wafer and substrate include doped and undoped semiconductors, epitaxial semiconductor layers supported by a base semiconductor or insulator, as well as other semiconductor structures well known to one skilled in the art. Substrate is also used herein as describing any starting material that is useable with the fabrication method as described herein.

The term battery used herein refers to one example of an energy-storage device. A battery may be formed of a single cell or a plurality of cells connected in series or in parallel. A cell is a galvanic unit that converts chemical energy, e.g., ionic energy, to electrical energy. The cell typically includes two electrodes of dissimilar material isolated from each other by an electrolyte through which ions can move.

The term adatom as used herein refers to a particle, molecule, or ion of material that has not yet been formed into a structure or film.

The term intercalation as used herein refers to a property of a material that allows ions to readily move in and out of the material without the material changing its phase. Accordingly, a solid-state intercalation film remains in a solid state during discharging and charging of an energy-storage device.

FIG. 1B shows an embodiment of an energy-storage device 50 according to the present invention. A substrate 55 is provided on which is formed a contact film 57. Contact film 57 acts as a current collector and is connected to a lead 58, which connects one pole of the energy storage device 50

to an external circuit. An electrode film 59 is formed on the contact film 57. In some embodiments, the electrode film 59 substantially covers a surface of the contact film 57 to as to minimize resistance by maximizing the area of the interface between the films. In some embodiments, the electrode film 59 is a cathode for a thin-film battery. In other embodiments, electrode film 59 is an electrode of a supercapacitor. An electrolyte film 61 is formed on the electrode film 59. An electrode film 63 is formed on the electrolyte film 61. The electrolyte film 61 isolates electrode film 59 from electrode film 63. A contact film 65 is formed on electrode film 63. Contact film 65 acts as a current collector and is connected to a lead 67, which connects one pole of the energy storage device 50 to an external circuit. In some embodiments, the contact film 65 substantially covers a surface of the electrode film 63 to as to minimize resistance by maximizing the area of the interface between these films. In some embodiments, the electrode film 63 is an anode for a thin-film battery. In other embodiments, electrode film 63 is an electrode of a supercapacitor.

FIG. 1C shows a cross sectional view of an embodiment of an energy-storage device 50C. A substrate 55 is provided and, in some embodiments, includes additional layers and/or devices formed therewith. In some embodiments, the substrate 55 includes a substrate as described herein. Contact films 57 and 59 are formed on the substrate 55 according to the methods described herein. In some embodiments, contact films 57 and 59 are metal films deposited on the substrate according to other methods as known in the art. Contact films 57 and 59 act as contacts for connecting the energy-storage device 50C to other circuit elements (not shown).

An electrode first film 59 is formed on contact 57. Electrode first film 59 includes a metal or intercalation material in some embodiments, for example, thin-film battery embodiments in which the electrode first film 59 functions as a cathode. In some such embodiments, the electrode first film 59 includes lithium metal and/or a lithium-intercalation material. In other embodiments, such as supercapacitors, electrode first film 59 is a metal oxide. It is desirable to maximize the contact interface between the electrode first film 59 and contact film 57. Accordingly, in some embodiments, the electrode first film 59 substantially covers contact film 57 except for a portion reserved for connection to external circuits.

An electrolyte film 61C is formed on, or at least partially on, the electrode first film 59. The electrolyte film 61C, in some embodiments, completely encloses the electrode first film 59. The electrolyte film 61C is formed using the systems and methods described herein. In one embodiment, a first material of the electrolyte film 61C is deposited using a first source, which directs a first electrolyte material (adatoms) to the location on the substrate or, as shown in FIG. 1C, to a location on the electrode first film 59.

An electrode second film 63 is formed on electrolyte film 61C and contact film 59. Electrolyte film 61C completely separates the electrode first film 59 from the electrode second film 63. The electrode second film 63 includes a metal or intercalation material in some embodiments, for example, thin-film battery embodiments in which the electrode second film is an anode. In other embodiments, such as supercapacitor embodiments, electrode second film 63 is a metal oxide. Electrode second film 63, in some embodiments is deposited according to the methods described herein. In other embodiments, electrode second film 63 is formed according to methods known in the art.

The electrolyte film 61C as deposited includes the electrolyte material. A first source (e.g., sources 311, 511, 511A, and 711 as described herein) of the electrolyte material, in one embodiment, is a physical vapor deposition source. In another embodiment, the first source is a chemical vapor deposition source. A second source provides energized particles to the location. The energized particles impinge on the electrolyte material and assist in forming a desired structure of the electrolyte film 61C. In some embodiments, the second source provides energized particles simultaneously with the first source supplying the electrolyte material. The use of the energized particles conforms the electrolyte film 61C to electrode first film 59 such that the electrolyte film provides the necessary insulative property, namely preventing electrons from travelling directly between the electrode first film 59 and the electrode second film 63, i.e., shorting the electrodes. In some embodiments, the second source is an ion source as described herein, e.g., sources 313, 413, or 713. The second source provides energized ions that supply energy to the electrolyte material from the first source. The energy that is supplied by the ions assists in conforming the formed electrolyte film 61C to the electrode first layer 59. It is believed that the use of the energized particles in the energy range referenced herein provides the growing electrolyte material an extended period of mobility upon the previous film surface, and this extended period of mobility allows the electrolyte material to grow in a more defect-free manner.

In some embodiments, it is desired to form the electrolyte film 61C as thin as possible to lower its contribution to the internal resistance of the energy-storage device. It is also desired to maintain the electrolyte's property of blocking the flow of electrons (which would result in a short of the cathode to the anode) while permitting the flow of the ions that provide the battery function across the electrolyte. Using the methods and systems described herein, the electrolyte film 61C is formed to a thickness 61C' of less than about 5000 Angstroms. In some embodiments, the electrolyte film 61C has a thickness 61C' of less than about 2500 Angstroms. In some embodiments, the electrolyte film 61C has a thickness 61C' of less than about 1000 Angstroms. In some embodiments, the electrolyte film 61C has a thickness 61C' of less than about 500 Angstroms. In some embodiments, the electrolyte film 61C has a thickness 61C' of less than about 250 Angstroms. In some embodiments, the electrolyte film 61C has a thickness 61C' of less than about 100 Angstroms. In some embodiments, the electrolyte film 61C has a thickness 61C' in a range of about 10 Angstroms to about 200 Angstroms. In some embodiments, the electrolyte film 61C has a thickness 61C' in a range of about 10 Angstroms to about 100 Angstroms.

In one embodiment, the electrolyte film 61C includes LiPON and is formed using the first source 311 with the second source 313 or 413. As used herein, LiPON refers generally to lithium phosphorus oxynitride materials. One example is $\text{Li}_3\text{PO}_4\text{N}$. Other examples incorporate higher ratios of nitrogen in order to increase lithium ion mobility across the electrolyte. In some embodiments, the first source 311 provides Li_3PO_4 in a nitrogen atmosphere. In other embodiments, the first source 311 provides Li_3PO_4 in a vacuum environment wherein the background pressure is less than 1 E-3 Torr. The second source 313 or 413 provides energized particles from a source gas. In some embodiments, the secondary source is an ion source supplying energetic ions from a source gas comprising oxygen (e.g., O_2) or nitrogen (e.g., N_2). The source gas, in other embodiments, comprises a noble gas, e.g., argon, xenon, helium,

neon, and krypton. The energized particles and/or ions increase the energy of the material forming the electrolyte film 61C, thus enhancing layer-by-layer growth. Accordingly, the electrolyte film is of a higher quality than conventional electrolyte layers.

An embodiment for forming a LiPON electrolyte film 61C includes the first source providing Li_3PO_4 at or to the location where the LiPON electrolyte film is to be formed and second source providing energized nitrogen particles to or near the same location. The energized nitrogen particles react with Li_3PO_4 provided at the location for forming the electrolyte film. This increases the amount of nitrogen in the LiPON electrolyte film. Increasing the nitrogen content is desirable to increase lithium ion mobility across the electrolyte.

In a further embodiment, the chamber in which the substrate 55 is positioned has a nitrogen enhanced atmosphere. A LiPON electrolyte film 61C is formed by the Li_3PO_4 supplied by the first source reacting with the nitrogen in the chamber. The second source provides energized particles assisting in the formation of the electrolyte film. In another embodiment, the second source also provides nitrogen to the Li_3PO_4 at the location. Thus, the Li_3PO_4 reacts with both the nitrogen in the chamber and with energized, nitrogen containing particles supplied by the second source. This increases the nitrogen content of the electrolyte film 61C. In some embodiments, increasing the nitrogen content in the electrolyte film 61C is desirable since published data from the Department of Energy lab at Oak Ridge, Tenn. indicates an increase in nitrogen content increases the ion conductivity or mobility in the electrolyte film.

As will be understood by reading the present invention, the systems shown herein for depositing films are adaptable to form the electrolyte film 61C according to the present invention. Examples of some such systems are shown in FIGS. 3-7.

FIG. 1D shows another embodiment of an energy storage device according to the teachings of the present invention. A supercapacitor 70 is formed on the energy-storage device 50C having the ultra-thin electrolyte film 61. The energy-storage device 50C being formed on the substrate prior to forming the supercapacitor 70 represents an embodiment of layer/devices being formed on the substrate prior to applying the techniques described herein to form energy-storage and/or energy conversion devices. The supercapacitor 70 includes an intermediate film 73 formed in physical contact with electrode films 71 and 75. In some embodiments, the intermediate film 73 is an electrolyte for storing and discharging electrical charge by a faradaic process. In some embodiments, the intermediate film 73 includes a dielectric material. The contact film 65 is in physical and electrical contact with electrode 71. Thus, in this embodiment contact film 65 is a shared contact film for both the energy storage device 50C and supercapacitor 70. In other embodiments, energy storage device 50C and supercapacitor 70 have separate contact films. In some embodiments, the intermediate film 73 includes LiPON. In some embodiments, the electrolyte film 73 includes TaO. In some embodiments, the electrode films are RuO_2 . A contact film 77 is formed on the electrode film 75. A lead 76 extends from the contact film 77 to contact one plate of the supercapacitor to an external circuit.

A method for fabricating the solid-state energy-storage device 50 will now be described with reference to FIGS. 1B and 2B. The method includes providing a substrate 55 (step 251) and depositing a cathode contact film 57 on the substrate 55 (step 253). In some embodiments, step 251

includes providing a substrate having insulator layers or other layers/devices formed thereon. The method further includes a step 255 of depositing an electrode material to a location on the substrate, while simultaneously supplying energized particles to the electrode material at the substrate. In one embodiment, an assist source provides the energized particles. In some such embodiments, the energized particle beam is directed to the same location on the substrate as the electrode material. In an embodiment, the energized particles are energized ions. The energized ions, in an embodiment, include a material that is different than the electrode material. The energized particles or the ion beam assist in controlling growth of the structure of the electrode material at the location. In some embodiments, step 255 is used to form a cathode film or layer 59 for a solid-state, thin-film battery. The cathode film 59 is in electrical and physical contact with the cathode contact. An electrolyte film 61 is deposited, step 257, on the cathode film 59. An anode film 63 is deposited, step 259, on the electrolyte film. The electrolyte film 61 separates the cathode and anode films 59 and 61 to prevent shorting the energy-storage device 50, e.g., battery. An anode contact is formed, step 261, in electrical and physical contact with the anode film. The thin-film battery according to the present invention is now formed and is subjected to post energy-storage device fabrication steps 263.

The deposition of the cathode film includes directing a first material (e.g., adatoms) to a location on the substrate, while simultaneously supplying energized particles (e.g., ions) of a second material to the location on the substrate. In some embodiments, the second material is different from the first material. The energized particles supply energy to the first material to assist in the growth of a desirable crystal structure in the cathode film. Moreover, this controls the stoichiometry of the growing film at the location on the substrate. In one embodiment, the first material is a lithium-intercalation material used as a solid-state, thin-film battery cathode. The assist source provides ions that provide energy in a range of 5 eV to 3000 eV to the lithium-intercalation material. Control of the energy in the ions produced by the assist source provides in situ control for growing a lithium-intercalation film having a crystalline structure. The energy from the ions assists the formation of lithium-intercalation materials into a crystalline structure at the time of deposition. In one embodiment, the gas used to form the ions is used to control the stoichiometry of the growing, crystalline film. For example, an ionized, assist beam of O_2 is used to control the growth and stoichiometry of a $LiCoO_2$ intercalation material. In some such embodiments, the O_2 in the ion assist beam combines with $LiCo$ at the location to form the $LiCoO_2$ intercalation material.

The crystalline structure of a thin film formed according to the teachings herein has a higher order than those achieved by conventional cathode film forming techniques. Conventional techniques rely on a high-temperature, post-cathode-deposition anneal to reorder and crystallize the structure of a conventional cathode film. Unfortunately, such conventional techniques anneal the entire structure to the same temperatures, which is undesirable in that the substrate must withstand such temperatures which eliminates many otherwise suitable substrate materials from consideration. Further, different layers cannot be provided with different anneals suited to their different requirements. A highly ordered crystalline cathode film is desirably achieved according to the teachings described herein by providing the required energy to form the desired, high-order and appropriately oriented crystal structure without subjecting the

substrate, and other layers formed on the substrate including the cathode-contact film to a high-temperature anneal. Further, each layer can be annealed using a different anneal process (such as using ion assist beams having different energies for different layers, or depositing and annealing at different rates or for different durations). Further, by annealing the surface layer of the previous layer, a subsequent layer can be deposited onto a surface that has been ordered in a specific way (for example, to achieve a specific crystal orientation, or a specific ion-bonding surface) that enhances the quality of that subsequent layer.

FIG. 2C shows one embodiment of a method for fabricating an energy-storage device. Steps 251, 253, 259, 261, and 263 are substantially similar to the steps described above with reference to FIG. 2B. Step 255C is a step for depositing a cathode film at least partially on the cathode contact film. In an embodiment, the cathode film is deposited as described above in step 255. In other embodiments, the cathode film is deposited according to other deposition processes known in the art. The electrolyte film is formed by depositing an electrolyte material to a location at least partially in contact with the cathode film (step 257C). In a preferred embodiment, the electrolyte material is in contact with a substantial portion of, if not all of, a surface of the cathode film. In some embodiments, an assist source simultaneously supplies energized particles to the electrolyte material as it forms the electrolyte film. In an embodiment, the assist source supplies a beam of energized ions of an assist material different than the electrolyte material. In one embodiment, the second material beam is directed to the same location on the substrate as the electrolyte material. The energized ion beam assists in controlling growth of the structure of the electrolyte film. The ion beam is unfocused in one embodiment. The ion beam is focused in another embodiment.

The deposition of the electrolyte film includes directing an electrolyte material to a location at least partially in contact with the cathode film, while simultaneously supplying energy to the electrolyte material. In one embodiment, the energy is supplied by energized particles. In some such embodiments, the energized particles are energized ions. In some such embodiments, the energized particles from the assist source are of a different material than the electrolyte material. The energized particles supply energy to the electrolyte first material to assist in the growth of a desirable, solid electrolyte-film structure. Moreover, this controls the stoichiometry of the growing electrolyte film.

In one example, the electrolyte material is a lithium phosphorus oxynitride. In some embodiments, the assist source provides ions that provide energy in a range of about 5 eV to about 5000 eV to the lithium phosphorus oxynitride ("LiPON"). Control of the energy in the ions produced by the assist source provides in situ control for growing a lithium phosphorus oxynitride structure at the location. The energy from the ions assists the formation of the lithium phosphorus oxynitride material into a desirable structure at the time of deposition. In one embodiment, the gas used to form the ions is used to control the stoichiometry of the growing electrolyte film. For example, an ionized assist beam of O_2 is used to control the growth and stoichiometry of a lithium phosphorus oxynitride material. In another embodiment, an ionized assist beam of N_2 is used. In this embodiment, the N_2 not only controls growth and stoichiometry of the electrolyte film, but also injects additional nitrogen into the electrolyte film. This is desirable due to the ionic transportivity of a LiPON electrolyte film is dependant on the amount of nitrogen in the film.

13

FIG. 2D shows one embodiment of a method for fabricating an energy-storage device. Steps 251, 253, 257, 261, and 263 are substantially similar to the steps described above with reference to FIG. 2B. Step 255C is a step for depositing a cathode film at least partially on the cathode contact film. In an embodiment, the cathode film is deposited as described above with reference to FIG. 2B. In other embodiments, the cathode film is deposited according to other deposition processes known in the art. Step 259D is a step for depositing an electrode material to a location at least partially on the electrolyte film, while simultaneously supplying energized particles to the electrode material. In one embodiment, the energized particles are directed to the same location as the electrode material. In an embodiment, the energized particles are energized ions. The energized ions, in an embodiment, include a second material that is different than the first material. The energized particles or the ion beam assist in controlling growth of the structure of the electrode material. Step 259D, in some embodiments, is used to form an anode film for a solid-state thin-film battery. The anode film is in electrical and physical contact with the anode contact and electrolyte films.

The deposition of the anode film includes directing an electrode material to a location at least partially in contact with the electrolyte film, while simultaneously supplying energized particles of a second material. The energized particles supply energy to the electrode material to assist in the growth of a desirable crystal structure in the anode film. Moreover, this controls the stoichiometry of the growing film. In one embodiment, the electrode material includes a lithium-intercalation material used as a battery anode. In an embodiment, the anode includes a lithium metal or a lithium alloy. In another embodiment, the anode includes a carbonaceous material, such as graphite or diamond-like carbon. In another embodiment, the anode includes a metal oxide, for example, RuO or VaO. In another embodiment, the anode includes a nitride material. A secondary source provides particles, which are ions in some embodiments, that provide energy in a range of about 5 eV to about 3000 eV to the lithium-intercalation material. Control of the energy in the ions produced by the secondary source provides in situ control for growing a lithium-intercalation crystalline structure at the location. The energy from the ions assists the formation of lithium-intercalation materials into a crystalline structure at the time of deposition. In one embodiment, the gas used to form the ions is used to control the stoichiometry of the growing, crystalline film.

The crystalline structure of an electrode thin film formed according to the teachings herein has a higher order than those achieved by conventional film forming techniques. Conventional techniques rely on a high-temperature, post-deposition anneal that affects the substrate and other layers as well as the film intended to reorder and crystallize the structure of that film. In contrast, the present invention provides a controlled energy source at the time of deposition or after the time of deposition that reorders the surface of the deposition film without substantially heating the underlying layers or substrate. In some embodiments, the energy is provided while depositing each atomic layer of a film such that each atomic layer is ordered as crystallizes into the film. Examples of such energy sources include an ion beam that either react with the adatoms being deposited and/or provide kinetic energy to assist in deposition of the film. Other examples of energy sources include high temperature, short duration heat sources, short duration plasma sources, lasers, other high intensity photo sources that reorder the crystal structure adjacent the surface of the film without effecting

14

other layers or the substrate. A highly ordered crystalline cathode or anode is desirably achieved according to the teachings described herein.

While the above fabrication process describes forming cathode and anode films in a certain order, other embodiments reverse the order of the cathode film and anode film. Moreover, the fabrication process describes forming cathode and anode films, for example in a battery. In some embodiments, the cathode and anode films are electrodes of a battery. Other embodiments include films forming various layers of supercapacitors. Supercapacitors operate in these embodiments, at least one of the films forming the supercapacitor, e.g., electrode films 71, 75 and electrolyte and/or dielectric film 73, have improved crystalline structure, crystallite size, or fewer defects without resorting to a high temperature anneal of the entire structure to provide these properties. Accordingly, techniques and systems for fabricating thin films for use in an energy-storage device as described herein are applicable to both solid-state batteries and solid-state capacitors.

In another embodiment, the thin-film energy-storage device is formed on a substrate. A contact film, which is electrically conductive and does not react with a subsequently deposited, adjacent cathode film, is formed on the substrate. The contact film acts as a barrier between the substrate and the cathode film. The contact film further acts as a current collector and as a connection between the cathode film and circuits that are external to the energy-storage device. In an embodiment, the contact film has a thickness of greater than 0.3 microns.

FIG. 3A shows a deposition apparatus 305 including a reaction chamber 307 in which is positioned a substrate 309 on which an energy-storage device is to be fabricated. Reaction chamber 307, in one embodiment, is a sealed chamber that holds gases for the reaction and that provides a sub-atmospheric pressure. In some embodiments, it is desirable to hold the pressure in the chamber less than about 1×10^{-3} Torr. A first material source 311 is provided in the chamber 307. The first source 311 produces a beam of adatoms 312 of a first material to be deposited on the substrate 309. In one embodiment, the first material source 311 is a physical vapor deposition source. In one such embodiment, the material source 311 is an e-beam source. In another such embodiment, the first source 311 is an arc source including, for example, a cathodic-arc source, an anodic-arc source, and a CAVAD arc source. Arc sources are particularly suited for use as a source as they effectively operate in a chamber that is operated at low temperatures. In another embodiment, the first source 311 is a physical deposition source including, for example, a sputtering source. In another embodiment, the source 311 is a chemical vapor deposition source including, for example, a direct ion source using a hydrocarbon precursor gas. Beam 312 is focused on a location 319 on the substrate 309 whereat the material of the beam 312 is deposited to form a film of an energy-storage device. An assist source 313 is provided in the chamber 307 and produces a beam of energized particles 314 directed at least adjacent to the location 319 on the substrate 309. In some embodiments, the assist source is an energized ion-producing source. In some embodiment, the assist source 313 is offset from the first source 311 such that the beams from these sources are not coincident. The energized particle beam 314 provides the energy that is required to control the growth and stoichiometry of the material in the first beam 312 into a crystalline structure on the substrate 309 as is explained in greater detail herein. In one embodiment, the energized particle beam 314 also

15

provides elements that are required in the film being deposited. In another embodiment, beam 314 is directed at least near location 319 such that sufficient energy to form the desired crystal structure and stoichiometry of the film being deposited is supplied by beam 314 to the material in first beam 312. In some embodiments, the deposition system 305 includes at least one additional assist source 313A. In some embodiments, each of the sources 313A provides an additional assist beam 314A that provides energy to arriving adatoms at the substrate. Various embodiments of assist beams 314 are described below.

FIG. 3B shows another embodiment of a deposition apparatus 305. The assist source 313 produces an energy beam 314 that travels along a path that is essentially normal to the substrate 319. The source of material to be deposited 311 is offset from assist source 313. In some embodiments, source 311 produces a beam of adatoms 312 that travels along a path that is non-normal to the substrate 319. The energy beam supplies energy to the adatoms from beam 312 as described herein.

FIG. 4 is a view substantially similar to FIG. 3A, except that depositing apparatus 405 includes an assist source 413 for producing the energized beam that is pivotally mounted to a bracket fixed in the chamber 307. The assist source 413 pivots to direct the energized particle beam 414 at a desired impingement angle to the surface of the substrate 309. In an embodiment, the impingement angle is in the range of about 15 degrees to about 70 degrees from normal to the substrate. Accordingly, in some embodiments, the impingement angle is variable. In one embodiment, the impingement angle is about 45 degrees. In some embodiments, the deposition system 405 includes at least one additional assist source 413A. In some embodiments, each of the sources 413A provides an additional assist beam 414A that provides energy to arriving adatoms at the substrate. In some embodiments, the energy provided by assist beam 414 differs from the energy provided by at least one of assist beams 414A. In some embodiments, the assist beam 414 and 414A need not simultaneously transmit energy to the adatoms. In some embodiments, the means by which the beams 414 and 414A transmit energy are different. In some embodiments, the material in beams 414 and 414A are different.

FIG. 5A is a view substantially similar to FIG. 3 except that depositing apparatus 505 includes a plurality of first deposition sources 511. In one embodiment, each one of the first deposition sources 511 directs its respective beam 512 to the location 319 on the substrate 309. In some embodiments, every one of the first sources 511 produces a beam 512 including the same material. In other embodiments, at least of the first sources 511 produces a beam 512 of a material that is different than that of another of the first sources 511. In some embodiments, the materials from the plurality of first beams 512 combine at the location 319 to form the desired film. In other embodiments, the materials in first beams 512 combine with material from assist beam 314 to form the desired film. In one embodiment, one of the first sources 511 directs its beam 512 to the substrate 319 but away from the location 319. In some embodiments, a plurality of assist sources 313 provide energy to the adatoms of beams 512.

FIG. 5B shows another embodiment of a depositing apparatus 505B. A plurality of assist sources 313 is positioned to provide energy to a forming film at the substrate 319. A plurality of material sources 511A, 511B, and 511C supply material to the chamber 307 and adjacent the surface of the substrate 319. In some embodiments, each of the material sources 511A, 511B, and 511C provide a same

16

material and, thus, have the ability to provide a greater quantity than one of the sources alone. In some embodiments, at least one of the material sources 511A, 511B, and 511C provides a material different than another of the material sources. In some embodiments, these different materials react at the in chamber 307 to create the adatom material that will form a film on the substrate 319. In some embodiments, at least one of the material sources 511A, 511B, and 511C provides a precursor material into chamber 307 and another of the material sources provides a reactant material into the chamber. The precursor and reactant material react together to create the material that will form the film. In some embodiments, at least one of the material sources 511A, 511B, and 511C includes a chemical reactor in which chemicals react. This source then injects the resultant material into the chamber. The resultant material is included in the film fabrication process.

FIG. 6 is a view substantially similar to FIG. 5A except that depositing apparatus 605 includes a plurality of first deposition sources 511 and a pivotable assist source 413. In some embodiments, this provides more material to a given deposition location. In some embodiments, this provides deposition at multiple locations. In still other embodiments, this allows different materials from different sources to be combined.

FIG. 7 shows another embodiment of a depositing apparatus 705 according to the teachings of the present invention. Depositng apparatus 705 includes a reaction chamber 707 in which is positioned an elongate, flexible substrate 709 on which an energy-storage device is to be fabricated. The substrate 709 is fed from a source roll 710 over an arched thermal control surface 715 and taken up by an end roll 718. A first material source 711 is provided in the chamber 707 and is a physical deposition source. First source 711 produces a beam of adatoms 712 of a material to be deposited on the substrate 709. In one embodiment, the first source 711 is an arc source including, for example, a cathodic arc source, an anodic arc source, and a CAVAD arc source. In another embodiment, the first source 711 is a physical vapor deposition source including, for example, a sputtering source. In another embodiment, source 711 is a chemical vapor deposition source. Moreover, source 711, in some embodiments, represents a plurality of different material sources. Beam 712 is focused on a location 719 on the substrate 709 whereat the adatoms in the beam are deposited to form a film layer of an energy-storage device. An assist source 713 is provided in the chamber 707 and produces a beam of energized particles 714 directed at the substrate 709. In an embodiment, the assist source 713 produces a beam of energized ions 714. The energized particle beam 714 provides the energy required to control growth and stoichiometry of the deposited material of the first beam 712. Thus, a crystalline structure is formed on the substrate 709 as is explained in greater detail herein. The substrate 709, in one embodiment, is an elastomer, polymer, or plastic web or sheet on which the energy-storage device is fabricated. Substrate 709, being elongate, allows a plurality of energy-storage devices to be deposited on successive locations of the substrate, thereby improving the rate of energy device production. Moreover, a plurality of deposition apparatuses 705 or sources 711, in some embodiments, are provided for simultaneously depositing a plurality of films at different locations on the substrate 709.

The thermal control surface 715 is connected to a thermal source 725, which controls the temperature of surface 715. The substrate 709 is in thermodynamic contact with surface 715 to thereby control the temperature of the substrate as

needed for a particular deposition process on a particular substrate. In one embodiment, the thermal source is a coolant source, for example a cryogenic vacuum pump that releases compressed helium toward the surface **715** to cool it. The use of a thermally controlled surface **715** in direct contact with the substrate **709**, especially when the direct contact is aligned or coincident with the location whereat a thin film is being formed, allows the use of substrates that have lower thermal degradation temperatures than are possible using conventional solid-state thin-film battery fabrication processes.

The above provides descriptions of various embodiments of systems in which the present invention is performed to produce energy-storage devices or energy-conversion devices. It is within the scope of the present invention to combine the elements of the systems in different ways than shown and described as long as the methods described herein are performable with such a system. For example, in some embodiments, the flexible substrate **709** and rolls **710**, **718** can be combined with any of the embodiments shown in FIGS. **3A–6**. In some embodiments, the thermal source **725** is also combinable with any of the embodiments of FIGS. **3A–6**. In some embodiments, the pivotable assist sources **413** are combinable with any of the embodiments of FIGS. **3A**, **3B**, **5A**, **5B**, and **7**. In some embodiments, the material sources **511A**, **511B**, and **511C** are combinable with embodiments of FIGS. **3A–5A** and **6–7**.

In one embodiment, the electrode second film, e.g., films **59** or **71** is a lithium-intercalation material which overlays at least part of the first film, e.g., contact films **57** or **63**, but does not extend beyond the boundary of the first film. Thus, the intercalation second film remains in a solid state during discharging and charging of the energy-storage device. In some embodiments, the second film is deposited using the first deposition source simultaneously with the secondary source supplying energetic ions to the growing second film. In some embodiments, the first deposition source is a physical vapor deposition source. In some embodiments, the secondary source is an ion source supplying energetic ions from a source gas comprising oxygen (e.g., O_2) or nitrogen (e.g., N_2). The source gas, in another embodiment, comprises a noble gas, e.g., argon, xenon, helium, neon, and krypton. The source gas, in yet another embodiment, comprises a hydrocarbon material such as a hydrocarbon precursor. Selection of the secondary source gas is based on the desired effect on the stoichiometry of the deposited film. The secondary source, in one embodiment, provides a focused beam of energized ions. The secondary source, in one embodiment, provides an unfocused beam of energized ions. The energized ions provide energy to the lithium-intercalation material in the range of about 5 eV to about 3,000 eV. In one embodiment, the energy range of is about 5 eV to about 1,000 eV. The energy range in a further embodiment is about 10 eV to about 500 eV. The energy range in a further embodiment is about 30 eV to about 300 eV. In another embodiment, the energy range is in the range of about 60 eV to 150 eV. In another embodiment, the energy range is about 140 eV. In an embodiment, the second film has a thickness of greater than 10 microns. In one embodiment, the second film has a thickness in the range of about 10 to 20 microns. In one embodiment, the second film has a thickness in the range of about 1 to 5 microns.

An electrolyte third film, e.g., films **61**, **61C** or **73**, having ionic transport qualities but not being electrically conductive (an electrolyte) is deposited so as to completely overlay the second deposited film. In one embodiment, the third film is deposited using a first deposition source and a secondary

source supplying energetic ions to the growing film. In some embodiments, the first deposition source is a physical vapor deposition source. In some embodiments, the secondary source is an ion source with the capability of supplying energetic ions having an energy greater than 5 eV. In another embodiment, the energy range is about 5 eV to about 3,000 eV. In one embodiment, the energy range of is about 5 eV to about 1,000 eV. The energy range in a further embodiment is about 10 eV to about 500 eV. The energy range in a further embodiment is about 30 eV to about 300 eV. In another embodiment, the energy range is in the range of about 60 eV to 150 eV. In another embodiment, the energy of the ions from the secondary source is about 140 eV. In some embodiments, the secondary source includes oxygen (e.g., O_2) or nitrogen (e.g., N_2) gas. The secondary source gas, in another embodiment, includes a noble gas, e.g., argon, xenon, helium, neon, and krypton. The secondary source gas, in another embodiment, includes a hydrocarbon material such as a hydrocarbon precursor. Selection of the secondary source gas is based on the desired effect on the stoichiometry of the deposited film. The secondary source, in one embodiment, provides a focused beam of energized ions. The secondary source, in one embodiment, provides a non-focused beam of energized ions. It is desirable to make the electrolyte, third layer as thin as possible and prevent the cathode and anode layers from shorting. In an embodiment, the third film has a thickness of less than 1 micron. In one embodiment, the third film has a thickness of less than 5,000 Angstroms. In another embodiment, the third film has a thickness of less than 1,000 Angstroms. In another embodiment, the third film has a range of about 10 Angstroms to about 100 Angstroms.

In another embodiment, the third film is deposited using a first source supplying energetic ions (5 to 3000 eV) to a material source (target) at an impingement angle of 15 to 70 degrees and a second source supplying energetic ions to the growing film. The first deposition source includes a beam of focused energetic ions from a source gas. The source gas includes one of the sources gases described herein.

An anode, fourth film, e.g., film **65** or **75** includes from a lithium-intercalation material that is deposited on and overlays the third film but not contacting first film (barrier) or second film (cathode). In one embodiment, the fourth film is deposited using a first deposition source simultaneously with a secondary source supplying energetic ions to the growing fourth film. In some embodiments, first deposition source is a physical vapor deposition source. In some embodiments, the secondary source is an ion source supplying energetic ions from a source gas that includes oxygen (e.g., O_2) or nitrogen (e.g., N_2). The source gas, in another embodiment, includes a noble gas, e.g., argon, xenon, helium, neon, and krypton. The source gas, in another embodiment, includes a hydrocarbon material such as a hydrocarbon precursor. Selection of the secondary source gas is based on the desired effect on the stoichiometry of the deposited film. The secondary source, in one embodiment, provides a focused beam of energized ions. The secondary source, in another embodiment, provides an unfocused beam of energized ions. The energized ions provide energy to the lithium-intercalation material in the range of about 5 eV to about 3,000 eV. In one embodiment, the energy range of is about 5 eV to about 1,000 eV. The energy range in a further embodiment is about 10 eV to about 500 eV. The energy range in a further embodiment is about 30 eV to about 300 eV. In another embodiment, the energy range is in the range of about 60 eV to 150 eV. In another embodiment, the energy range of the ions from the secondary source is about 140 eV.

In an embodiment, the fourth film has a thickness of greater than 10 microns. In one embodiment, the fourth film has a thickness in the range of about 10 to 40 microns.

In another embodiment, the fourth film is deposited by plasma decomposition of hydrocarbon pre-cursor(s) at the surface of the substrate thereby forming a lithium-intercalation anode. In some embodiments, deposition is performed by plasma enhanced CVD using hydrocarbon precursors. In one embodiment, the deposition includes dopants such as N₂. In one embodiment, a secondary source provides energized ions to assist in the deposition of the fourth film. The energized ions provide energy in the range as described herein. In some embodiments, the secondary source is the same as any described herein.

In another embodiment, the anode, fourth film is deposited by direct ion beam deposition of a lithium-intercalation material using hydrocarbon precursors. The first deposition source provides a beam of focused energetic ions (5 to 3000 eV) from a source gas hydrocarbon precursor directed at the target material. In one embodiment, a secondary source supplies energetic ions to assist in growing the fourth film and is a secondary source as described herein.

A contact, fifth film, e.g., film **65** or **77**, which is electrically conductive and does not react with the fourth film is formed in contact with at least part of the fourth film. The fifth film does not contact the second film (cathode). In an embodiment, the fifth film has a thickness of greater than 0.5 microns. The fifth film acts as an anode current collector for contact to external circuitry.

In some embodiments, a passivation, sixth film **79**, which is electrically non-conductive and chemically inert, essentially overlays the energy-storage device as formed thus far, i.e., all the second, third, and fourth films, so that same are packaged and free from environmental contaminants that may react with these films and degrade performance of the energy-storage device. Environmental contaminants may include further fabrication materials for devices with the energy-storage device integrated therewith. In some embodiments, the first and fifth contact films are partially exposed outside the sixth film for connection to circuitry outside the energy-storage device.

The substrate **55**, **309** or **709**, on which the films described herein are deposited, includes any material capable of supporting a thin film and being able to withstand the deposition process described herein. In one embodiment, the substrate is formed of a material having a temperature at which it will begin to degrade due to thermal effects of less than 700 degrees Celsius. A further embodiment includes a substrate having such a temperature at which it experiences thermal degradation of less than or equal to about 300 degrees Celsius. Thermal degradation of the substrate includes loss of shape of the substrate, loss of sufficient rigidity to support an energy-storage device, chemical breakdown of the substrate, cross-linking of materials on the substrate and/or films, melting, and combustion. Examples of substrates include silicon wafers and silicon on insulator structures. Other examples of substrate materials include metals on which an insulator layer is formed prior to formation of the energy-storage device as described herein. In another example, the metal may act as a contact for the energy-storage device with insulator layers electrically separating the electrolyte film, the anode film and the anode contact from the metal substrate. Examples of other materials that have a low thermal degradation temperature that are suitable for fabricating an energy-storage device as disclosed herein include paper, fabrics (natural and synthetic), polymers, plastics, glasses, and ceramics.

The substrate **55**, **309**, or **709** has a form that is applicable to the type of apparatus used to fabricate the energy-storage device according to the teachings herein. One example of the substrate shape is a semiconductor wafer. Other forms of the substrate include elongate webs, weaves, foils, and sheets. It is within the scope of the present invention to provide a substrate having sufficient size on which a plurality of energy-storage devices and/or a plurality of energy conversion devices are fabricated.

One embodiment of the substrate **55**, **309**, or **709** includes a substrate that retains its support characteristics during an in situ temperature treatment. In the in situ temperature treatment, the substrate is placed in intimate contact with a thermally controlled surface, e.g., surface **715**. In one embodiment, the thermally controlled surface is a cooled surface such that heat associated with deposition of any of the films described herein are thermally balanced so as not to thermally degrade the substrate or any other structural element previously formed on the substrate. Thus, in some embodiments, substrates having low thermal degradation temperatures, such as low melting points or low combustion temperatures, are used as substrates in the present fabrication methods. For example, substrates include ceramics, glasses, polymers, plastics and paper based materials. In an embodiment according to the teachings herein, the substrate is a plastic or metal substrate on which a plurality of energy-storage devices is deposited. The substrate is then divided into separate dies having at least one energy-storage device thereon. The dies then can be worked, e.g., cold worked, into a desired shape as dictated by the energy-storage device application.

In another embodiment, the substrate is made of a flexible material, e.g., substrate **709**. The flexible substrate is formed into an elongate roll that is caused to pass over a curved object, which forces the material into intimate contact with the surface of the curved object. The curved object is a thermally controlled device (e.g., device **725** as shown in FIG. 7) to control the temperature of the substrate and balance the effect of heat generated on the substrate and films thereon during deposition. For example, the object is hollow and sealed from the environment of the deposition vessel. In some embodiments, the hollow space is filled with a coolant, e.g., cryogenic gas such as gas obtained from LN₂ or liquid helium, with the coolant being constantly replenished. An area of intimate contact between the substrate and object is coincident and opposite the location of material impingement on the substrate from the deposition source. In another embodiment, the coolant is chilled water that is constantly being replenished. In another embodiment, the curved object is thermally controlled by an electro-thermal cooling apparatus. In another embodiment, the curved object is a drum, which is either stationary or rotatable about its axis in the direction of substrate movement.

In another embodiment, the substrate **55** or **309** is formed of a strip of rigid material. The rigid substrate is made to pass over a cooled, thermally controlled surface. Examples of the cooled surface are described herein. One such example is a cooled surface that is cooled by the release of cryogenic fluid such as liquid N₂ or liquid helium into passages within the body of object having the surface but sealed from the environment of the deposition chamber. Other coolant sources include chilled water, cryogenic gas, and electro-thermal devices.

FIG. 8 shows a photovoltaic cell **800**, e.g., solar cell, that includes a transparent electrode **810**. Transparent electrode **810** includes a transparent supporting film **820** and a transparent, electrically conductive film **830** formed on film **820**.

Examples of supporting film **820** include glass and transparent plastics. In some embodiments, conductive film **830** includes indium tin oxide or tin oxide. In use, light **890**, enters solar cell **800** through the transparent electrode **810**. In some uses of embodiments, light **890** is solar light. A first semiconductor film **840** is positioned in contact with the transparent electrode **810**. A second semiconductor film **860** is positioned in contact with the first semiconductor film **840**, thereby, forming a semiconductor junction **850**. In some embodiments, second semiconductor film **860** includes a bulk, highly doped region **862** and a high quality region **863** adjacent the first semiconductor film **840**. In this embodiment, the junction is formed by the first semiconductor film **840** and region **863**. An electrical contact film **870** contacts the second semiconductor film **860**. First and second conductive leads **880** respectively contact the transparent, electrically conductive film **830** and the electrical contact film **870** to carry power away from the cell.

In some embodiments, the materials and compositions of photovoltaic cell **800** are conventional CdS/CdTe materials such as is described in U.S. Pat. No. 4,207,119, which is incorporated by reference; with the additional processing according to the present invention to anneal or treat the surface (e.g., by ion-assist beam) of the films as they are deposited. In other embodiments, the compositions used are as described in the following publications, each of which is incorporated by reference: R. W. Birkmire et al, "Polycrystalline Thin Film Solar Cells: Present Status and Future Potential," *Annu. Rev. Mater. Sci.* 1997.27:625-653 (1997); T. L. Chu et al, "13.4% Efficient thin-film CdS/CdTe Solar Cells," *J. Appl. Phys.* 70 (12) (15th Dec. 1991); T. Yoshida, "Photovoltaic Properties of Screen-Printed CdTe/CdS Solar Cells on Indium-Tin-Oxide Coated Glass Substrates," *J. Electrochem. Soc.*, Vol. 142, No. 9, (September 1995); T. Aramoto et al., "16% Efficient Thin-Film CdS/CdTe Solar Cells," *Jpn. J. Appl. Phys.* Vol. 36 pp 6304-6305 (October 1997); R. B. King, ed. "Encyclopedia of Inorganic Chemistry" Vol 3., pp 1556-1602, John Wiley & Sons Ltd., (1994).

The brief description of the operation of a heterojunction, photovoltaic solar cell that follows is to illustrate how the methodology of the present invention is applied to the fabrication of heterojunction, photovoltaic solar cells. It is believed that the present invention provides means and methods for fabricating photovoltaic cells having superior efficiency.

In a heterojunction photovoltaic cell, the semiconductor films are formed of different materials. For a rectifying junction, the semiconductor films must also be of different type, that is p or n type. The junction between the two semiconductor films is both a pn junction and a heterojunction. The first semiconductor film on which solar light is incident has a band gap higher than that of the second semiconductor film. The band gap of a semiconductor is the energy separation between the semiconductor valance band and the conduction band. The band gap of this first semiconductor film is chosen so that it corresponds to light in the short wavelength region of the solar spectrum. Photons of light having energy equal to or greater than the band gap of the first semiconductor film are strongly absorbed, but photons of light of energy less than the band gap of the first semiconductor pass through the first semiconductor and enter the second semiconductor film. Examples of materials used for the first semiconductor film include CdS, ZnS, CdZnS, CdO, ZnO, CdZnO, or other wide band gap semiconductors like SiC, GaN, InGaN, and AlGaN. The second semiconductor film is chosen from materials that have band

gaps that correspond well to the long wavelength onset of solar radiation. Materials such as CdTe, CuInSe₂, InP, GaAs, InGaAs, InGaP, and Si are examples of materials for the second semiconductor film.

A "built in" electric field exists at the junction between the two semiconductor films due to the migration of majority carriers from one semiconductor type into the other. That is, electrons from the n-type semiconductor migrate into the p-type semiconductor leaving a net positive charge on the n-semiconductor side of the junction. The converse happens to the p-type semiconductor. Holes from the p-type semiconductor migrate into n-type semiconductor leaving a net negative charge on the p-semiconductor side of the junction. Absorption of a photon in one of the semiconductor films **840**, **860** results in the creation of an electron and a hole. When the photon is absorbed in the vicinity of the pn junction, the built in electric field separates the two carriers in opposite directions, electrons are driven to the n-type material and holes are driven to the p-type film. The separated charges result in a potential difference between the two semiconductor films **840**, **860**. This potential difference is used to drive a current through an external circuit thereby converting solar energy (photons) into electrical energy.

One embodiment of a heterojunction, photovoltaic solar cell is an n-type, polycrystalline CdS film as the first semiconductor film **840** and a p-type, polycrystalline CdTe film as the second semiconductor film **860**. CdS has a band gap of 2.43 eV that corresponds to 510 nm. CdTe has a band gap of 1.44 eV that corresponds to 860 nm. Solar radiation shorter than 860 nm and longer than 510 nm is absorbed in the p-type CdTe semiconductor film **860**. Each absorbed photon creates an electron hole pair. If the minority carrier, the electron in p-type CdTe, has a lifetime sufficiently long so that it can drift to the pn junction and be swept across the junction to the n-type CdS film, the absorbed photon contributes to solar cell photocurrent. Minority carrier lifetimes in p-type CdTe are long, which results in high quantum efficiencies (number of electrons created per number of photons absorbed at a particular wavelength) of ~90% between 860 nm and 510 nm. Most photons absorbed in the CdTe film contribute to the solar cell photocurrent.

Solar light at wavelengths shorter than 510 nm is absorbed in the n-type CdS film and creates an electron-hole pair. Minority carriers in n-type CdS, holes, have short lifetimes. Most photogenerated holes recombine with electrons in the n-type CdS film before they can be swept across the junction to the p-type CdTe film. Recombined electron-hole pairs do not contribute to the solar cell photocurrent. Creation of electron-hole pairs by absorption of solar radiation in the CdS film is detrimental to the overall efficiency of the solar cell. High-efficiency solar cells make the CdS film as thin as possible, ~50 nm, so that some fraction of solar radiation shorter than 510 nm can pass through the CdS film and be absorbed in the CdTe film where the photogenerated electron-hole pairs can be efficiently collected. A problem with this procedure is that, in some embodiments, thinning the n-type CdS film increases the series resistance of the cell, which also decreases the efficiency. Additionally, the CdS film must have some reasonable thickness, ~50 nm, to form a stable pn junction.

The deposition methods according to the present invention are used to enhance the performance of heterojunction solar cells by creating higher quality semiconductor films **840**, **860**. In some embodiments, semiconductor films **840**, **860** have structures that provide sufficiently long minority-carrier lifetimes to allow the minority carriers to be swept across the junction and contribute to the solar cell photo-

current. In some embodiments, higher quality films **840**, **860** are produced by providing energy focused at the surface where a film is being formed. In some embodiments, the energy is supplied simultaneously with the material to be deposited on a substrate. In some embodiments, higher quality films are created by depositing the primary material, for example, CdS in the film **840**, using a physical vapor deposition technique while impinging energized particles from a second source on the film surface during the deposition. In some embodiments, the second source includes an ion source. In some embodiments, the ion source provides a beam of ions. In some embodiments, the beam of ions includes argon or xenon. In some embodiments, the beam of ions includes sulfur for depositing sulfide materials. In some embodiments, the beam of ions includes oxygen for depositing oxide materials. The effect of supplying focused energy is to increase the extent of crystallinity of the material being deposited. Another effect of supplying focused energy is to decrease defects that provide sites for electron-hole recombination. A further enhancement of the solar cell efficiency is achieved by using the focused energy to control the quality of the physical interface between the first semiconductor film **840** and the second semiconductor film **860**.

In an embodiment, the first film **840** is fabricated by providing energy to the material being deposited so that the material has fewer defects. With fewer defects the minority carriers will have longer lifetimes in film **840** as the will be fewer recombination sites. In some embodiments, first film **840** includes an n-type CdS material. In some embodiments, the first film **840** is formed in a range of about 40 nanometers to about 100 nanometers. In some embodiments, the first film **840** has a thickness of about 50 nanometers. In some embodiments, the first film **840** is formed in a range of about 40 nanometers to about 100 nanometers.

In some embodiments, the second film **860** includes two regions **862**, **863**. Region **863** is a high-quality region formed according to the teachings of the present invention. In some embodiments, region **862** is grown in a faster manner using conventional methods. In other embodiments, film **862** is merely a further growth of film **863** using the teachings of the present invention. High quality includes, among other things, fewer defects, larger crystal size, or certain structures being formed. Specifically, energy is supplied to the material of region **863** as the material is formed on the first film **840**. The energy is supplied according to the teachings herein, for example, by an ion-assist beam. In some embodiments, the energy is supplied by energized particles. In some embodiments, the energy is supplied by energized ions. In some embodiments, the energy is supplied by light or heat, e.g., a brief laser sweep of the surface. Due to the application of energy while the region **863** is being formed, a post-deposition high-temperature anneal is not required.

In some embodiments, the high quality region **863** has fewer defects than p-type regions of other photovoltaics. In some embodiments, region **863** has a thickness of at least about 50 nanometers. In some embodiments, region **863** has a thickness in a range of about 50 nanometers to about 100 nanometers.

In some embodiments, region **862** is larger than region **863**. In some embodiments, region **862** has a thickness of greater than 500 nanometers. In some embodiments, region **862** has a thickness in a range of 1 micron to 5 microns. In some embodiments, region **862** has a thickness of greater than 3 microns. In addition, region **862** is a highly doped p-type material.

In some embodiments, a chamber in which the films **840**, **860** are being deposited is held at a temperature of less than 650 degrees Celsius. In some embodiments, the temperature of the chamber is less than about 300 degrees Celsius. In some embodiments, the temperature is between about 30 degrees Celsius and about 275 degrees Celsius. In some embodiments, the temperature is between about 100 degrees Celsius and about 200 degrees Celsius. In an embodiment, the substrate, e.g., glass layer **820** and conductor layer **830** for depositing film **840**; glass layer **820**, conductor layer **830**, and film **840** for depositing region **863**; and glass layer **820**, conductor layer **830**, film **840**, and region **863** for depositing region **862**, is not externally heated. Thus, the temperature of the substrate is generally equal to the temperature of the chamber plus minor heating effects of depositing the film. In contrast to prior methods for fabricating layers having sufficient quality such that the cell approaches about 10 percent efficiency, an embodiment of the present invention does not heat the substrate. Accordingly, manufacturing efficiencies are achieved while maintaining sufficient efficiency.

It is believed that some embodiments of the present invention will have conversion efficiencies of greater than about 5 percent. It is believed that some embodiments of the present invention will have conversion efficiencies of greater than about 6 percent. It is believed that some embodiments of the present invention will have conversion efficiencies of greater than about 7 percent. It is believed that some embodiments of the present invention will have conversion efficiencies of greater than about 8 percent. It is believed that some embodiments of the present invention will have conversion efficiencies of greater than about 9 percent. It is believed that some embodiments of the present invention will have conversion efficiencies of greater than about 10 percent. It is believed that some embodiments of the present invention will have conversion efficiencies of greater than about 11 percent.

Other embodiments for fabricating energy conversion devices, such as a photovoltaic cell **800**, are fabricated according to many of the embodiments described herein with reference to energy storage devices. The thin films of the energy conversion devices are improved in a similar manner as described herein for the thin films of energy storage devices.

In contrast to some conventional methods for improving performance of a photovoltaic cell, the present methods can produce photovoltaic cells having an enhanced conversion efficiency without heat treating during deposition, e.g., heating the substrate, or a post-deposition high temperature anneal.

FIG. 9A shows a thin-film energy-storage device **910A** according to the teachings of the present disclosure and an integrated circuit **940**, here shown as a "flip chip". Energy-storage device **910A** includes substrate **920** on which is formed a patterned wiring layer **922**. The wiring layer **922** is an electrically conductive layer for connecting energy-storage device **920** to the integrated circuit **940**. In some embodiments, layer **922** is formed of a metal. In one embodiment, the wiring layer **922** is patterned copper. In another embodiment, the wiring layer is formed of nickel. In other embodiments, the wiring layer is formed of a noble metal. Wiring layer **922** includes a cathode wiring pattern **922A** and an anode wiring pattern **922B**, which are separate from each other and form opposite polarity connectors **923A** and **923B** to external circuitry, such as integrated circuit **940**. Device **910A** further includes a cathode contact film **924** formed on at least a portion of cathode wiring pattern **922A**.

25

and an anode contact film 926 formed on at least a portion of the anode wiring pattern 922B. A cathode film 927 is formed on the cathode contact film 924 according to the teachings herein. An electrolyte film 928 is formed over the cathode film 926, cathode contact film 924 and a portion of the cathode-wiring pattern 922A. Electrolyte film 928 separates the cathode films 922A, 924 and 927 from respective anode films 922B, 926 and 932. Anode film 932 is formed on the electrolyte film and in contact with the anode contact film 926 according to the teachings herein. It will be appreciated that, in one embodiment, cathode contact film 924 and cathode wiring pattern 922A are formed as a single layer. It will be further appreciated that, in one embodiment, anode contact film 926 and anode wiring pattern 922B are formed as a single layer. A passivation layer 934 is formed over all of the films except portions 923A and 923B of the wiring patterns 922A and 923B, which portions are left exposed. Passivation layer 934 protects the films from contact to other layers, which may be formed on substrate 920, and the environment, which may include elements that may react with and damage the films of the energy-storage device 910A.

In some embodiments, the cathode materials and other materials used in the batteries above include materials discussed more in N. J. Dudney et al, "Nanocrystalline $\text{LiMn}_{1-x}\text{O}_4$ Cathodes for Solid-State Thin-Film Rechargeable Lithium Batteries," Journal of the Electrochemical Society, 146(7) 2455-2464 (1999) which is incorporated by reference.

The integrated circuit 940 includes a first ball contact 941 and a second ball contact 942 both extending outside a package. The first ball contact 941 aligns with the exposed portion 923A of the cathode wiring pattern 922A. The second ball contact 942 aligns with the exposed portion 923B of the anode wiring pattern 922B. Integrated circuit 940 is positioned so that the ball contacts 941 and 942 physically and electrically contact the wiring contacts 923A and 923B, respectively. Integrated circuit 940 is fixed in position relative to the device 910A such that device 910A provides electrical energy to circuit 940. In some embodiments, circuit 940 is provided with circuitry for recharging energy-storage device 910A. It will be recognized that the present invention is not limited to only integrated circuit 940 being connected to wiring contacts 923A and 923B. Other circuits, including integrated circuits fabricated on substrate 920 and circuits with leads connected to wiring contacts 923A and 923B, are within the scope of the present invention.

FIG. 9B shows another embodiment of the thin-film energy-storage device 910B, substantially similar elements to those described above are designated by the same reference numerals. After forming wiring patterns 922A, 922B, an insulator layer 930 is formed on the substrate 920. Insulator layer separates the thin-film energy-storage device 910 from other layers that may be included with substrate 920. Insulator layer 930 includes vias 931 through which cathode contact film 924 and anode contact film 926 extend downward to connect to cathode contact wiring pattern 922A and anode wiring pattern 922B, respectively.

In one example of an energy-storage device 910 according to the present invention, the cathode film 927 is a LiCoO_2 deposited using a first source of LiCoO with a secondary source of oxygen. The electrolyte film 928 is LiPON deposited using a first source of LiPO (such as Li_3PO_4) and an assist of nitrogen. The anode film 932 is a metal, e.g., copper, and is deposited by a first source of copper and a secondary source of an inert material, e.g.,

26

xenon. In another embodiment, the anode film includes carbon. In yet another embodiment, the anode is formed of pure lithium. In some embodiments, the anode is a lithium alloy. In some embodiments, the anode includes an oxide.

FIG. 9C shows a further embodiment of a thin-film energy-storage device 910C. This device 910C includes a seed layer 950 formed on the cathode contact 924. Seed layer 950 is formed on the cathode contact 924 prior to forming the cathode film 927, as described herein, on the seed layer 950 and substrate 920. Seed layer 950 is formed using deposition techniques as described herein, e.g., physical vapor deposition such as arc source deposition. Seed layer 950 is a very thin, electrically conductive layer and has a small crystal size. The seed layer 950 also has a high sheet resistance and is non-reactive with the materials of adjacent films. In an embodiment, seed layer 950 has a thickness that is substantially thinner than the adjacent electrode film 927. The material of the seed layer 950 is chosen such that the arriving adatoms of the subsequent material (e.g., in some embodiments, the material from the first source 311, 511 or 711) would have sufficient mobility to allow a period of activity once the adatom contacts the seed layer surface. This improves nucleation of the first few molecular layers of arriving material, minimizes strain associated with lattice mismatch and assists the arriving material to grow in a manner consistent with the desired crystal structure for cathode film 927.

In some embodiments, a seed layer 955 is formed on the electrolyte layer 928 prior to forming anode film 932, as described herein, on the seed layer 955. Seed layer 955 improves nucleation of the first few molecular layers of arriving material, minimizes strain associated with lattice mismatch and assists the arriving material to grow in a manner consistent with the desired crystal structure for anode film 932.

The ion transport properties of the materials used in the fabrication of energy-storage devices 910C, e.g., rechargeable batteries, greatly influence the operation and quality of the device. For example, the total energy-storage capability of solid-state, lithium-ion batteries of a given area is limited by a depletion region that forms at or near the cathode/electrolyte interface. The depletion of this region and the inability for additional lithium ions to be transported out of the bulk of the cathode film 927 results in limited capacity and, thus, more frequent recharges. Additionally, the efficiency of the lithium ion transport through the electrolyte film 928 controls and dictates the maximum discharge rate that can be achieved for a given structure. The seed layer 950 improves the crystalline structure of the materials subsequently deposited, i.e., a cathode film 927 or an anode film. The growth of the first few atomic layers of a material significantly impacts its overall structure even when the final film is very thick relative to the initial few atomic layers. If the "seed" material is chosen such that the surface energy kinetics are conducive to pseudo-epitaxial growth of the subsequent material, high quality cathode and anode (electrode) films 927 and 932 are achieved. Examples of materials for seed layer 950 include chromium, chromium nitride, tantalum, tantalum nitride, tungsten, tungsten nitride, ruthenium and ruthenium nitride.

The thin-film energy-storage device fabricated according to the present teachings stores electrical energy by introducing ions into a storage layer and removing the ions from the storage layer to create an electrical potential at the contacts. In one embodiment, lithium ions are stored in an anode formed of a lithium-intercalation material with the battery in a charged state. In some embodiments, the anode is formed

of a metal or a carbonaceous material. The lithium ions travel from the anode through the electrolyte layer to a cathode, which is also formed of a lithium-intercalation material, to discharge electrical energy from the battery. In order to achieve sufficient energy density to operate external circuitry, the lithium-intercalation material cathode and anode must intercalate (i.e., add) and de-intercalate (i.e., remove) of a substantial mole fraction of lithium ions. It has been found that the choice of intercalation material and fabrication techniques for the cathode determine many operating parameters of a solid-state, thin-film battery. The operating parameters include, but are not limited to, operating voltage range, capacity, specific power, and specific energy. One method of measuring the transport properties of ions in a battery is diffusivity, which is measured by a diffusion coefficient. The diffusion coefficient is a measure of how well a particular material allows ions to diffuse into and out of the material.

FIG. 10 shows comparative data for LiCoO₂ cathode films in the form of X-ray diffraction spectra. The LiCoO₂ cathode films were created according to the teachings herein and according to a control process that did not include a secondary source assist. A first source supplied a LiCoO₂ material using an electron-beam evaporation process. An assist, second source provided energy in the form of oxygen ions impinging at the location on the substrate whereat it is desired to grow a thin electrode (cathode) film from the LiCoO₂ first material. The beam of oxygen ions from the second source is not co-incident with the LiCoO₂ material from the first source. Four samples of LiCoO₂ thin films were grown according to the data in Table I.

TABLE I

Deposition Parameters	Film a	Film b	Film c	Film d
Electron beam power* (W)	500	500	500	500
Total gas flow, O ₂ + Ar, (sccm)	0	10.8	10.8	10.8
O ₂ gas ratio, O ₂ /(O ₂ + Ar), (%)	NA	0.48	0.48	0.48
Chamber pressure (Torr)	9.2×10^{-7}	2.6×10^{-6}	3.7×10^{-6}	5.0×10^{-6}
Ion source power (W)	0	123	128	135
Ion source acceleration voltage	0	41	64	135

The electron beam voltage for each first source used in forming films a-d is 5 kV with an emission current of 100 mA.

FIG. 10 shows that the LiCoO₂ films deposited with lower energy oxygen ions from the second source, samples "b" and "c", enhanced the formation of the desirable crystallite structure of the grown film relative to the non-assisted sample "a". Specifically, a more distinct (003) orientation of the crystal structure is found in ion-assisted samples "b" and "c" than in non-assisted sample "a". A strong (003) X-ray diffraction peak indicates one desired crystal orientation of the LiCoO₂ thin film. The (003) X-ray diffraction peak indicates that the film has lattice planes parallel to the substrate, e.g., layer on which the film was deposited. The (003) peak width, full width at half maximum ("FWHM") decreases and the X-ray peak increases in this series of samples as the energy of the oxygen ions impinging the deposited material increases. These examples indicate an increasing crystallite grain size and a larger fraction of ordered grains for sample films "b" and "c" than are found in sample film "a". The (003) orientation of samples "b" and

"c" is preferable over an essentially non-ordered, non-crystallized structure of sample "a".

FIG. 10 further shows a sample "d" that was deposited using the highest energy secondary source of this example. Sample "d" was deposited using a secondary source energy of 135 eV. X-ray diffraction of sample "d" shows it has the most distinct (101) orientation of all the samples described herein. The desired (101) orientation has lattice planes, which contain lithium ions in a LiCoO electrode material, nearly perpendicular to the substrate. In this orientation, the lattice planes are essentially parallel to the direction of travel of the ions and in the direction nearly perpendicular to the substrate. As this is the direction lithium ions must travel in a lithium battery fabricated according to the embodiments described herein, the preferential (101) orientation leads to superior charging and discharging characteristics. As lithium transport through the LiCoO₂ film in the (101) preferential orientation does not rely on diffusion along grain boundaries, which can trap lithium ions and prevent their utilization, the preferential (101) orientation also leads to greater capacity and cycle lifetime. Consequently, this preferred orientation of the LiCoO₂ thin film is produced without additional anneal fabrication steps and the internal resistance is lower with lower capacity loss at high discharge rates.

FIG. 11 shows a comparison of the (003) x-ray diffraction peak of an ion assisted LiCoO₂ film fabricated according to the teachings of the present invention and a conventionally magnetron sputtered LiCoO₂ film. Both spectra are for as-deposited films. The ion assisted LiCoO₂ film in this spectrum is the same as the "c" sample shown in FIG. 10. The sputtered LiCoO₂ film was fabricated in an MRC 8667 using 1200 watts RF power, 10% O₂ in Argon, 80 sccm total gas flow (8 sccm O₂ and 72 sccm Ar), 20 mTorr pressure, with the substrate table grounded. Film thickness of the sputtered LiCoO₂ film is 5460 Angstroms. The significantly sharper peak for the ion-assisted film indicates the higher degree of long range order in this film. The peak width for this film is approaching that obtained by high temperature annealing of a similar conventionally magnetron sputtered film and exceeds that achieved for 300 degree Celsius annealed films of LiMn₂O₄. Accordingly, the LiCoO₂ film fabricated according to the teachings of the present invention provides a higher degree of order than conventional LiCoO₂ films without resorting to a post deposition anneal step to provide the desired crystal structure in the film. This results in significant manufacturing efficiencies.

FIG. 12A shows a X-ray diffraction spectra of a LiCoO₂ layer fabricated according to a conventional method of magnetron sputtering without the subsequent anneal step. The magnetron sputter was performed in MRC 8667 sputter, with 1200 W of RF power, in an environment of argon with 10% oxygen and 80 sccm total gas flow, at a pressure of 20 mTorr. The resulting film thickness is 5460 Angstroms. The x-ray peak full width at half maximum ("half height width") of the peak at 19 degrees of this conventional sample is 2.61 degrees. The half height width is a measure of the crystallite size, which can be calculated from this data as according to known formulas. The crystallite size for this conventionally magnetron sputtered film is 34 Angstroms. This conventional film must be annealed at high temperature to achieve sufficient crystallite size to have adequate electrical properties such that the film is part of a functional and practical battery.

In other conventional film materials, like LiMn₂O₄, nanocrystalline structures have been sputtered into films and prior to their anneal they have a crystallite size of about 40 Angstroms to about 50 Angstroms. Annealing this film at a

temperature of about 300 degrees Celsius produces a crystallite size of about 130 Angstroms to about 160 Angstroms. In some embodiments of the present invention, these crystallite sizes are achieved at the time of deposition. Moreover, in some embodiments, superior crystallite sizes are achieved at the time of deposition.

FIG. 12B shows an X-ray diffraction spectrum for a LiCoO_2 film fabricated according to the teachings of the present disclosure. Specifically, this film was deposited using a first source and a secondary source of energized ions as discussed above with respect to samples "b" and "c" of FIG. 11. The peak for the ion assisted deposition film is significantly higher than the non-assisted spectra of FIG. 12A. This indicates a higher degree of long range order in the ion assisted deposition film. The half height width of the peak of the ion-assisted film at 19 degrees is 0.45 degrees. The crystallite size is 242 Angstroms. Accordingly, the present fabrication techniques yield an as deposited film having a crystallite size of greater than seven times that of the conventional deposition methods without post-deposition anneal. Moreover, the present fabrication techniques yield a superior crystallite size even when compared to the conventional film after it has been annealed. The present fabrication technique yields a factor of crystallite size improvement of about a 1.8 to about a 2.6 over the conventional technique. Consequently, the present fabrication method can thus achieve superior crystallite size in the film as they are deposited resulting in faster, more efficient fabrication of thin-film batteries. Such an improved crystallite structure is highly desirable in the cathode film due to the limitations imposed on energy storage in thin-film batteries due to cathode film performance.

Another aspect of the present fabrication method is the ability to fabricate thin films at essentially room temperature with a crystalline orientation that is essentially perpendicular to a boundary with adjacent films and crystallite size. Ions must travel through these boundaries to charge and discharge the battery. The boundaries include a first boundary that is between the cathode film and the electrolyte film and a second boundary that is between the electrolyte film and the anode film. The crystallite orientation is preferably perpendicular to the boundary planes. That is, the lithium ion lattice planes are parallel to the lithium ion direction of travel during charging and discharging the thin-film battery. This orientation lowers the internal battery resistance and lowers capacity loss at high discharge rates. The crystallite size is preferably large, e.g., over 100 Å, and more preferably over 200 Å. The larger the crystallite size improves electrical properties. Crystallite size is strongly correlated to the ion diffusion coefficient, a measure of how freely lithium ions can be added to, or extracted from the intercalation material.

While the above-described embodiments focus on lithium-intercalation materials and, more specifically, LiCoO_2 , it will be recognized that the some embodiments are adaptable to other intercalation materials for producing energy-storage devices. Other types of intercalation material include LiMn_2O_4 , V_2O_5 , and carbonaceous materials, lithium, lithium alloys, oxides, and nitrides

Using the fundamental teachings herein, i.e., the in situ assist of the growing film with appropriate energy and/or species of ionized gasses, processes involving the manufacture of photovoltaic panels, supercapacitors/ultracapacitors, and fuel cells could be made more robust and efficient. A corresponding cost, fabrication efficiency, and performance advantage can be gained.

For example, Solid Oxide Fuel Cells (SOFC) require the manufacturer to deposit a ceramic material on a support structure. See U.S. Pat. No. 6,007,683, incorporated herein by reference. This ceramic is then coated with a conductive material such as platinum, which is the catalyst for the fuel cell. The cost of these materials and the efficiency with which they conduct the appropriate ions from one side of the cell to the other determines, in large measure, the cost of manufacture and operation of the fuel cell. The application of the techniques described herein to a fuel cell manufacturing process would yield substantially higher quality catalyst with higher ionic transport capability. Moreover, the present techniques further provide the ability to produce a thinner catalyst by virtue of the structural properties of materials deposited via the methods described herein. This allows lower temperature operation of the fuel cell, thus, widening product latitude.

Supercapacitor/ultracapacitor performance is also enhanced by the application of the present techniques. See e.g., U.S. Pat. No. 5,426,561, incorporated herein by reference. High energy density and high power density ultracapacitors and supercapacitors are improved by reduction in crystalline defects and improvement in the growth mechanism such that the electrolyte layer could be significantly thinned. This thinning improves the volumetric energy density of the device. The improved crystal structure enhances the voltage stability of the electrolyte.

While some of the above embodiments include an ion source for providing the focused energy to arriving adatoms at a surface of a substrate to form films having fewer defects and/or certain crystal properties, other source of the focused energy are within the scope of some embodiments of the present invention. Examples of such other sources include high intensity photo sources, lasers, short duration, high intensity (flash) heat sources, short duration plasma sources. Each of these sources provides the required energy to a film and does not harm previously deposited layers, previously connected devices, or the substrate. In some embodiments, these sources provide the energy to the adatoms as they arrive at the surface on which the adatoms will form a film.

By way of introduction, one aspect of the invention deals with the field of batteries and, more specifically, to the use of a thin film battery for enclosures for devices and also for devices which include an integrated battery.

FIG. 13 is an exploded perspective view of an electronic device 1000 having a separate printed circuit board 1010 and a separate battery 1020. The enclosure 1000 typically includes a first portion 1001 and a second portion 1002. The first portion 1001 may also be termed as a bottom portion and typically may include pegs 1011 upon which the printed circuit card 1010 rests. The pegs 1111 are also used to position the printed circuit card 1010 with respect to the bottom portion 1001 of the enclosure 1000. In addition, there are typically several other sets of stops 1112, which are used to position the battery 1020 with respect to the bottom portion 1001 of the enclosure 1000. The second portion 1002 will include openings 1030 and 1032. The opening 1032 may be for a display such as an LCD or liquid crystal display (not shown in FIG. 13). The opening 1030 is typically for an access panel 1040, which fits within the opening 1030. The access panel 1040 provides access to the battery 1020. The printed circuit board 1010 includes a battery connector 1022, which fits over the terminals of the battery 1020. The battery connector 1022 provides an appropriate amount of current to the electrical components on the printed circuit board 1010. The second portion 1002 of the enclosure 1000 includes several plastic hooks, which are

31

used to mate the second portion **1002** with the first portion **1001** to form the enclosure **1000**. The prongs or hooks **1050** fit within corresponding slots **1052** on the first portion **1001** of the enclosure **1000**.

These enclosures are typically made of plastic, and housed within the enclosure **1000** is a separate battery **1020** and a separate printed circuit board **1010**. These particular types of devices have several problems. First of all, the whole housing or enclosure, or at least a portion of it, has to be removed in order to replace a battery or in order to recharge a battery. The batteries **1020** typically include a gel-type electrolyte which can be very toxic and dangerous and, for that reason, difficult to dispose. From a manufacturing standpoint, there is a need to assemble many parts, including the separate circuit board **1010** and a battery **1020** and an LCD (not shown). These also must be accurately placed within the first portion **1001** to produce a quality-looking enclosure **1000** for the entire electrical device. Each time a separate component must be placed together or into one portion or a first portion of the device requires an additional process step. In addition, mating the second portion **1002** of the enclosure **1000** with the first portion **1001** is still a further process device. From a manufacturing point, it would be advantageous if there were less process steps involved in manufacturing an electronic device such as the one shown. With less manufacturing steps, the device can be made more simply and more cost effective.

Still a further disadvantage is that the separate components, such as the separate printed circuit card **1010** and the separate battery **1020**, require a lot of space in terms of the enclosure. The tendency these days is to form electronic products or electronic devices that save on space. In most instances, a smaller electronic device is better than a larger electronic device. Therefore, there is a need for a process that can reduce the number of process steps and save on space and yet produce a reliable battery and circuit for an enclosure.

The above-described method (see FIGS. 1–12) for placing a battery onto a substrate can be used in many different ways in devices to produce a more compact and reliable electronic package having a battery which is capable of being recharged a very large number of times. The batteries and electronics could be placed directly onto an enclosure portion therefore saving space. As a result, the design of the various electronic devices could be smaller than corresponding devices that are currently used.

FIG. 14A is an exploded perspective view of a portion of an enclosure that includes both a battery **1110**, which is deposited directly onto the enclosure portion **1100**. The enclosure portion **1100** includes an interior surface **1101** and an exterior surface **1102**. In this particular embodiment, the battery **1110** is deposited onto the interior surface **1101** of the enclosure portion **1100**. It should be noted that the enclosure portion **1100** resembles the first portion **1101** or the bottom portion, as shown in FIG. 13. The interior **1101** of the enclosure portion **1100** also includes a plurality of traces **1120** for electrically coupling the battery **1110** to various electronic components **1130**, **1131**, which are attached to sites **1140** and **1141**. The sites **1140** and **1141** include the electrical contact pads for electrically connecting the electrical components **1130** and **1131** to the sites **1140** and **1141**. The pads associated with the sites **1140**, **1141** are also directly deposited onto the interior surface **1101** of the enclosure portion **1100**. Advantageously, the battery **1110** can be deposited onto the interior portion **1101** of the enclosure portion **1100** as well as the traces **1120** and the pads associated with the sites **1140** and **1141**. Advanta-

32

geously, in order to complete an electronic circuit, the only process steps that need to be accomplished are to add the electronic components **1130** and **1131**. In some instances it also may be possible to produce some of the electronic components during the manufacturing steps required to place the thin film battery **1110** onto the interior portion **1101** of the enclosure **1100**. Optionally, a protective layer **1150** may be placed over the battery **1110** or other select portions deposited on the interior surface **1101** of the device enclosure **1100**. The optional protective layer is shown in phantom and is referenced by reference numeral **1150**.

FIG. 14B is an exploded perspective view of a portion **1100** of an enclosure for an electronic device according to another embodiment of this invention. The enclosure portion **1100** includes an interior and an exterior surface **1102**. In this particular embodiment, the battery **1110** is deposited on the exterior surface **1102** of the enclosure portion **1100**. The battery **1110** includes a post **1160** for the cathode and another post **1162** for the anode. The posts **1160** and **1162** terminate or attach to through holes **1161** and **1163**. The through holes **1161** and **1163** provide electrical communication to various components located inside the enclosure portion **1100**. In essence, the chief difference between the embodiment shown in FIG. 14A and the embodiment shown in this FIG. 14B is that the battery portion **1110** is deposited on the exterior surface **1102** of the enclosure portion **1100**. A protective coating **1150** may be placed over the battery portion **1110** and, more specifically, over the battery portion **1110** and the electrical posts **1160** and **1162** and the through holes **1161** and **1163**. The protective layer **1150** may be translucent or may be colored to match the exterior surface **1102** of the enclosure portion **1100**.

FIG. 14C is an exploded perspective view of a portion of enclosure **1103** for an electronic device according to yet another embodiment of this invention. The enclosure portion **1103** includes a battery **1110** that is deposited on the interior surface of the enclosure portion **1103**. The enclosure portion **1103** includes an interior portion **1101** and an exterior portion **1102**. The enclosure portion **1103** corresponds to a top portion including a display that can be viewed by the consumer during use. The battery **1110** is deposited on the interior surface **1101** of the enclosure portion **1103**. Also included are traces **1120** as well as electronic components **1130** and **1131**. Completing the circuit is an LCD or liquid crystal display **1170**. The LCD is positioned near or at an opening in the enclosure device **1103** so that the readable portion of the LCD **1170** can be viewed from the exterior surface **1102** of the enclosure portion **1103**. Enclosure portion **1103** roughly corresponds to the second enclosure portion **1102** or on top of the electronic device shown in FIG. 13.

An addition to depositing a device or a battery device or energy device **1110** onto the surface of an enclosure, another embodiment of this invention is to produce a sheet including multiple cells or batteries **1110**. The batteries **1110** are formed on a sheet of flexible or plastic material **1300**. It should be noted that the size of the cells **1110** and the placement of the cells or individual batteries **1110** can be varied for producing various different sizes and styles of formed batteries.

FIGS. 15A through 15E disclose a method whereby the battery is formed into a conformed or conformable sheet having roughly the same shape as either the interior or exterior surface of an electronic device. The conformed sheet can then be placed or adhered directly to the interior surface or exterior surface of an electronic device. The sheet is produced with a number or plurality of cells **1110**, as will

33

be discussed later in this application. Once the sheet is formed as described later in this application, the sheet **1300** is diced into individual cells or individual battery portions **1310**. In other words, a battery **1110** will be formed on a dice sheet **1310** from the main sheet **1300**. The individually diced battery portion **1310** can then be formed into a variety of shapes, as shown by FIGS. **15C**, **15D** and **15E**. These shapes can be any desired shapes. In some embodiments or in most embodiments, the shape of the sheet will conform or will be able to be placed on the interior or exterior surface of an electronic device. FIG. **15C**, for example, shows a roughly square battery that has folded up sides or vacuum formed sides **1320**. This particular device could be placed on the interior surface of an electronic device such as a garage door opener or any other like device.

FIG. **15D** shows a more rectangular portion or diced sheet which resulted from a more rectangular battery laid down upon a sheet and diced into an individual battery portion **1310**. This more rectangular formation may be glued or adhered to the inner surface of an electronic enclosure for a personal data assistant. In the alternative, the form shown in FIG. **15D** may also be suitable for placement on the exterior surface of an electronic device, such as a portable data assistant.

FIG. **15E** shows a more formed device that might be found on a cell phone or similar device. FIG. **15E** may be formed to fit on the interior surface of a cell phone or the exterior surface of a cell phone or calculator. In other words, a diced sheet **1310** is used as a starting point for vacuum forming or for otherwise forming a battery that can be attached either to the interior or exterior surface of an electronic device. An electronic device to which it is attached can be anything including hearing aides, calculators, personal data assistants, smart cards or other credit card, watches, laser pens, power tools, surgical devices or even catheters. The list above is not exhaustive but is merely set forth as examples of the type of the devices that may include a battery shown and formed in FIGS. **15A** through **15E**.

In some instances, it may be advantageous to include a battery having multiple cells **1110**, **1110'** and **1110''**. In this particular instance, a dice is made **1320** that includes cells **1110**, **1110'** and **1110''**. The sheet can also be formed with fold lines **1321** and **1322**, as shown in FIG. **15G**.

FIG. **15H** shows that the batteries have been folded along the fold lines to form a stack of three batteries **1110**, **1110'** and **1110''**. The folds shown in FIG. **15H** are a fan fold. Once the fan fold is formed, as shown in FIG. **15H**, the fan folded battery, including three cells **1330**, can be formed in any desired shape, such as square-sided shape **1503** of FIG. **15C**, angle-sided shape **1504** of **15D** and curve-sided shape **1505** of **15E**. The three-celled or multi-celled unit **1330** can be adhered to the interior or exterior surface of any electronic device, as discussed above. It should be noted that the fan fold can include more than three batteries or less than three batteries. The inventive aspect is that it includes a plurality of batteries. The cells **1110**, **1110'** and **1110''** can be attached to one another so that the cells are in series after they are diced. Another possibility is that the electrical contacts for each of these could be put in contact with one another as a result of fan folding the multi-celled unit **1330**.

FIGS. **15I**, **15J** and **15K** show yet another embodiment of the invention. In this particular embodiment of the invention, the sheet of electrical cells **1300** includes a plurality of cells including **1110** and **1110'**. The entire sheet **1300** is then vacuum formed to form more or less an egg carton **1350** with individual battery cells **1110** and **1110'** being formed

34

within well **1360** and **1362** in the sheet **1300**. Between the wells **1360** and **1362** is a living hinge **1370**. The batteries **1110** and **1110'** are at the bottom of each well **1360** and **1362**, as shown in FIG. **15K**. The living hinge **1370** is positioned between the two wells **1360** and **1362**. The first cell **1360** can be folded on top of the second well **1362** to form an electronic device enclosure **1380**, as shown in FIG. **15L**. It should be noted that the size of the battery portions **1110** and **1110'** can be limited or placed so that other traces and room for other electronic devices can be added so that a total circuit can be formed within a disc enclosure. This provides for an advantage that wherein the electronic component could be directly placed into the wells **1160** and **1162** at sites formed at the same time as the batteries were deposited onto the sheet **1300**. After placing all the various electronics, the electronic device can be formed merely by dicing two of the wells **1360** and **1362** so that they form a top and bottom of the device enclosure **1380**. All sorts of electronic devices could be included, including an LCD or other display device. The LCD may be readable directly through a sheet if it is transparent or the sheet, or one of the wells **1360** and **1362**, may be provided with an opening that would correspond to an opening or face of the display of an LCD or other display device. Thus, the sheet and the deposited battery thereon can ultimately become the exterior surface or the enclosure for the device formed on the sheet. This has a great advantage in that the process steps necessary to form a device are or can be quite easily and efficiently done in a continuous process. This would lead to very efficient manufacturing of electronic devices.

FIG. **16A** is a plan view of a sheet including a plurality of cells **1110** according to this invention. FIGS. **16A**, **16B** and **16C** show a way to form a laminated battery cell and possibly laminated battery cell and electronics for a smart card or other invention that includes a battery and electronics within a card. The sheet **1300** shown in FIG. **16A** includes cells **1110**. The sheet also includes fold lines **1390** and **1392**. The sheet **1300** is diced into individual sections, which include fold lines **1390** and **1392**, as well as a battery cell site **1110**. The battery cell site might also include electronics that are also deposited with the battery or energy source onto the sheet **1300**. The diced portion **1400** includes one portion including the cell **1110** and two blank portions **1402** and **1403**. The diced portion **1400** is then fan folded, as shown in FIG. **16C**. Once a fan fold has been formed, the cell portion **1110** is captured between the two unpopulated sheet portions **1402** and **1403** and will provide an extra protective layer. The excess portions of the sheet **1300** can be trimmed, as shown in FIG. **16D** to produce a smart card or card including both a battery **1110** and electronic, as shown as item **1600E** in FIG. **16E**.

FIG. **17** is an exploded perspective view of a diced portion of a sheet **1300** which includes one battery cell **1110** rolled around an electrical motor **1500**. In this case, the diced portion, which includes a cell **1110**, is an elongated strip **1510** from the original sheet **1300**. The elongated strip **1510** may include several batteries placed in series or one elongated battery that is laid down as a strip on the sheet **1300**. The electrical motor is electrically connected to the anode and cathode of the battery and then rolled on to the electrical motor **1500**. In this case, the strip **1510**, on which the battery has been deposited, becomes the case for the electrical motor or also can be viewed as being a part of the case of the electrical motor. The electrical motor can be provided with a sprocket **1520** that is used to drive another gear **1530** having a shaft **1532** attached thereto. As shown in FIG. **17**, a chuck **1540** is placed upon the shaft **1532** to form a drill

35

or other power tool. Advantageously, the power tool could be light and compact, as well as being capable of being recharged a multiplicity of times. The power tool could be a hand held drill for homeowner use or a smaller device, such as a Dremel-brand rotary hand tool.

FIGS. 18A, 18B, 18C and 18D show several other embodiments of an LED light device in which the diced portion of a sheet 1300 becomes the outside case for the pen light or light device.

FIG. 18A is a planned view of a diced battery cell 1600 which includes a battery or energy device 1110 and a switch 1602 and an LED 1604. The switch 1602, battery 1110 and the LED 1604 form a flashlight or LED lighting device. The sheet, including the diced battery cell and LED, is rolled across its shorter distance starting at the end including the LED 1604. The LED is merely rolled into the battery and the battery is formed around the first roll to form a spiral, as shown in FIG. 18B.

FIG. 18B is a perspective view of the diced battery cell and LED after it has been formed into a lighting device in which the sheet 1600 in which the battery is deposited becomes an outer case. The LED can be activated by enabling the switch 1604. By enabling the switch 1604, the LED can be turned on. The sheet 1600 acts as an outer case of the lighting device formed 1620.

FIGS. 18C and 18D show another embodiment of the invention for a lighting device. In this particular embodiment, again a strip 1600 is provided with a switch 1602 and an LED 1604. In this particular embodiment, the LED is positioned so that it extends beyond the length of the sheet 1600. In this particular embodiment, the sheet 1600 is rolled along its longer dimension around the LED 1604 to form an elongated case having the LED 1604 at one end of the case and a switch 1602 at the other end of the case. This forms a light emitting diode light 1630 in which the sheet 1600 is part of the case.

FIGS. 19A, 19B and 19C, in some instances, is necessary to keep the battery portions 1110 and 1110' of a power source or energy source flat and not curved when it is formed.

FIG. 19A shows a sheet 1300 which includes a plurality of individual cells such as 1110 and 1110' which are an elongated strips and include fold lines, such as 1710. FIG. 19B is a plan view of a diced strip 1700 including a plurality of battery cells 1110, 1110' and 1110". It should be noted that the battery cells 1110", which are located near one end of the strip 1700, are smaller than the battery cells formed at the other end of the strip 1700. For example, battery cell 1110" has a very thin width while the battery cell 1110 is roughly more rectangularly shaped. The strip 1700 is folded successively along fold lines 1710 to form a box of cells, as shown in FIG. 19C. The smaller cells 1110" are in the inside or inner core of the box while the larger cells 1110 form the outer sides of the box. Each of the cells 1110, 1110' and 1110" and the cells in between those particular cells are placed in series with one another. The end result is a cubically formed battery cell 1720, as shown in FIG. 19C.

FIG. 20 is a cutaway side view of an enclosure portion that includes a sheet having a plurality of battery cells. It should be noted that we have discussed thus far that a sheet of battery cells, such as the one shown in FIG. 15H, can either be placed on the outside surface of an enclosure or on the inside surface of an enclosure or it can be formed or deposited upon an inside or outside surface of the enclosure. FIG. 20 shows that an enclosure portion 1800 having an interior surface 1801 and an exterior surface 1802 can be injection molded around a battery formed on a sheet. The battery could be a single battery, as is shown in FIG. 15B,

36

or it could be a multi-celled battery, as shown in FIG. 15H. In other words, a sheet 1820 including one or more, or at least one battery cell 1110 formed by the above methods, could be held within a mold and a suitable plastic could be injection molded about or around the battery cell 1820. The mold could also include pins that electrically connect the battery 1820 to the interior surface 1801 of the enclosure portion 1800. The pins are shown by reference numerals 1821 and 1822.

FIG. 21A is a flow chart that depicts a process for recycling device enclosure portions or for recycling batteries 1110 or battery cells 1110. Because the battery cell 1110 and batteries made from a number of these battery cells 1110 can be recharged many, many times, it is contemplated that any electronics associated with this circuit may become obsolete over time and, therefore, a method of recycling the batteries is also part of this invention.

The first step, depicted by reference numeral 1900, is to determine if the electronics within a circuit are obsolete. Electronics are typically obsolete due to technology advances in the electronics, which may occur over a number of years. If the electronics are obsolete, then the battery 1110 or series of cells 1110 may be removed from a device cover or enclosure portion, as depicted by reference numeral 1910. The next step is to replace the old electrical components with new electrical components, as depicted by reference numeral 1920. This first process is useful for enclosure portions where the battery or number of cells 1110 cannot be easily removed from the enclosure portion.

A second process is shown in FIG. 21B. The second process shown in FIG. 21B is useful for devices in which the battery 1110 may be removed easily from the enclosure portion. As before, the first step, depicted by reference numeral 1930, is to determine if the electronics are obsolete. If they are, the battery 1110 is merely removed from the case for the enclosure portion and recycled for use in another enclosure portion having a similar contour, as depicted by reference numeral 1950.

In some embodiments, multiple cells are stacked in the original device, the manufacture method would include connection tabs that are coupled together to form the appropriate cell capacity and voltage for some particular electronic device. Upon reaching the end of the device's life, such battery stacks could have the tabs clipped or otherwise disconnected from each other so that the battery stack could be disassembled and re-assembled in a different capacity/voltage configuration.

Design and Fabrication of Solid-state Power Sources Cofabricated with Solid-state Integrated Circuitry

FIG. 22A shows a schematic circuit of an embodiment of a device 2200 having an integrated battery 2320 and circuit 2330 sharing a common terminal 2318. In other embodiments, more than one terminal is common between battery 2320 and circuit 2330, for example, when battery 2320 includes a stack having plurality of series-connected cells, and circuit 2330 connects to two or more different taps in the cell stack (e.g., if each cell of a two-cell stack provided an open-circuit potential of 3.6 volts, circuit 2330 could connect to the top of the cell stack for a portion of its circuitry needing 7.2 volts, and also to a center tap of the cell stack for a portion of its circuitry needing 3.6 volts, or a split voltage battery supply could be wired to provide a ground connection at the center tap and plus and minus 3.6 volts at the top and bottom of the stack). Common terminal 2318

37

connects battery 2320 to circuit 2330, and optionally can be brought out as a connection to other components. In some embodiments, common terminal connects the cathode of battery 2320 to circuit 2330; in other embodiments, terminal 2318 connects the anode of battery 2320 to circuit 2330 as shown in FIG. 22A. In some embodiments, circuit 2330 includes one or more conductors 2317 that are used to connect to other components and/or to the other connections to battery 2320. In some embodiments, battery 2320 includes one or more conductors 2319 that are used to connect to other components and/or to the other connections to circuit 2330. In other embodiments, terminal 2317 of circuit 2330 is connected directly to terminal 2319 of battery 2320 to form a complete device, and no connection is made to other external devices using terminals 2317, 2318, or 2319. Note that circuit 2330 can include any type of circuitry, for example, as shown in FIGS. 23–26, wiring traces 2332–2337, one or more active or passive devices such as integrated circuit 2340, switches, light sources, LCD displays, photovoltaic cells, etc.

FIG. 22B shows a block diagram perspective view of an integrated device 2201 implementing circuit 2200 of FIG. 22A having the circuit 2330 built on the battery 2320. According to the present invention, in some embodiments such as shown in FIG. 22B, battery 2320 is deposited or fabricated first (for example, onto a polymer substrate), and later circuit 2330 is deposited or fabricated to a surface of battery 2320. In some embodiments as shown in FIG. 22B, a top surface of the device implementing circuit 2330 includes one or more conductors 2317 that are used to connect to other components and/or to the other connections to battery 2320. In some embodiments, a bottom surface of battery 2320 includes one or more conductors 2319 that are used to connect to other components and/or to the other connections to circuit 2330. In some embodiments, a top surface of battery 2320 (the surface fabricated adjacently to circuit 2330) is partially exposed and includes one or more conductors 2318 that are used to connect to other components and/or to the other connections to circuit 2330. FIG. 23 and FIG. 24A show some examples of devices 2300 and 2400 that are exemplary embodiments of device 2201 of FIG. 22B.

FIG. 22C shows a block diagram perspective view of an integrated device 2202 implementing circuit 2200 of FIG. 22A having the battery 2320 built on the circuit 2330. According to the present invention, in some embodiments such as shown in FIG. 22C, circuit 2330 is deposited or fabricated first (for example, an integrated circuit chip built onto a silicon substrate), and later battery 2320 is deposited or fabricated to a surface of battery 2320. In some embodiments as shown in FIG. 22B, a top surface of the device implementing circuit 2330 is left partially exposed and includes one or more conductors 2317 that are used to connect to other components and/or to the other connections to battery 2320. In some embodiments, a top surface of battery 2320 includes one or more conductors 2319 that are used to connect to other components and/or to the other connections to circuit 2330. In some embodiments, a top surface of circuit 2330 (the surface fabricated adjacently to circuit 2330) is partially exposed and includes one or more conductors 2318 that are used to connect to other components and/or to the other connections to circuit 2330. FIG. 25A and FIG. 26A show some examples of devices 2500 and 2600 that are exemplary embodiments of device 2202 of FIG. 22C.

FIG. 22D shows a schematic circuit 2205 of an embodiment of an integrated battery 2320 and circuit 2330 each

38

having separate, electrically isolated terminals. Such embodiments are substantially identical to the embodiments of FIGS. 22A, 22B, and 22C, except that an insulator between terminal 2318 of the battery 2320 and terminal 2316 of the circuit 2330 keeps these electrically separate.

FIG. 22E shows a block diagram perspective view of an integrated device 2206 implementing circuit 2205 of FIG. 22D having the circuit built on the battery. Such embodiments are substantially identical to the embodiments of FIG. 22B except that an insulator 2331 is deposited on battery 2320 before the rest of circuit 2330 is deposited or fabricated. In some embodiments, a portion of the top surface of battery 2320 is left partially exposed and includes one or more conductors 2318 that are used to connect to other components and/or to the other connections to circuit 2330. In some embodiments, a portion of the top surface of insulator layer 2331 is coated with a conductor and is left partially exposed and includes one or more conductors 2316 from circuit 2330 that are used to connect to other components and/or to the other connections to battery 2320.

FIG. 22F shows a block diagram perspective view of an integrated device 2207 implementing circuit 2205 of FIG. 22D having the battery 2320 built on but insulated from the circuit 2330. Such embodiments are substantially identical to the embodiments of FIG. 22C except that an insulator 2331 is deposited on circuit 2330 before the rest of battery 2320 is deposited or fabricated. In some embodiments, a portion of the top surface of circuit 2330 is left partially exposed and includes two or more conductors 2316 and 2317 that are used to connect to other components and/or to the other connections to battery 2320. In some embodiments, a portion of the top surface of insulator layer 2331 is coated with a conductor and is left partially exposed and includes one or more conductors 2318 from battery 2320 that are used to connect to other components and/or to the other connections to circuit 2330.

FIG. 22G shows a block diagram perspective view of an integrated device 2203 implementing circuit 2200 of FIG. 22A having the battery 2320 and the circuit 2330 built side-by-side on a substrate 2310. In some embodiments, a pattern of conductive areas or traces is deposited on substrate 2310, and the successive layer(s) of battery 2320 and circuit 2330 are then deposited. In some embodiments, circuit 2330 consists only of these conductive traces. In other embodiments, one or more of the process steps or deposited layers of battery 2320 and circuit 2330 are common, and thus performed at substantially the same time for both circuit 2330 and battery 2320, thus increasing the reliability, speed and yield of fabrication and lowering the cost of fabrication. In the embodiment shown, trace 2318 is deposited on substrate 2310 and forms a common bottom electrical connection for both circuit 2330 and battery 2320. Other aspects of FIG. 22G can be understood by reference to FIGS. 22A–22C.

FIG. 22H shows a block diagram perspective view of an integrated device 2208 implementing circuit 2205 of FIG. 22D having the battery 2320 and the circuit 2330 built side-by-side on a substrate 2310. This embodiment is substantially identical to that of FIG. 22G, except that separate traces are provided for signals 2316 and 2318.

FIG. 23 shows a perspective view of an embodiment 2300 of the present invention having a battery 2320 overlaid with circuitry. In some embodiments, substrate 2310 is a conductor such as a thin sheet of metal, and is overlaid with an insulator layer 2312, and then the bottom conductor layer 2322 of battery 2320. In other embodiments, insulator layer 2312 and bottom conductor layer 2322 are omitted, and a

conductive substrate **2310** itself forms the bottom conductive layer for battery **2320**. In some embodiments, battery **2320** is a thin-film battery deposited by a process, and having a structure, as described in FIGS. 1B to 8 herein. In the embodiment shown, battery **2320** includes a bottom conductive layer/electrical contact **2322** and a top conductive layer/electrical contact **2324**, and is covered by a protective/electrically insulating layer **2331** having one or more openings or vias for electrical connections, for example, a via through which pad/trace **2332** connects to battery **2320**. In some embodiments, the top conductor **2324** of battery **2320** is the anode connection. In the embodiment shown, the connection to the lower conductive layer/electrical contact **2322** from pad/trace **2334** is a conductive trace deposited over the side of battery **2320** to extended contact area **2333**. In some embodiments, additional connection pads/traces **2335**, **2336**, and **2337** are deposited, for example, using a shadow mask that defines where the traces will go, and a metal-evaporation source, PVD source, CVD source, sputter source or other source to supply the conductor being laid down. In other embodiments, a conductive layer for circuit **2330** is deposited over an entire upper surface, and the unneeded portions are removed, for example, using photolithography and etching techniques. In some embodiments, multiple layers are successively deposited, wherein these layers include conductors, insulators, semiconductors (e.g., polysilicon or polymer semiconductors), electrolytes, passivation layers, mechanical-protection layers, sealants, reactants (such as sensor materials that react with, e.g., smoke, carbon dioxide, antibodies, DNA, etc.) and/or decorative pattern, topography, design or color layers.

Some embodiments further include a separately fabricated circuit **2340** that is bonded (e.g., by adhesive or solder) to the rest of the deposited circuitry **2330**, for example, a flip-chip integrated circuit **2340** having bump, ball or ball-grid array connections **2341** as shown in FIG. 23. In other embodiments, packaged chips are used, e.g., J-leaded, gull-wing leaded, in-line-pin, or other plastic- or ceramic-encapsulated chip packages.

FIG. 24A shows a perspective view of an embodiment **2400** of the present invention having a battery **2320** overlaid with an integrated device **2430**. In some embodiments, integrated device **2430** is a so-called supercapacitor relying on either charge accumulation on opposing sides on an insulator (as in a capacitor) or ion transport across an electrolyte (as in a battery), or both charge accumulation and ion transport to store electrical energy. In some embodiments, integrated device **2430** includes a photovoltaic cell of conventional construction deposited directly on battery **2320**.

Some embodiments further include a separately fabricated circuit device such as an integrated circuit chip **2440** that is wire-lead bonded to device **2430** using wire **2441**, to device-battery common terminal **2324** using wire **2443**, and to bottom battery contact **2322** using wire **2442**. For example, in one embodiment having a supercapacitor device **2430**, integrated circuit **2440** includes a wireless communication circuit that uses the battery for overall power needs and uses supercapacitor device **2430** for quick-burst power needs such as for transmitting short burst of data to an antenna. Other embodiments include other fabricated circuit devices such as switches, LEDs or other light sources, LCD displays, antennas, sensors, capacitors, resistors, etc., wired to device **2400**.

In one embodiment, battery **2320** includes a bottom conductor layer of platinum (e.g., 0.5 micrometers thick), a

cathode of lithium cobalt oxide covered by a LiPON electrolyte and a carbon anode, and a top electrode of platinum. On top of these depositions, device **2430** includes a layer of ruthenium oxide, an electrolyte of LiPON, another layer of ruthenium oxide and a top layer of platinum. Such a device **2430** would store energy by transporting lithium ions derived from the LiPON electrolyte from one to another of the top and bottom surface of the electrolyte, as well as perhaps moving charge (electrons) to an opposing surface. Such a device exhibits a higher-current discharge rate than a comparable battery, and a higher energy storage than a comparable capacitor. The present invention including ion-assist deposition provides for higher quality cathode films (better crystal orientation) and better electrolyte films (more complete isolation and fewer pinhole defects for any given thickness, thus allowing thinner electrolyte films that increase ion transport rates), and better capacitor dielectric films (more complete isolation and fewer pinhole defects for any given thickness, thus allowing thinner dielectric films that increase dielectric isolation, capacitance, and charge storage). In some embodiments, a capacitor insulator layer is made of a barium strontium titanate.

In some embodiments, a cathode layer of lithium-cobalt-oxide is covered by a LiPON electrolyte layer and a lithium (0.5)-cobalt-oxide anode layer. This anode layer is non-stoichiometric deposited using a source that has excess cobalt and oxygen relative to lithium as compared to that used for the cathode, and various embodiments use different lithium ratios.

Design and Fabrication of Solid-state Power Sources Fabricated as a Laminate on a Rigid or Flexible Direct Energy Conversion Material such as Photovoltaic

Virtually all electronics require energy to operate and perform the designed functions. This energy typically comes from either an AC source such as a home wall electrical outlet or a battery mounted in the packaging of the electronic device. More recently, advances in the conversion of heat and light into energy have fueled research in the area of direct energy conversion (e.g., by photovoltaic cells). This has the potential to supply a large percentage of the world energy needs in a clean and safe manner. One problem with these methods of energy supply has been the cyclical nature of the energy being converted. Whether heat or light, the source usually goes away for a 6- to 12-hour period resulting in zero output from the unit. One way around this problem is to supply a battery with the unit to supply power during periods of low light or heat input. This is however not an ideal solution as today's rechargeable batteries are bulky and failure prone after several charge/discharge cycles. The present invention solves this problem by integrating its solid-state Lithium battery directly on the energy conversion substrate. The present battery has a distinct advantage over current technologies, in that it is not prone to failure or memory problems over tens of thousands of charge/discharge cycles, has very high capacity, is lightweight, can be fabricated on nearly any substrate and is cheap to manufacture. The resultant product is a reliable, portable power source with steady output over extended periods or rain or shine, night or day, warm or cold.

According to the present invention, solid-state processes are used to cofabricate direct energy conversion materials and energy storage on the same substrate. This is possible by using the low-temperature processes for solid-state batteries described above.

41

FIG. 24B shows a block diagram of a battery-layer-deposition system 2460. In some embodiments, system 2460 includes a supply reel 2461, a deposition chamber 2462 that deposits one or more layers of battery 2320 onto a substrate 2410 as described above, and a takeup reel 2463. Typically, deposition chamber 2462 is a vacuum chamber that encloses supply reel 2461 and takeup reel 2463, and successively deposits a plurality of layers, wherein each of one or more of the layers is immediately treated (e.g., by ion assist, laser surface anneal, heat surface anneal, or kinetic treatment), according to the present invention, to impart a high-quality surface structure to that layer or those layers before subsequent layers are deposited, and without substantial heating of the underlying layer(s) or substrate. For layers that need to be thicker, a longer deposition station is provided than the station for thinner layers. In some embodiments, the lower contact layer 2322 is deposited onto a starting substrate film, fabric, or foil 2410, then the cathode, electrolyte, anode, and anode-contact layers are deposited, wherein the cathode layer and/or the electrolyte layer are treated (e.g., by an ion-assist beam) before subsequent layers are deposited.

FIG. 24C shows the resulting item 2464, which is a continuous sheet of substrate material 2410 having batteries 2320 deposited on it. This partially built item 2464 is then used as the supply reel 2466 of layer-deposition system 2465 of FIG. 24D.

FIG. 24D shows a block diagram of an energy-conversion-layer-deposition system 2465. In some embodiments, system 2565 deposits layers that form a photovoltaic cell 2430 onto battery 2320 of FIG. 24A. In some embodiments, system 2460 and system 2465 are merged into a single system having a single supply reel 2461 and a single takeup reel 2468, and having layers of the battery 2320 and of the photovoltaic cell 2430 successively deposited. In other embodiments, other types of devices 2430 are deposited such as capacitors, antennae, circuitry, transducers, sensors, magneto-resistors (e.g., of the giant magneto-resistor type), etc.

FIG. 24E shows a perspective view of a processed sheet 2469 that is the result of processing by system 2460 and system 2465. Sheet 2469 is then cut or diced into individual devices 2400. FIG. 24F shows a perspective view of three diced final devices 2400. In other embodiments, sheet 2469 is cut into any desired number of devices 2400.

In other embodiments, system 2460 and system 2465 deposit a battery 2320 and a photovoltaic cell 2330 side-by-side on one face of substrate 2310, such as shown in FIG. 22G and FIG. 22H. In some such embodiments, one or more of the layers deposited for battery 2320 are also deposited for photovoltaic cell 2330 simultaneously of the same deposition material, thus saving process steps but making a wider device than if stacked as in FIG. 24A.

FIG. 25A shows a perspective view of an embodiment 2500 of the present invention having an integrated circuit 2510 overlaid with a battery 2320. In some embodiments, integrated circuit 2510 includes a top insulator layer 2511 having a plurality of vias or openings 2512 to the active surface of the integrated circuit 2510 (the side with devices and connectors). Two of these vias are used as contacts 2514 and 2515 between integrated circuit 2510 and battery 2320. Battery 2320 is deposited as described for FIG. 23. In some embodiments, battery 2320 is deposited on an integrated circuit wafer before integrated circuit 2510 is diced apart from the other integrated circuits. In some embodiments, battery 2320 is deposited onto integrated circuit 2510 after integrated circuit 2510 is diced apart from the other inte-

42

grated circuits. Some embodiments further include a passivation layer over the top and sides of battery 2320 such as layer 2331 of FIG. 23.

In other embodiments, a circuit such as circuit 2330 of FIG. 23 is used in place of integrated circuit 2510 of FIG. 25A. Thus, a pattern of vias and/or other devices or circuitry is deposited on a substrate, and battery 2320 is deposited on the top of the predefined circuitry/substrate, as in FIG. 25A. In some embodiments, a photovoltaic cell is used as such a circuit device/substrate, and battery 2320 is deposited directly on the premanufactured photovoltaic cell. In some embodiments, an integrated circuit such as 2440 of FIG. 24A is wired to the battery 2320 and the premanufactured photovoltaic cell to control charging of the battery from the cell and/or to control using power for other devices (such as a light source or hearing aid) from the photocell during periods of high amounts of light and power available from the photovoltaic cell, and using power from the battery during periods of little or no light and power available from the photovoltaic cell.

Virtually all electronics require energy to operate and perform the designed functions. This energy typically comes from either an AC source such as a home wall electrical outlet or a battery mounted in the packaging of the electronic device. Until the last few years, this approach has proved to be acceptable even though the inefficiencies caused waste of both energy and natural resources in that the device housing had to be made large enough to incorporate the energy package or conversion electronics. As electronic complexity increases, the wasted real estate and energy begin to become an issue as the demands of operator interface begin to compete with the energy source for area on the device. The application of the solid-state battery process of the present invention allows the cofabricating of electronics and the associated power source together on chip.

Solid-state processes are used to cofabricate electronics and solid-state rechargeable battery on a common substrate such as silicon used for IC processing. This is possible by using the low-temperature processes for solid-state batteries described above.

Referring to FIG. 25A, in some embodiments, the integrated circuit (IC) 2510 in wafer form is processed normally through final passivation including bond-pad etch. All thermal processing necessary for the electronics is performed conventionally. The IC in wafer form is sent to backend energy processing. In some embodiments, the design of the IC includes electronics for control of recharge for the solid-state energy source; contact vias for connecting the cathode plate and anode plate to the circuit. Using shadow masks with sufficient overlay accuracy, the necessary components of the energy structure 2320 are deposited using PVD or CVD as described above. A final passivation coating (such as 2331 of FIG. 23) is applied to the energy stack. The IC in wafer form with energy source integrated is sent for test, dicing and packaging. This provides integration of electronics and solid-state rechargeable batteries by cofabrication.

Design and Fabrication of Solid-state Power
Sources Fabricated as a Laminate on the Packaging
for the Device the Energy Source will Power

Solid-state processes are used to cofabricate electronics and packaging. This is possible by using the low-temperature processes for solid-state batteries described above.

FIGS. 25B–25E show a fabrication sequence for cofabrication of solid-state integrated circuits and solid-state

energy source such as that described above, but onto a packaged IC **2540**. FIG. **25B** shows a plan view and FIG. **25C** shows an elevational view of IC **2540**. In some embodiments, IC **2540** includes a silicon chip **2545** having integrated components such as transistors, resistors, memory, etc., a lower substrate **2546**, and a wiring superstrate **2544** having deposited wires **2543** that extend to bonding vias **2542**. FIG. **25D** shows a plan view and FIG. **25E** shows an elevational view of an integrated battery-IC **2501**. Battery-IC **2501** includes a cathode **2326** (e.g., lithium cobalt oxide), electrolyte layer **2327** (e.g., LiPON), and anode layer **2328** (e.g., including copper, carbon, lithium, lithium-magnesium, and/or other suitable anode material). Passivation overcoat layer **2329** suitable to protect the inner components of battery **2320** is then deposited or grown.

In one embodiment, the package IC **2540** product is formed by conventional means. All machine work and cleaning is accomplished. The package **2540** is sent to energy processing for deposition of battery **2320** or other energy-storage device. The design of the package included a suitable area **2549** for deposition of battery components. Using shadow masks with sufficient overlay accuracy, the necessary components of the energy structure (e.g., a battery and/or photovoltaic cell) are deposited using the methods described above. A final passivation coating **2329** is applied to the energy stack structure. The package with energy structure integrated is sent for assembly.

In one embodiment, further electronics are attached to the package/energy entity **2501** by way of adhesive. The electronics are then hardwired to the package/energy entity. In a second embodiment, the electronics are mounted directly to the package/energy entity by **2501** way of solder bumps. In some embodiments, the entire assembly is optionally potted, then sealed by the package cover. In other embodiments, the battery is formed on a substrate suitable as a packaging material. The substrate is formed into individual package form factors. The package with energy structure integrated is sent for assembly.

Thus, the present invention provides integrated product packaging and solid-state rechargeable batteries by cofabrication where the battery is deposited on the already-formed package. The present invention also provides integrated product packaging and solid-state rechargeable batteries by cofabrication where the battery is deposited on a suitable package material, then formed into the package.

The present invention also provides a method of attaching electronics to a package/energy hybrid wherein the electronics are mounted with adhesive, then hardwired to the energy source. The present invention further provides a method of attaching electronics to a package/energy hybrid wherein the electronics are attached to the energy source via solder bumps.

FIG. **25F** shows a block diagram of a layer-deposition system **2560** much the same as that of FIG. **24B**, however rather than using a sheet of polymer or other homogenous substrate material **2410**, system **2560** starts with a sheet **2561** having a plurality of processed packaged ICs **2540** that are received by takeup reel **2563**.

FIG. **25G** shows a perspective view of a processed sheet **2569**. Sheet **2569** includes a plurality of preprocessed circuits **2540** each having a battery **2320** deposited on it by system **2560**. Sheet **2569** is then cut or diced into individual devices **2501**.

FIG. **26A** shows a perspective view of an device **2600** of the present invention having an integrated circuit **2510** overlaid on its back with a battery **2320**. This embodiment is similar to that of FIG. **25A**, except that the battery **2320**

is deposited on the back of IC **2510**, and is wire-lead bonded to contact **2514** using wire **2614** from battery contact **2519** and to contact **2515** using wire **2615** from battery contact **2518**.

In some embodiments, device **2600** further includes device **2650** such as a photovoltaic cell fabricated on a surface of integrated circuit **2510**, for example, on the opposite side as that facing battery **2320**. In some embodiments, such a photovoltaic cell **2650** provides power to IC **2510** for both operation of IC **2510** and for charging of battery **2320** during periods of relatively bright light, and then battery **2320** provides power to IC **2510** for operation during periods of relatively dim or no light. In some embodiments, device **2600** includes one or more devices **2650** such as sound transducers for such applications as a hearing aid having an combined transducer-battery-amplifier device. In some such embodiments, both a photovoltaic cell **2650** and one or more sound transducers **2650** are deposited in order to provide a light-rechargeable hearing aid which could be taken out of the ear at night and placed in a light-emitting recharging stand (e.g., that of FIG. **27L**), avoiding the need to replace batteries or even to electrically connect to an external recharging circuit. In some embodiments, a photovoltaic cell and/or a sound transducer is/are deposited on one face of device **2600** for recharging and for sound pickup, and a sound transducer is deposited on an opposing face for use as a speaker for applications such as a hearing aid.

In yet other embodiments, **2600** further includes device **2650** such as a magnetoresistive sensor fabricated on a surface of integrated circuit **2510**, for example, on the opposite side as that facing battery **2320**. Such a device **2600** could be used in a compass, for example.

In some embodiments, embodiment **2600** further includes an antenna or electromagnetic radiation receiving loop **2662** fabricated on a surface of integrated circuit **2510**, for example, on the opposite side as that facing battery **2320**. In some such embodiments, device **2600** also includes one or more devices **2650** such as sound transducers for such applications as a hearing aid having an combined transducer-battery-amplifier device in order to provide a radio frequency-wave-rechargeable hearing aid which could be taken out of the ear at night and placed in an RF-emitting recharging stand (e.g., that of FIG. **27M**), avoiding the need to replace batteries or even to electrically connect to an external recharging circuit.

In various embodiments, such an antenna or electromagnetic radiation receiving loop **2662** is fabricated on device **2202**, **2203**, **2204**, **2206**, **2207**, **2208**, **2300**, **2400**, or **2500** (or **2700** described below) or other battery devices described herein. In some such embodiments, electromagnetic radiation received wirelessly by antenna **2662** can be such low-frequency radiation as 50- or 60-hertz magnetic radiation from a coil connected to house current (e.g., that of FIG. **27L**). In other such embodiments, RF radiation such as radio, TV, cellular, etc. having frequencies up to and exceeding 2.4 GHz is received. In some embodiments, multiple antennae are used, e.g., one for transducing communications signals and another for receiving recharging signals.

FIG. **26B** shows a block diagram of a layer-deposition system **2660**. System **2660** is much the same as system **2560** of FIG. **25B**, except that the battery material is deposited on the back of the sheet, i.e., on the side opposite the active parts or connections of circuit **2510**.

FIG. **26C** shows a perspective view of a processed sheet **2669**. Sheet **2669** includes a plurality of devices or circuits **2510** each having a battery **2320** on the back. FIG. **26D** shows a perspective view of diced final devices **2600** after

45

being dices or cut apart. FIG. 26E shows a perspective view of wired diced final device 2600 after being wired, e.g., by wires 2615 and 2616 as shown, or by deposited traces (not shown) that extend electrical connections from the top to the bottom of device 2600.

In some embodiments, a roll of flexible fabric 2661 suitable for use as a substrate for direct energy conversion has deposited on it the necessary elements and/or layers to form the desired unit (such as a photovoltaic cell) using roll-to-roll concepts. The roll is then taken to the energy deposition tool 2660 which is also configured to operate in a roll-to-roll mode. The battery 2320 is fabricated on the backside (the side opposite the active side of the device, e.g., the side having the light-reception face of a photovoltaic cell) of the roll. Electrical connection is made after fabrication using hardwire techniques, such as shown in FIG. 26E.

In other embodiments such as shown in FIGS. 24B–24F, a roll of flexible fabric 2461 suitable for use as a substrate for direct energy conversion (e.g., for a photovoltaic cell) is deposited with materials to form a solid-state lithium battery using roll-to-roll concepts in system 2460. The resulting roll 2463 is then taken to the direct energy conversion materials deposition tool 2465 which is also configured to operate in a roll-to-roll mode. The direct energy conversion material 2430 is deposited directly on the solid-state battery 2320. In some embodiments, electrical connection is made through vias formed during battery and device fabrication such as shown in FIG. 23.

In yet other embodiments, roll 2461 above is replaced by a different substrate, such as wafer 2961 of FIG. 29A described below, also suitable for use in direct energy conversion. The fabrication tools 2960 and 2965 are also configured to handle the new substrate form factor such as square plates or round wafers.

In still other embodiments, roll 2661 above is replaced by a different substrate, such as wafer 2971 of FIG. 29E below, also suitable for use in direct energy conversion. The fabrication tools 2960 and 2965 are also configured to handle the new substrate form factor such as square plates or round wafers.

Thus, the present invention provides a method for integrating solid-state lithium batteries with direct energy conversion materials on a flexible fabric. Further, the present invention provides a method for integrating solid-state lithium batteries with direct energy conversion materials on a rigid substrate.

FIG. 26F shows a perspective view of a hearing aid 2690 incorporating a wired diced final device 2600. In some embodiments, device 2600 includes a photovoltaic cell 2650 for recharging battery 2320 the operates hearing aid 2690. In some embodiments, sound transducers of conventional materials such as piezo-electric materials are deposited as layers by system 2660 to be used as the microphone and speaker of hearing aid 2690.

FIG. 27A shows a plan view of a starting substrate 2710 of an embodiment that will have an integrated battery and device sharing a common terminal. FIG. 27F shows an elevation view of the starting substrate of FIG. 27A. FIG. 27B shows a plan view of the substrate 2710 of FIG. 27A after deposition of the integrated battery 2320 and device 2430 sharing a common terminal. In some embodiments, integrated battery 2320 and device 2430 are a thin-film battery and supercapacitor having electrical connections 2322, 2324, and 2431 such as shown and described in FIG. 24A above. FIG. 27G shows an elevation view of the partially built device of FIG. 27B. FIG. 27C shows a plan

46

view of the substrate of FIG. 27B after placing and wiring a separately fabricated chip 2440 connected by wires 2441, 2442, and 2443 to the integrated battery 2320 and device 2430 sharing common terminal 2324. FIG. 27H shows an elevation view of the partially built device of FIG. 27C. FIG. 27D shows a plan view of the substrate 2710 of FIG. 27C after placing and wiring a loop antenna 2750. FIG. 27I shows an elevation view of the partially built device of FIG. 27D. FIG. 27E shows a plan view of the final device 2700 having the partially built device of FIG. 27D after a top encapsulation layer 2760 has been deposited. FIG. 27J shows a cross-section elevation view of the device 2700 of FIG. 27E. The elevational views of FIGS. 27E–27J are not to scale. In some embodiments, device 2700 is approximately the size and thickness of a common credit card. In some embodiments, a magnetic strip 2770 and raised lettering 2780 are also fabricated on device 2700.

FIG. 27K shows a perspective view of the device of FIG. 27E at a magnetic-recharging station. In the embodiment shown, coil 2790 uses house current to generate a 60 Hz magnetic field, and together with coil 2750, form a transformer inducing current flow in coil 2750, which is rectified and used to recharge battery 2320.

FIG. 27L shows a perspective view of a device 2700 of FIG. 27E, but further including a photovoltaic cell 2650, at a light-recharging station that includes lamp 2791. In some embodiments, device 2700 is fabricated in a shape to fit in the ear, includes sound transducers, and functions as a hearing aid that can be recharged an indefinite number of times, eliminating the need to replace its battery.

FIG. 27M shows a schematic of the device of FIG. 27E at a radio-wave-recharging station 2792. Radio waves from radio-wave-recharging station 2792 are picked up by antenna 2750, and the received radio wave's power is scavenged to recharge battery 2320 using a conventional recharging circuit, e.g., implemented in circuit 2440.

Solid-state rechargeable batteries such as those described above have the unique ability of being integrated directly with the electronics they will power. Further integration of thin-wire antenna/coil 2662 or 2750 to be used as one of the coils of a two-part transformer such as shown in FIG. 27K and/or RF-scavenging technology such as that used in keyless entry systems allows the recharging of the solid-state thin-film battery 2320 wirelessly (through the air). Using techniques already common in RF I.D. tagging, the communicated energy is converted into a D.C. voltage and used to perform functions on board. In the case where a battery already exists on board, the D.C. voltage is used to power up recharge circuitry to wirelessly recharge the on-board battery.

Certain needs exist within industry that would benefit from the integration of energy, storage communication and electronics on a single platform. One example is control of warehouse inventories where a small “credit card” is attached to an item in the warehouse. On board the “credit card” is an antenna, supercapacitor, solid-state battery and all required electronics. When the controller needs to know something about the package, the warehouse is queried via cellular or other wireless means with the I.D. of the package in question. The query “wakes up” the package and entices it to respond with whatever data is programmed to be released. The supercapacitor discharges into the antennae-driving circuitry bursting the data out to the central computer. At the same time, the electronics on the credit-card form factor device perform a self evaluation to see if any anomalies have or are occurring such as “battery needs charging.” If the answer is yes, the central computer sends

47

a signal of appropriate length to recharge the on-board battery using technology described herein.

Another application seeing significant enhancement from the integration of energy, communication and electronics on a single platform is an implantable device such as a pacemaker. This technology allows a battery having a very large number (if not infinite) charge/discharge cycles to be implanted as part of a pacemaker. When a “battery-low condition” is encountered, the battery is remotely recharged through the body using AC magnetic fields, sound or ultrasound, radio-frequency or other energy sources.

Solid-state processes are used to integrate electronics, solid-state rechargeable battery, and antenna on a single platform such as a “credit card” form factor. This is possible by using the low-temperature processes for solid-state batteries and supercapacitors described.

The present invention provides a platform integrating electronics, solid-state rechargeable batteries, and antenna on a single platform such as a credit card or implantable device allowing remote wireless recharging of the on-board battery.

FIGS. 27A–27J show a fabrication sequence if some embodiments of an example of a credit-card form factor I.D. tag with remote recharge capability.

FIG. 31B shows a fabrication sequence for an example of an implantable device such as a pacemaker 3101. This method starts with a substantially flat sheet deposited with batteries, which is then cut apart and formed into a three-dimensional shape. The method is otherwise similar to that of FIG. 31C.

FIG. 31C shows one method for making a pacemaker 3102. The method includes a plurality of steps carrying the reference numbers 3194, 3195, 3196 and 3197. The pacemaker 3102 includes a first half 3131 and a second half 3130. In the initial step, 3194, the second half 3130 is provided. A battery cell 1110 is formed on an interior surface of the pacemaker 3102, as shown by step 3195. The single cell 1110 is deposited on the interior surface, as shown by step 3195. The electronics 3150 are then placed onto the battery 1110 to form a circuit with the battery 1110, as depicted by step 3196. The first half 3131 of the enclosure is placed over the second half 3130 to form the assembled pacemaker 3102, as depicted by step 3197.

Solid-state rechargeable batteries such as those described above have the unique ability of being integrated directly with the electronics they will power. Further integration of thin-wire antenna and an energy burst device such as a supercapacitor would allow the device to communicate over large distances via any possible number of current communication methods including but not limited to cellular.

This invention relates to solid-state rechargeable batteries and the integration of such with wireless communication (antennae and electronics), supercapacitor and conventional electronics on a single platform.

Certain needs exist within industry that would benefit from the integration of energy, communication and electronics on a single platform. One example is control of warehouse inventories where a small “credit card” is attached to an item in the warehouse. On board the “credit card” are an antenna, supercapacitor, solid-state battery and all required electronics. This “credit card” allows tracking of location, time at location, description of item in question and/or information on the environment. When the controller needs to know something about the package, the warehouse is queried via cellular or other wireless means with the I.D. of the package in question. The query “wares up” the package and entices it to respond with whatever data is programmed

48

to be released. The supercapacitor discharges into the circuitry driving the antennae bursting the data out to the central computer. At the same time, the electronics on the “credit card” performs a self evaluation to see if any anomalies have or are occurring such as battery needs charging. If the answer is yes, the central computer could send a signal of appropriate length to allow recharge of on-board battery using technology described above.

Solid-state processes are used to integrate electronics, solid-state rechargeable battery, supercapacitor and antenna on a single platform such as a “credit card” form factor. This is possible by using the low-temperature processes for solid-state batteries and supercapacitors described above.

Thus, the present invention provides for integrating electronics, solid-state rechargeable batteries, supercapacitors and antenna on a single platform such as a credit card or implantable device.

Method of Recycling and Re-using Solid-state Lithium-ion Batteries

FIG. 28A shows an elevation view of a battery 2800 having stacked cells 2801. Each cell includes an anode tab 2802 and a cathode tab 2803, wherein all of the anode tabs 2802 are soldered together, and all of the cathode tabs 2803 are soldered together. Optionally, battery 2800 is encapsulated with a potting material.

FIG. 28B shows a plan view of a single battery cell 2801 after recycling. In some embodiments, the anode tab 2802 and the cathode tab 2803 are “tinned” (covered with fresh solder) and/or solder bumped to facilitate reassembly soldering operations.

FIG. 28C shows a process 2810 used for recycling. Process 2810 includes providing batteries 2800 to be recycled into input bin 2820. In some embodiments, the batteries are de-potted at de-pot station 2822, de-soldered at de-solder station 2824, tested at test station 2826, and outputted into sorted output bins 2828 based on the testing results.

Of the 2 billion rechargeable batteries consumed in the United States in 1998, only about 300 million were actually recycled. That means about 1.7 billion recyclable batteries made it into landfills. Although more and more of these batteries are technically environmentally safe, this still represents a significant load on the landfill situation in the USA. The present invention provides a solution that will have its greatest impact as solid-state lithium-ion batteries begin to dominate the rechargeable battery market. In this invention, solid-state lithium-ion batteries have a date code and/or recycle value associated with them. Because of the very large (over 40,000) number of charge/discharge cycles possible with solid-state lithium batteries, the average expected life of a cell could exceed 100 years. It is therefore very likely that the product in which the cell is placed will lose its usefulness well before the battery cell is depleted. Thus, when the battery reaches the end of its useful life based on the obsolescence of the product it was in, the consumer will be enticed to recycle the battery based on the value returned to the consumer in exchange for recycling. This value could be a function of the date code and application the battery was used in. The recycler 2810 then disassembles the unit 2800, tests the single cells 2801, then rebuilds the cells in whatever configuration is most in demand at that time. The rebuilt unit could then be sold at an appropriate cost and warranty on performance.

This invention relates to recycling of rechargeable batteries, specifically the recycling of batteries that are manufac-

tured in such a way so as to allow the disassembly of the individual battery cells upon recycling.

For years the automotive industry has recycled certain high-cost components of the automobile. Using this philosophy, the present invention applies those principles to the recycling of rechargeable batteries. As battery technology advances, the batteries are actually outlasting the products they were designed for. The conventional solution is to depend on the consumer to recycle the no-longer useful battery by taking it to some place that will accept the battery. The data suggests that this is wishful thinking, as fully 80% of Americans do not recycle their rechargeable batteries. Rather, they throw them into the garbage and the battery ends up in a landfill. Although the newer battery chemistries are relatively benign to the environment, the sheer bulk of the disposed batteries can represent an enormous strain on landfills. This invention allows enticement of the consumer to recycle the batteries by offering a cash reward, or other inducement such as reduced cost on new batteries, in exchange for recycling. Since money is involved, this program should be able to be implemented on a wide scale making participation likely.

In one embodiment, rechargeable battery manufacturers are encouraged to manufacture their products in such a way that upon recycling, the battery can be broken down into individual cells and these cells rebuilt into "new" batteries. In some embodiments of the present invention provide such a recycling program, and provide batteries with features to facilitate recycling, for example, marking one or more of the cells of a battery with a code indicating such information as date of manufacture, voltage, capacity, value, composition physical size, and/or weight. An example is a cell-phone battery having a capacity of 1000 mAh (milliampere hours). Some embodiments involve the parallel assembly of approximately 10 individual cells into a battery pack that would have a capacity of 1000 mAh. These individual cells are fabricated on a grid that provides bonding tabs allowing the configuration of the cells in a variety of modes. Upon recycling, the batteries are de-potted, de-soldered and analyzed for robustness. Cells having data codes and test results indicating substantial life remaining would be repackaged according to market needs. In some embodiments, recycling rechargeable batteries involves the breaking down of the battery pack into individual cells which are tested and re-assembled into usable battery packs. Some embodiments include a method of determining the viability of recycled battery cells for use in rebuilt batteries such as measuring the charge-discharge voltage-current curve over one or more cycles. Some embodiments include a method of de-potting batteries such that the individual cells are accessible and not damaged, such as using a plastic potting compound that can later be dissolved using a solvent and/or heat that does not deteriorate the battery. Some embodiments include a method of disconnecting cells from the original battery pack and re-connecting into a new configuration, such as having solder tabs that extend beyond the battery pack so that the solder tabs can be desoldered without substantially heating the battery itself. Some embodiments include a recycling system based loosely on the system used by the automotive industry in rebuilding of starters, alternators etc. and the techniques used by lead acid battery outlets.

FIG. 29A shows a block diagram of a layer-deposition system 2960. System 2960 has layer deposition sections 2962 much the same as those of system 2460 of FIG. 24B, except that it is set up to deposit layers onto wafers 2961 (or onto diced ICs 2510 rather than onto flexible substrates), resulting in processed wafers 2963. FIG. 29B shows a

perspective view of a partially processed wafer 2964 having battery material 2320 on wafer 2961 or IC 2410.

FIG. 29C shows a block diagram of a layer-deposition system 2965. System 2965 has layer deposition sections 2962 much the same as those of system 2465 of FIG. 24D, except that it is set up to deposit layers onto wafers 2966 (or onto diced ICs 2510 rather than onto flexible substrates) by layer-deposition sections 2967, resulting in processed wafers 2968. FIG. 29D shows a perspective view of a processed sheet 2969 having battery material 2320 on wafer 2961 or IC 2410 and covered by a device 2430 such as a photovoltaic cell.

FIG. 29E shows a block diagram of a layer-deposition system 2965. In some such embodiments, system 2965 deposits layers forming a photovoltaic cell device 2650 onto a wafer 2971 or IC 2510. FIG. 29F shows a perspective view of a partially processed wafer 2974. FIG. 29G shows a block diagram of a layer-deposition system 2960. In some such embodiments, system 2960 deposits layers of a battery 2320. FIG. 29H shows a perspective view of a processed wafer 2979. In some embodiments, wafer 2979 represents a single device, and in other embodiments, wafer 2979 is diced or cut into a plurality of individual devices and then wired as necessary to connect the signals on the top of the device to the bottom of the device. FIG. 29I shows a perspective view of wired diced final device 2600 having wires 2914 and 2915.

Turning now to FIGS. 30, 31 and 32, specific examples of devices will now be provided. FIG. 30 shows an implantable device 3000 used to stimulate specific portions of the brain. One use of such device 3000 is for deep brain neural stimulation, for example, in order to treat Parkinson's Disease. By sending signals to a specific portion of the brain the tremors associated with Parkinson's Disease may be reduced. In the past, a lead or conductor was implanted in the brain so that electrical signals may be sent to the specific area of the brain for reducing tremors. The lead passes under the skull and through the neck to a pocket near the patient's chest in current versions. As shown in FIG. 30, after a burr hole has been made in the skull, a port 3010 is placed in the burr hole. The port 3010 includes a cap 3012, which is used to hold the lead in place during implantation as well as after implantation. In this particular invention, the cap 3012 is made of a suitable biocompatible material. Imbedded within the cap is a battery cell 1110 or a series of battery cells 1110. The electronics necessary to deliver the signals at a desired rate or programmable rate is also imbedded within the cap 3012. An RF antenna 3014 is also placed within the cap so that the battery 1110 imbedded within the cap 3012 can be recharged by passing radio frequency into the cap or inductively coupling the required energy into the cap. Another embodiment may use the lead 3020 for an energizing antenna and may include a separate antenna for programming the electronics used to deliver signals to the brain.

FIG. 31A is directed toward a pacemaker 3100. Rather than include separate batteries within the case of the pacemaker 3100, the enclosure, or at least one enclosure portion, includes a battery 1110 or a series of cells 1110. The pacemaker 3100 may include an antenna 3120 which is used to direct radio frequency toward the pacemaker for recharging of the battery 1110 that is positioned within the case or enclosure of the pacemaker 3100.

FIG. 31B shows the method for making the pacemaker 3101. The method is comprised of a plurality of steps carrying the reference numbers 3190, 3191, 3192 and 3193. The pacemaker 3100 includes a first half 3131 and a second half 3130. A plurality of battery cells 1110 are formed on a

51

substrate material **3140**, as shown by step **3190**. The substrate material **3140** is diced or cut resulting in a single cell **1110** on the sheet as diced. The single cell **1110** is adhesively bonded to the second half **3130** of the pacemaker **3100**, as shown in step **3191**. The electronics **3150** are then placed onto the battery **1110** to form a circuit with the battery **1110**, as depicted by step **3192**. The first half **3131** of the enclosure is placed over the second half **3130** to form the assembled pacemaker **3100**.

FIG. 32A is a perspective cutaway view of a watch **3200**. The watch includes a case **3210** and a band **3212** for strapping onto a person's wrist. Within the case **3210** is a solar cell **3220** and an LCD **3222**. The solar cell **3220** is attached to the battery or series of battery cells **1110**. The LCD **3222** is attached to the battery and electronic (not shown). The battery powers the LCD **3222** and is associated to electronics associated with the watch **3200**. The solar cell **3220** recharges the battery **1110** more or less continuously. Both the solar cell **3220** and the LCD **3222** appear at the crystal or glass portion of the watch. Advantageously, this type of watch can be sealed forever so that it can be made absolutely watertight.

Another embodiment of a watch is shown in FIG. 32B. In this particular instance, a circular-shaped solar cell **3240** is positioned atop a circular-shaped battery cell **1110**. The circular-shaped solar cell includes an opening **3241** therein. A set of hands for an analog watch may be inserted through the opening. The crystal or glass face of the watch will then be opened to the solar cell **3240** so that it can continuously charge the battery **1110**, which in turn powers the working portion of the watch.

SUMMARY OF THE INVENTION

A method and system is described for fabricating solid-state energy-storage devices. Some embodiments include fabricating films for an energy-storage device without an anneal step, especially without a cathode anneal. The present invention provides energy focused at the location where it is needed to form a film having certain structural characteristics. Accordingly, the total energy applied to the film and its support is less than if the energy was applied to the entire device, e.g., high temperature annealing the entire device. Thus, the present invention provides methods for applying energy to cure defects and/or create desired crystal structure at the time of depositing a film. In some embodiments, the energy is applied essentially at a few atomic layers at a time during deposition of a film.

In an embodiment as described herein, a film of an energy-storage device is fabricated by depositing a first material layer to a location on a substrate. Energized ions of a second material are directed to the first material to supply energy thereto, thereby assisting the growth of the crystalline structure of the first material. In some embodiments, the first material includes an intercalation material, which releasably stores ions therein. In one embodiment, the intercalation material is a lithium intercalation material. In energy-storage devices, and specifically in thin-film batteries, it is desirable to have large crystal size and a specific crystal orientation to improve electrical characteristics of the energy-storage device.

Another aspect of the invention includes fabricating a layer of an energy-storage device using a first source for supplying component material for the layer and a second source for supplying energy to a location on the substrate at which the layer is to be deposited. In one embodiment, the fabricated layer is the cathode for a thin-film battery. In

52

another embodiment, the thin-film battery is a rechargeable, solid-state lithium-ion battery.

Another feature of the present invention is fabricating the electrolyte film by depositing a first material layer to a location on a substrate. Energized ions of a second material are directed to supply energy to the first material, thus assisting the growth of the crystalline structure of the first material. Another feature of the present invention includes fabricating the anode film by depositing a first intercalation material layer to a location on a substrate. Energized ions of a second material are directed to supply energy to the first material, thereby assisting the growth of the crystalline structure of the first material and controlling stoichiometry of the crystalline structure of the first material.

Another aspect of the present invention includes controlling the energy provided by the second source energized ions. The energized ions provide energy to the intercalation material of about 5 eV or greater.

It is yet another aspect of the present invention to provide a seed layer on which an intercalation film is grown. The seed layer assists the formation of desired crystal structures to improve energy-storage device performance.

Another feature of the present invention includes fabricating an energy-storage device on any one of a plurality of different substrates. Some of the substrates have thermal degradation temperatures that are less than temperatures used for processes conventionally used for making thin-film batteries. It is another feature to provide systems and fabrication techniques that do not cause temperature degradation of a substrate or other layers thereon.

It is an aspect of the present invention to fabricate energy-storage devices under economical manufacturing conditions.

It is another aspect of the present invention to provide improved energy storage device structures that lower internal resistance.

One aspect of the present invention is a method for fabricating an electrolyte film. The method includes depositing an electrolyte material using a deposition source and supplying energized particles to control growth of the electrolyte film. In some embodiments, a second source supplies energized ions that provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure. In some embodiments, the ions have energy of greater than about 5 eV.

Another aspect of the present invention is an energy-storage device having an ultra-thin electrolyte film. In some embodiments, the electrolyte film is less than 5,000 Angstroms.

CONCLUSION

The present invention includes systems and methods for fabricating energy-storage devices and the energy-storage devices per se. The energy-storage devices include an ultra-thinned electrolyte film interposed between two electrode films. Such ultra-thinned electrolyte films improve electrical performance of the energy-storage devices by decreasing the resistance within the electrolyte layer while still maintaining the required insulative property between the two electrodes. By using the methods described herein, such ultra-thin electrolyte films of high structural quality and stoichiometric control are fabricated.

One example of a method according to the teachings herein includes forming an electrolyte second film by depositing electrolyte material using a deposition source, and supplying energized particles from a second source such that

the particles provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure. In some embodiments, the energized particles have energy above 5 eV. In other embodiments, the energy of the particles is less than 3000 eV. In some embodiments, the source gases used to form the ionized particles include oxygen (e.g., O₂) or nitrogen (e.g., N₂). The source gas, in other embodiments, includes one or more noble gas or gasses, e.g., argon, xenon, helium, neon, and/or krypton. In some embodiments, the source gas is a hydrocarbon precursor such that via a chemical vapor deposition methodology, an ultrathin electrolyte is formed on the surface of the cathode. In some embodiments, an electrolyte film fabricated according to the teachings herein has a thickness of less than about 5000 Angstroms. Other embodiments of the electrolyte film have a thickness of less than about 2500 Angstroms, less than about 1000 Angstroms, less than about 500 Angstroms, less than about 250 Angstroms, or less than about 100 Angstroms. Still other embodiments of the electrolyte film have a thickness in the range of about 10 Angstroms to about 200 Angstroms. Yet other embodiments of the electrolyte film have a thickness in the range of about 10 Angstroms to about 100 Angstroms.

In some embodiments, the electrolyte film includes at least one of a plurality of electrolyte materials. In one embodiment, the electrolyte film includes LiPON. Other embodiments of the electrolyte film include at least one of an aluminum oxide or silicon dioxide.

One aspect of the present invention provides a method of fabricating an energy-storage device. This method includes providing a substrate, forming an electrode first film, forming an electrolyte second film (wherein forming the electrolyte second film includes depositing electrolyte material using a deposition source, and supplying energized particles from a second source such that the particles provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure), and forming an electrode third film.

In some embodiments, supplying energized particles includes supplying ions having energy of greater than about 5 eV. In some embodiments, supplying energized particles includes supplying ions having energy of greater than about 3 eV. In some embodiments, supplying energized particles includes supplying ions having energy of greater than about 4 eV. In some embodiments, supplying energized particles includes supplying ions having energy of greater than about 6 eV. In some embodiments, supplying energized particles includes supplying ions having energy of greater than about 7 eV. In some embodiments, supplying energized particles includes supplying ions having energy of greater than about 9 eV. In some embodiments, supplying energized particles includes supplying ions having energy of greater than about 10 eV.

In some embodiments, supplying energized particles includes supplying ions having energy of less than 5000 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 4500 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 4000 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 3500 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 3000 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 2500 eV. In some embodiments, supplying energized

particles includes supplying ions having energy of less than about 2000 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 1500 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 1000 eV. In some embodiments, supplying energized particles includes supplying ions having energy of less than about 500 eV.

In some embodiments, supplying energized particles includes supplying ions having energy in the range of about 5 eV to about 500 eV. In some embodiments, supplying energized particles includes supplying ions having energy in the range of about 5 eV to about 400 eV. In some embodiments, supplying energized particles includes supplying ions having energy in the range of about 5 eV to about 300 eV. In some embodiments, supplying energized particles includes supplying ions having energy in the range of about 5 eV to about 250 eV. In some embodiments, supplying energized particles includes supplying ions having energy in the range of about 5 eV to about 200 eV. In some embodiments, supplying energized particles includes supplying ions having energy in the range of about 5 eV to about 150 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 100 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 50 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 40 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 30 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 20 eV.

In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 500 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 400 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 300 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 250 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 200 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 150 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 100 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 50 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 40 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 30 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 20 eV.

In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 500 eV. In some embodiments, supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 400 eV.

In some embodiments, forming the electrode third film includes depositing at least one of a metal and an intercalation material. In some embodiments, forming the electrode third film includes depositing a metal and an intercalation material. In some embodiments, forming the electrode third film includes depositing an intercalation material. In some embodiments, forming the electrode third film includes depositing a metal. In some such embodiments, the metal is lithium. In some such embodiments, the intercalation material includes a lithium intercalation material.

57

In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 1 nanometer to about 250 nanometers. In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 1 nanometer to about 100 nanometers. In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 2 nanometers to about 250 nanometers. In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 2 nanometers to about 100 nanometers. In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 5 nanometers to about 250 nanometers. In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 5 nanometers to about 100 nanometers. In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 10 nanometers to about 250 nanometers. In some embodiments, forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 10 nanometers to about 100 nanometers.

In some of the above embodiments, the electrolyte second film is lithium phosphorus oxynitride. In some of the above embodiments, the electrolyte second film is a silicon dioxide. In some of the above embodiments, the electrolyte second film is an aluminum oxide.

Another aspect of the present invention provides a solid-state energy-storage device that includes an electrode first film, an electrolyte second film, an electrode third film, wherein the electrolyte second film has a thickness of less than 5000 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 4500 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 4000 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 3500 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 3000 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 2500 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 2000 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 1500 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 1000 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 750 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 500 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 400 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 300 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 250 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 200 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 150 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 100 Angstroms. In some embodiments, the electrolyte second film has a thickness of less than about 50 Angstroms.

In some embodiments, the electrolyte first film includes a lithium intercalation material. In some embodiments, the

58

electrolyte first film includes a lithium metal material. In some embodiments, the third film includes one or more of a metal, a carbon material, and an intercalation material. In some embodiments, the third film includes a metal. In some embodiments, the third film includes a carbon material. In some embodiments, the third film includes an intercalation material. In some embodiments, the third film includes a lithium intercalation material.

In some embodiments, the first film includes a vanadium oxide, the second film includes lithium phosphorus oxynitride, and the third film includes a lithium intercalation material.

In some embodiments of the method, the gas used to form the energetic ions includes one or more of oxygen (e.g., O₂), or nitrogen (e.g., N₂), or a noble gas, e.g., argon, xenon, helium, neon, and krypton.

In some embodiments, the gas used includes a hydrocarbon precursor such that via a chemical vapor deposition methodology, a ultrathin electrolyte is formed on the surface of the cathode.

The invention claimed is:

1. A method of fabricating a thin-film battery, comprising: providing a substrate; forming an electrode first film on the substrate; forming an electrolyte second film electrolyte on the first film, wherein the electrolyte second film blocks the flow of electrons while permitting the flow of ions, and wherein forming the electrolyte second film includes: depositing electrolyte material using a deposition source; and supplying energized particles from a second source such that the particles provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure; and forming an electrode third film on the second film, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than 1000 Angstroms.
2. The method of claim 1, wherein supplying energized particles includes supplying ions having an energy of greater than about 5 eV.
3. The method of claim 1, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.
4. The method of claim 1, wherein supplying energized particles includes supplying ions having an energy of less than about 3000 eV.
5. The method of claim 4, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.
6. The method of claim 1, wherein supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 500 eV.
7. The method of claim 6, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.
8. The method of claim 1, wherein supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 250 eV.
9. The method of claim 8, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

59

10. The method of claim 1, wherein supplying energized particles includes supplying ions having an energy in the range of about 0 eV to about 40 eV.

11. The method of claim 10, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

12. The method of claim 1, wherein depositing electrolyte material includes depositing Li_3PO_4 electrolyte material.

13. The method of claim 12, wherein supplying energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the Li_3PO_4 electrolyte material.

14. The method of claim 13, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

15. The method of claim 12, wherein forming the electrolyte second film includes providing a nitrogen-enriched atmosphere in which the Li_3PO_4 electrolyte material is deposited.

16. The method of claim 15, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

17. The method of claim 12, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

18. The method of claim 1, wherein forming the electrolyte film includes forming the electrolyte film to a thickness sufficient to insulate the electrode first film from the electrode second film and to allow ion transport between the electrode first film and the electrode second film.

19. The method of claim 18, wherein forming the electrode first film includes depositing at least one of a metal and an intercalation material.

20. The method of claim 19, wherein forming the electrode third film includes depositing at least one of a metal and an intercalation material.

21. The method of claim 20, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

22. The method of claim 19, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

23. The method of claim 18, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

24. The method of claim 1, wherein forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 1 nanometer to about 250 nanometers.

25. The method of claim 24, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

26. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 500 eV.

27. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 400 eV.

60

28. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 300 eV.

29. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 250 eV.

30. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 200 eV.

31. The method of claim 30, wherein depositing electrolyte material includes depositing Li_3PO_4 electrolyte material.

32. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 150 eV.

33. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 100 eV.

34. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 300 eV.

35. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 250 eV.

36. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 200 eV.

37. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 150 eV.

38. The method of claim 1, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 100 eV.

39. The method of claim 1, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than 500 Angstroms.

40. The method of claim 39, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

41. The method of claim 1, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 400 Angstroms.

42. The method of claim 1, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 300 Angstroms.

43. The method of claim 1, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 250 Angstroms.

44. The method of claim 43, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

45. The method of claim 1, wherein the forming of the electrode first film includes depositing an intercalation material.

46. The method of claim 45, wherein the forming of the electrode third film includes depositing a metal.

47. The method of claim 1, wherein the forming of the electrode first film includes depositing a metal.

48. The method of claim 47, wherein the forming of the electrode third film includes depositing an intercalation material.

49. The method of claim 1, wherein the supplying of energized particles includes supplying energized nitrogen particles and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

61

50. The method of claim 1, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

51. The method of claim 1, wherein the forming of the second film includes depositing lithium phosphorus oxynitride.

52. An apparatus comprising:

means for providing a substrate;

means for forming an electrode first film on the substrate;

means for forming an electrolyte second film on the first film, wherein the electrolyte second film blocks the flow of electrons while permitting the flow of ions, and wherein the means for forming the electrolyte second film includes:

means for depositing electrolyte material using a deposition source; and

means for supplying energized particles from a second source such that the particles provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure; and

means for forming an electrode third film on the second film, wherein the electrolyte second film is deposited to a thickness of less than about 1000 Angstroms.

53. The apparatus of claim 52, wherein the electrolyte second film is lithium phosphorus oxynitride.

54. The apparatus of claim 52, wherein the electrolyte second film is deposited to a thickness in a range of about 10 Angstroms and about 200 Angstroms.

55. The apparatus of claim 52, wherein the electrolyte second film is deposited to a thickness in a range of about 10 Angstroms and about 50 Angstroms.

56. The apparatus of claim 52, wherein the means for supplying of energized particles supplies energized nitrogen particles, and the nitrogen particles react with the electrolyte material to form lithium phosphorus oxynitride.

57. A method of fabricating a thin-film battery, comprising:

providing a substrate;

forming an electrode first film on the substrate;

forming an electrolyte second film electrolyte on the first film, wherein the electrolyte second film blocks the flow of electrons while permitting the flow of ions, and wherein forming the electrolyte second film includes: depositing electrolyte material using a deposition source; and

supplying energized particles from a second source such that the particles provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure; and

forming an electrode third film on the second film, wherein the supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 50 eV, and wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than 1000 Angstroms.

58. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 30 eV.

59. The method of claim 58, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

60. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 20 eV.

62

61. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 5 eV to about 20 eV.

62. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 40 eV.

63. The method of claim 62, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

64. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 30 eV.

65. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 20 eV.

66. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 10 eV to about 20 eV.

67. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 50 eV.

68. The method of claim 67, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

69. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 40 eV.

70. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV to about 30 eV.

71. The method of claim 57, wherein the supplying energized particles includes supplying ions having an energy in the range of about 20 eV.

72. The method of claim 57, wherein depositing electrolyte material includes depositing Li_3PO_4 electrolyte material.

73. The method of claim 57, wherein the forming of the second film includes depositing lithium phosphorus oxynitride.

74. A method of fabricating a thin-film battery, comprising:

providing a substrate;

forming an electrode first film on the substrate;

forming an electrolyte second film electrolyte on the first film, wherein the electrolyte second film blocks the flow of electrons while permitting the flow of ions, and wherein forming the electrolyte second film includes: depositing electrolyte material using a deposition source; and

supplying energized particles from a second source such that the particles provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure; and

forming an electrode third film on the second film, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 200 Angstroms.

75. The method of claim 74, wherein forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 100 Angstroms.

76. The method of claim 75, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

63

77. The method of claim 74, wherein forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 10 Angstroms to about 200 Angstroms.

78. The method of claim 77, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

79. The method of claim 77, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

80. The method of claim 74, wherein forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 10 Angstroms to about 100 Angstroms.

81. The method of claim 80, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

82. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 150 Angstroms.

83. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 10 Angstroms and about 50 Angstroms.

84. The method of claim 83, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.

85. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 75 Angstroms.

86. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 50 Angstroms.

87. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than about 30 Angstroms.

88. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of about 20 Angstroms.

89. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of about 20 Angstroms.

90. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of about 10 Angstroms.

91. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness in a range of about 20 Angstroms and about 200 Angstroms.

92. The method of claim 74, wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of about 20 Angstroms and about 200 Angstroms.

93. The method of claim 52, wherein the electrolyte second film is lithium phosphorus oxynitride.

94. The method of claim 74, wherein depositing electrolyte material includes depositing Li_3PO_4 electrolyte material.

95. A method of fabricating a thin-film battery, comprising:
providing a substrate;
forming an electrode first film on the substrate;

64

forming an electrolyte second film electrolyte on the first film, wherein the electrolyte second film blocks the flow of electrons while permitting the flow of ions, and wherein forming the electrolyte second film includes:

depositing electrolyte material using a deposition source; and

supplying energized particles from a second source such that the particles provide energy to the electrolyte material to deposit the electrolyte material into a desired film structure; and

forming an electrode third film on the second film,

wherein the forming of the first film includes depositing a vanadium oxide, the forming of the second film includes depositing lithium phosphorus oxynitride, and the forming of the third film includes depositing a lithium intercalation material, and

wherein the forming the electrolyte second film includes forming the electrolyte film to a thickness of less than 1000 Angstroms.

96. A method comprising:

providing a substrate;

depositing an electrolyte second film on the first film, wherein the electrolyte second film blocks, the flow of electrons while permitting the flow of ions, and wherein the electrolyte second film includes LIPON electrolyte material deposited using an electrolyte deposition source and energized nitrogen particles from a second source such that the energized nitrogen particles provide energy to the electrolyte material during its deposition to form the electrolyte material into a desired film structure; and

depositing an electrode third film on the second film,

wherein the electrolyte second film is deposited to a thickness in a range of about 10 Angstroms and about 200 Angstroms.

97. The method of claim 96, wherein the electrolyte second film is deposited to a thickness in a range of about 10 Angstroms and about 100 Angstroms.

98. The method of claim 96, wherein the electrolyte second film is deposited to a thickness in a range of about 10 Angstroms and about 50 Angstroms.

99. The method of claim 96, wherein the forming of the second film includes depositing lithium phosphorus oxynitride.

100. An apparatus comprising:

means for providing a substrate;

means for depositing an electrode first film on the substrate;

means for depositing an electrolyte second film on the first film, wherein the electrolyte second film blocks the flow of electrons while permitting the flow of ions, and wherein the electrolyte second film includes LIPON electrolyte material deposited using an electrolyte deposition source and energized nitrogen particles from a second source such that the energized nitrogen particles provide energy to the electrolyte material during its deposition to form the electrolyte material into a desired film structure; and

65

means for depositing an electrode third film to form a battery that includes the electrolyte second film and the electrode first film,

wherein the electrolyte second film is deposited to a thickness of less than about 1000 Angstroms.

101. The apparatus of claim **100**, wherein the electrolyte second film is deposited to a thickness in a range of about 10 Angstroms and about 200 Angstroms.

66

102. The apparatus of claim **100**, wherein the electrolyte second film is deposited to a thickness in a range of about 10 Angstroms and about 50 Angstroms.

103. The apparatus of claim **100**, wherein the electrolyte second film is lithium phosphorus oxynitride.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 7,194,801 B2
APPLICATION NO. : 09/815983
DATED : March 27, 2007
INVENTOR(S) : Mark Lynn Jenson and Victor Henry Weiss

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 58, Line 43 (line 1 of claim 3):	Delete "The method of claim 1, wherein the supplying of" and insert --The method of claim 2, wherein the supplying of-- therefor.
In Column 61, Lines 1-4 (entire claim 50):	Delete "The method of claim 1, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride."
In Column 61, Line 60 (line 3 of claim 58):	Delete "in the range of about 5 eV to about 30 eV" and insert --in the range of about 5 eV to about 40 eV-- therefor.
In Column 61, Line 67 (line 3 of claim 60):	Delete "in the range of about 5 eV to about 20 eV" and insert --in the range of about 5 eV to about 30 eV-- therefor.
In Column 62, Line 6 (line 3 of claim 62):	Delete "in the range of about 10 eV to about 40 eV" and insert --in the range of about 10 eV to about 50 eV-- therefor.
In Column 62, Line 13 (line 3 of claim 64):	Delete "in the range of about 10 eV to about 30 eV" and insert --in the range of about 10 eV to about 40 eV-- therefor.
In Column 62, Line 16 (line 3 of claim 65):	Delete "in the range of about 10 eV to about 20 eV" and insert --in the range of about 10 eV to about 30 eV-- therefor.
In Column 63, Line 53 (line 4 of claim 91):	Delete "200 Angstroms" and insert --150 Angstroms-- therefor.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 7,194,801 B2
APPLICATION NO. : 09/815983
DATED : March 27, 2007
INVENTOR(S) : Mark Lynn Jenson and Victor Henry Weiss

Page 2 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 63, actual Lines 58-59 (entire claim 93):

Delete "93. The method of claim 52, wherein the electrolyte second film is lithium phosphorous oxynitride."

and insert --93. The method of claim 92, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.-- therefor.

In Column 64, actual Line 21 (insertion after line 2 of claim 96):

After "providing a substrate;"
insert --depositing an electrode first film on the substrate; --

In Column 64, actual Line 25 (line 6 of claim 96):

Delete "LIPON" and insert
--LiPON-- therefor.

In Column 64, Line 52 (line 8 of claim 100):

Delete "LIPON" and insert --LiPON--
therefor.

Signed and Sealed this

Second Day of October, 2007



JON W. DUDAS

Director of the United States Patent and Trademark Office

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 7,194,801 B2
APPLICATION NO. : 09/815983
DATED : March 27, 2007
INVENTOR(S) : Mark Lynn Jenson and Victor Henry Weiss

Page 2 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 63, actual Lines 58-59 (entire claim 93):

Delete "93. The method of claim 52, wherein the electrolyte second film is lithium phosphorous oxynitride."

and insert --93. The method of claim 92, wherein the supplying of energized particles includes supplying energized nitrogen particles, and reacting the nitrogen particles with the electrolyte material to form lithium phosphorus oxynitride.-- therefor.

In Column 64, actual Line 21 (insertion after line 2 of claim 96):

After "providing a substrate;"
insert --depositing an electrode first film on the substrate; --

In Column 64, actual Line 25 (line 6 of claim 96):

Delete "LIPON" and insert
--LiPON-- therefor.

In Column 64, Line 52 (line 8 of claim 100):

Delete "LIPON" and insert --LiPON--
therefor.

Signed and Sealed this

Second Day of October, 2007



JON W. DUDAS

Director of the United States Patent and Trademark Office