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(56) Documents Cited:
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by electron cyclotron resonance (ECR) plasma
sputtering method and its application to all-solid-
state thin-film lithium batteries", pp. 990 - 995.

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Other: **WPI, EPODOC, Patent Fulltext, XPESP,**
SPRINGER
updated as appropriate

Additional Fields
Other: **None**

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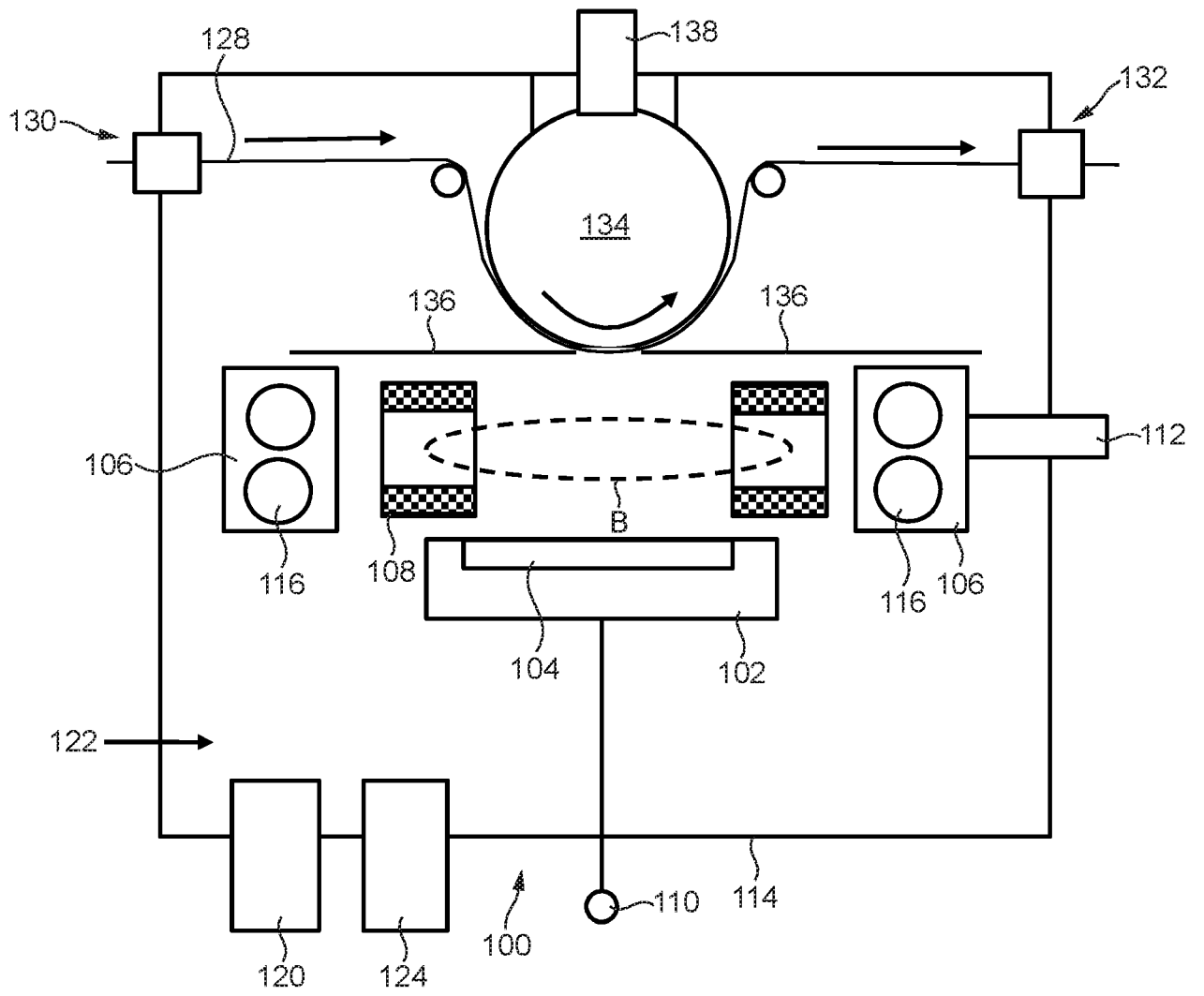


FIG. 1a

1001 ↘

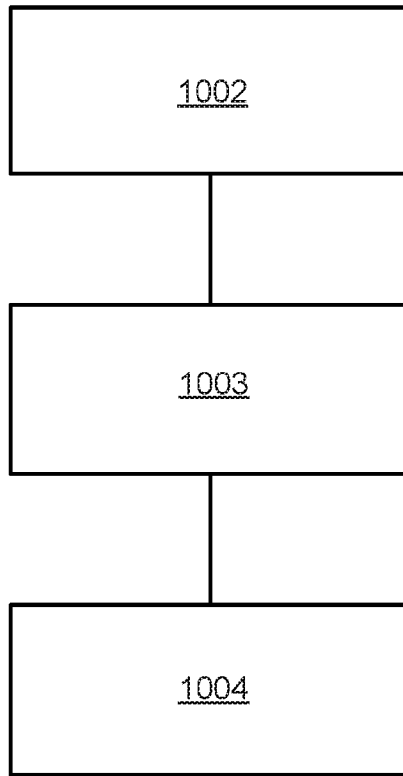


FIG. 1b

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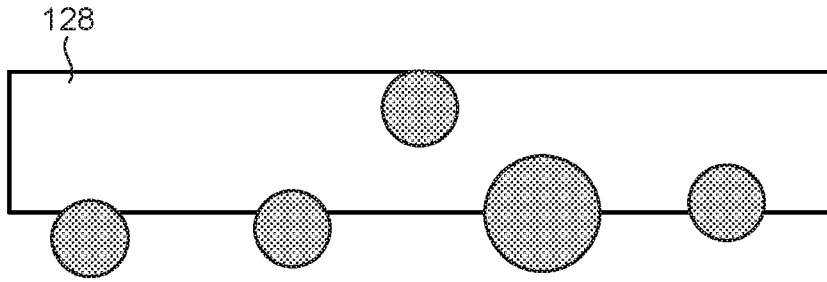


FIG. 1c

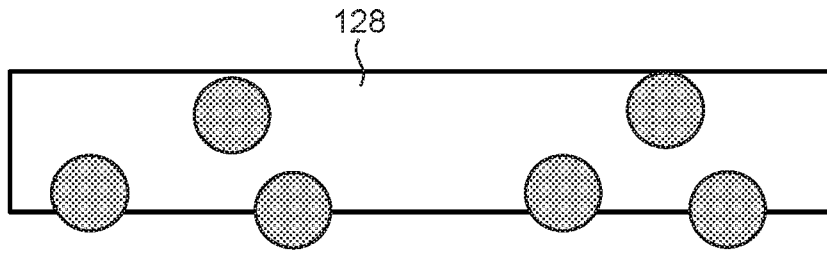


FIG. 1d

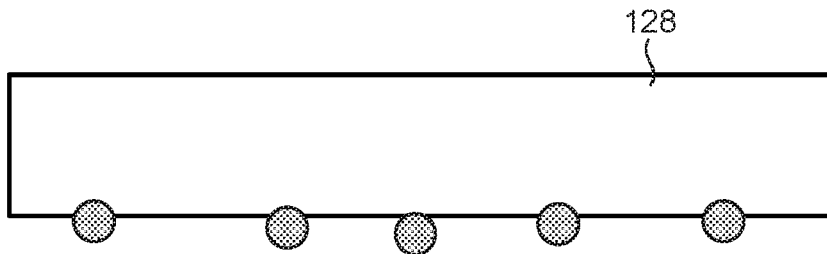


FIG. 1e

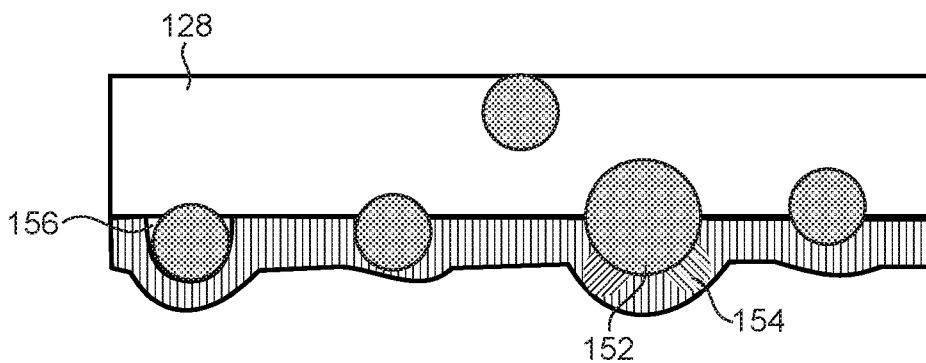


FIG. 1f

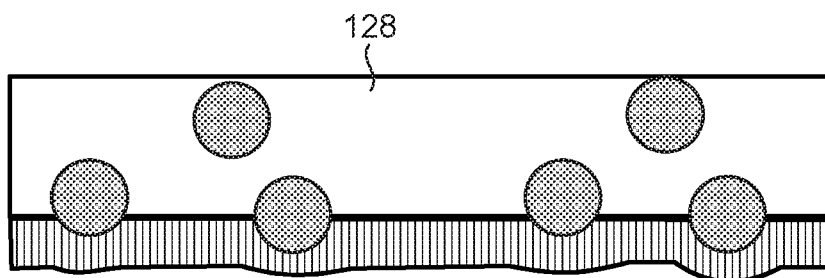


FIG. 1g

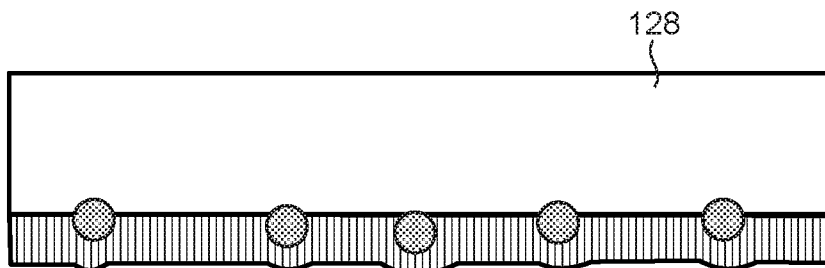


FIG. 1h

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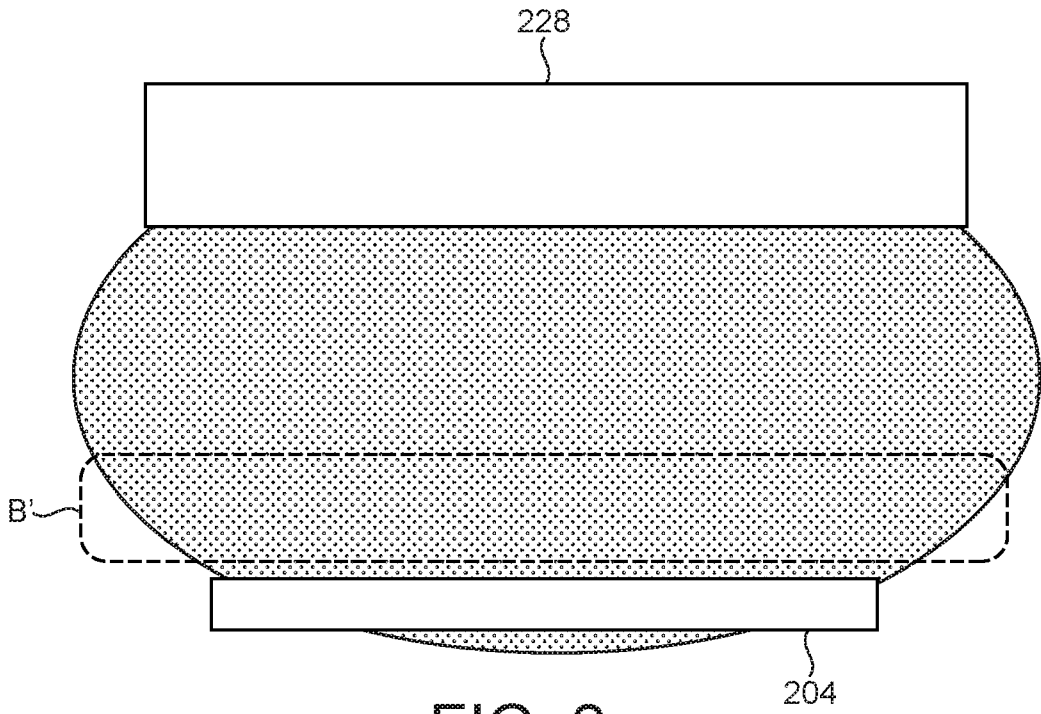


FIG. 2a

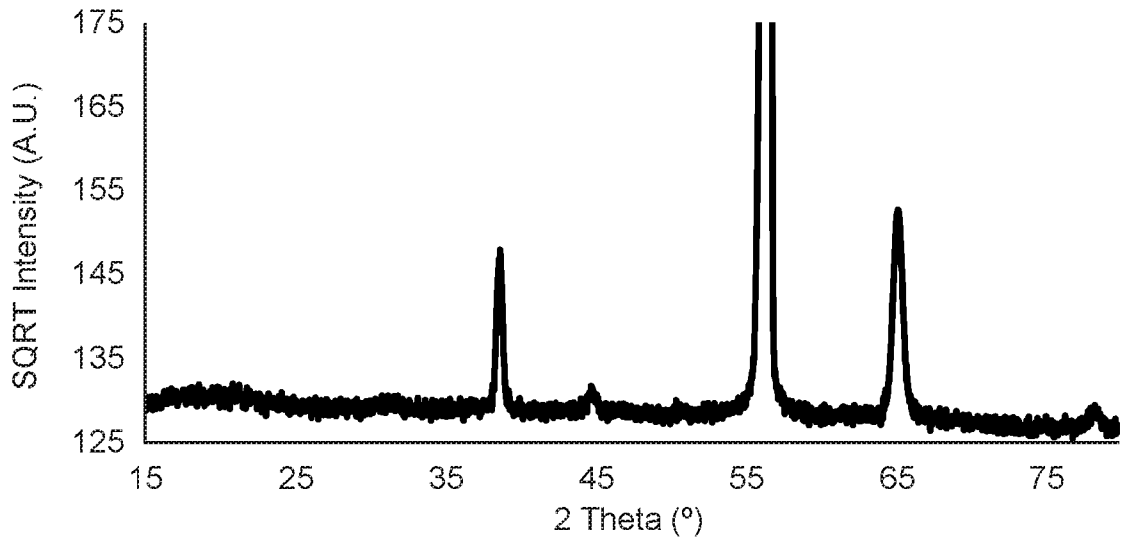


FIG. 2b

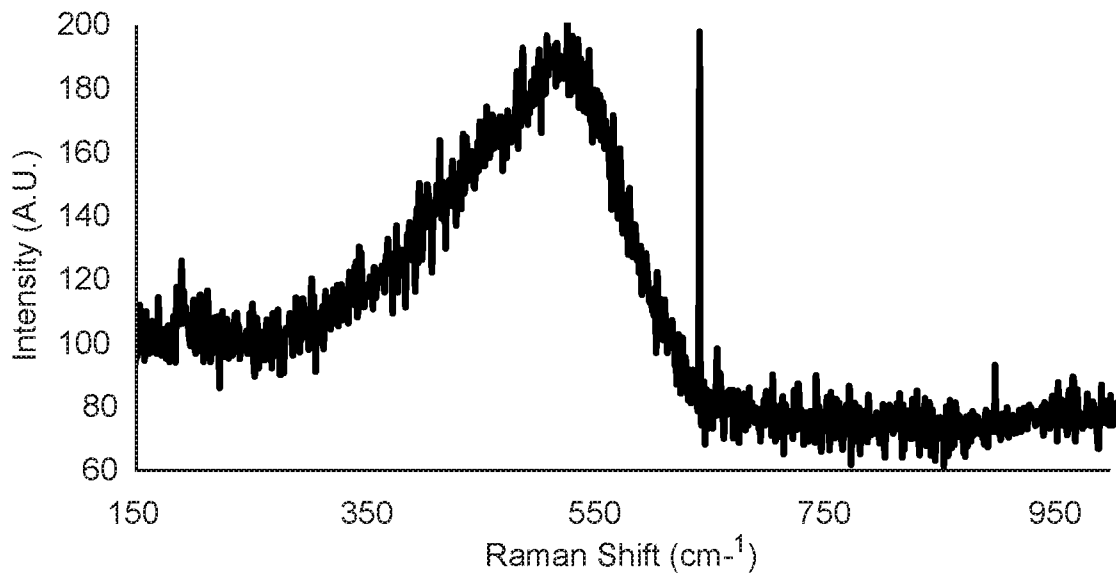


FIG. 2c

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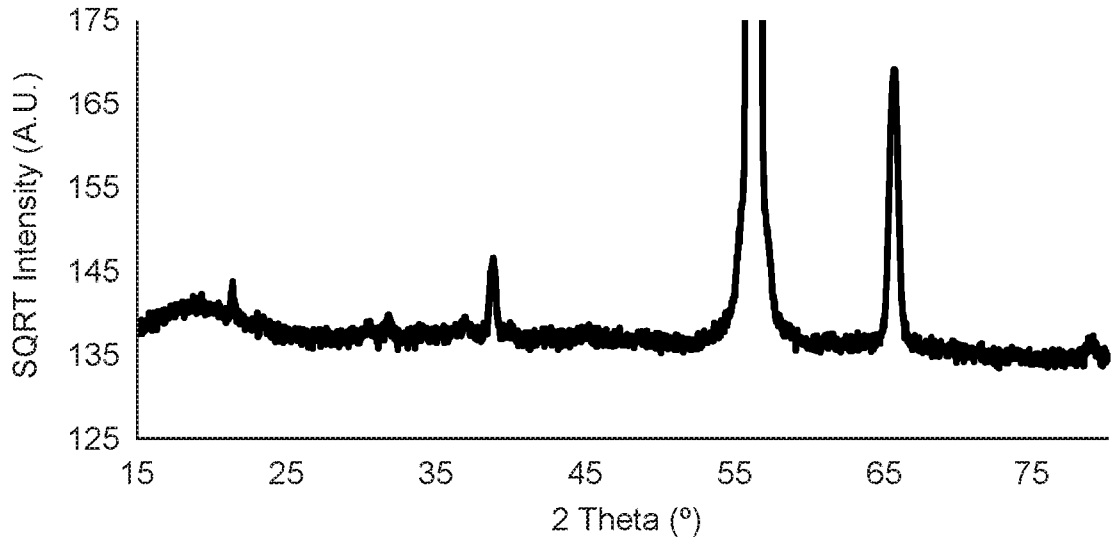


FIG. 2d

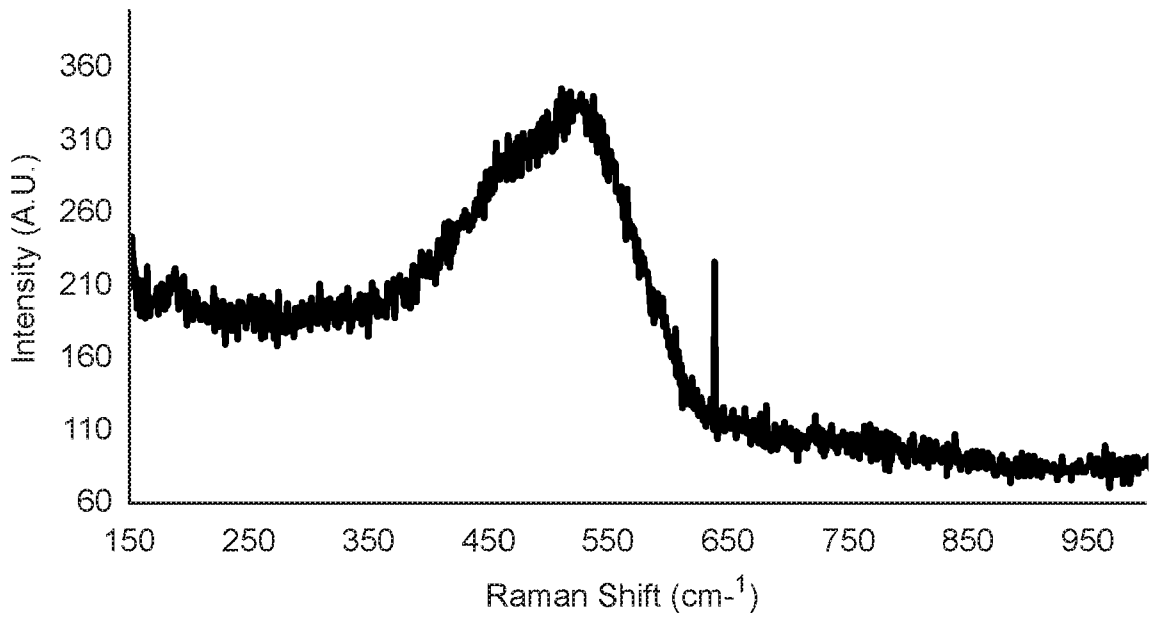


FIG. 2e

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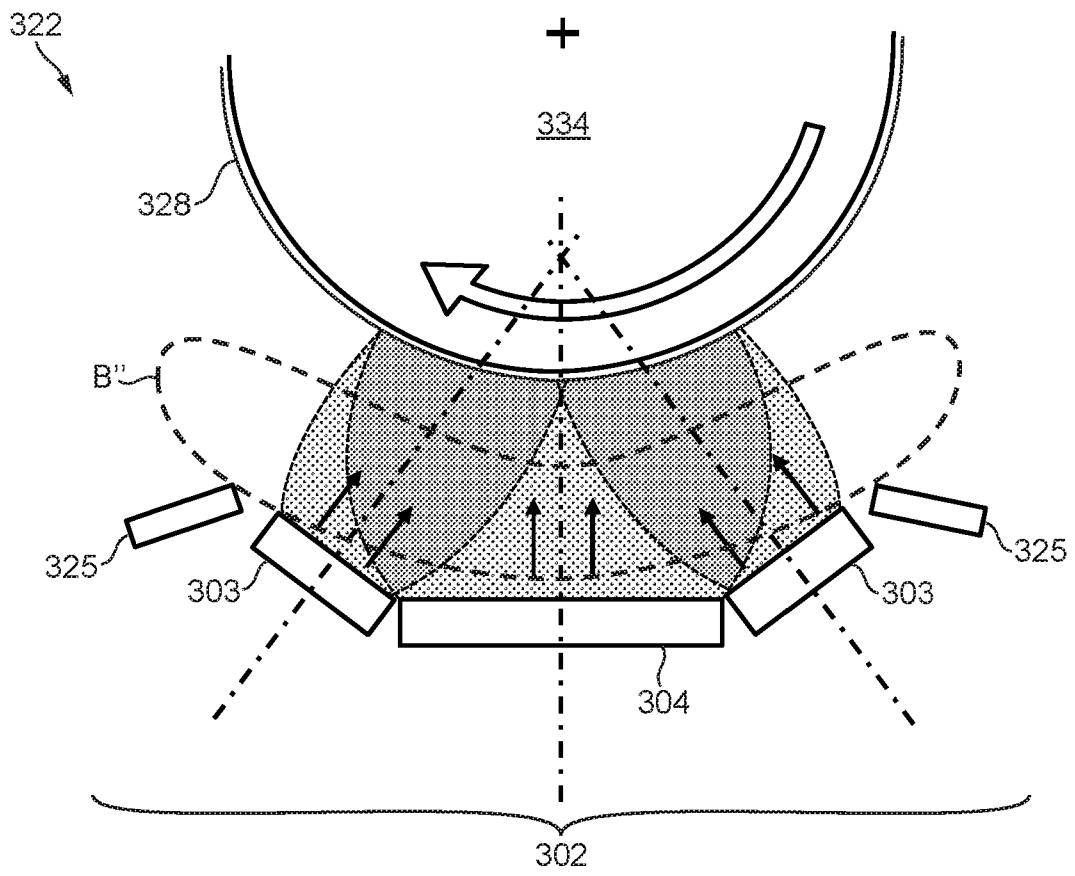


FIG. 3a

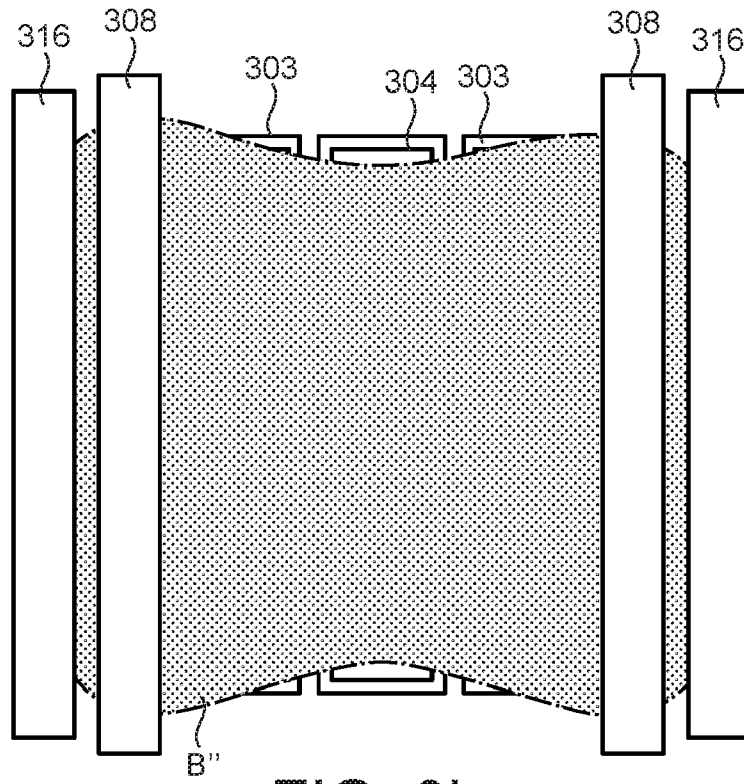


FIG. 3b

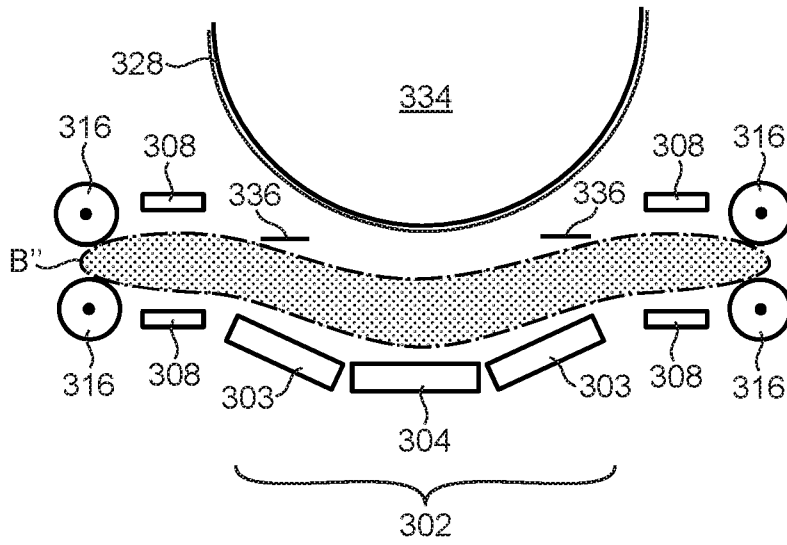


FIG. 3c

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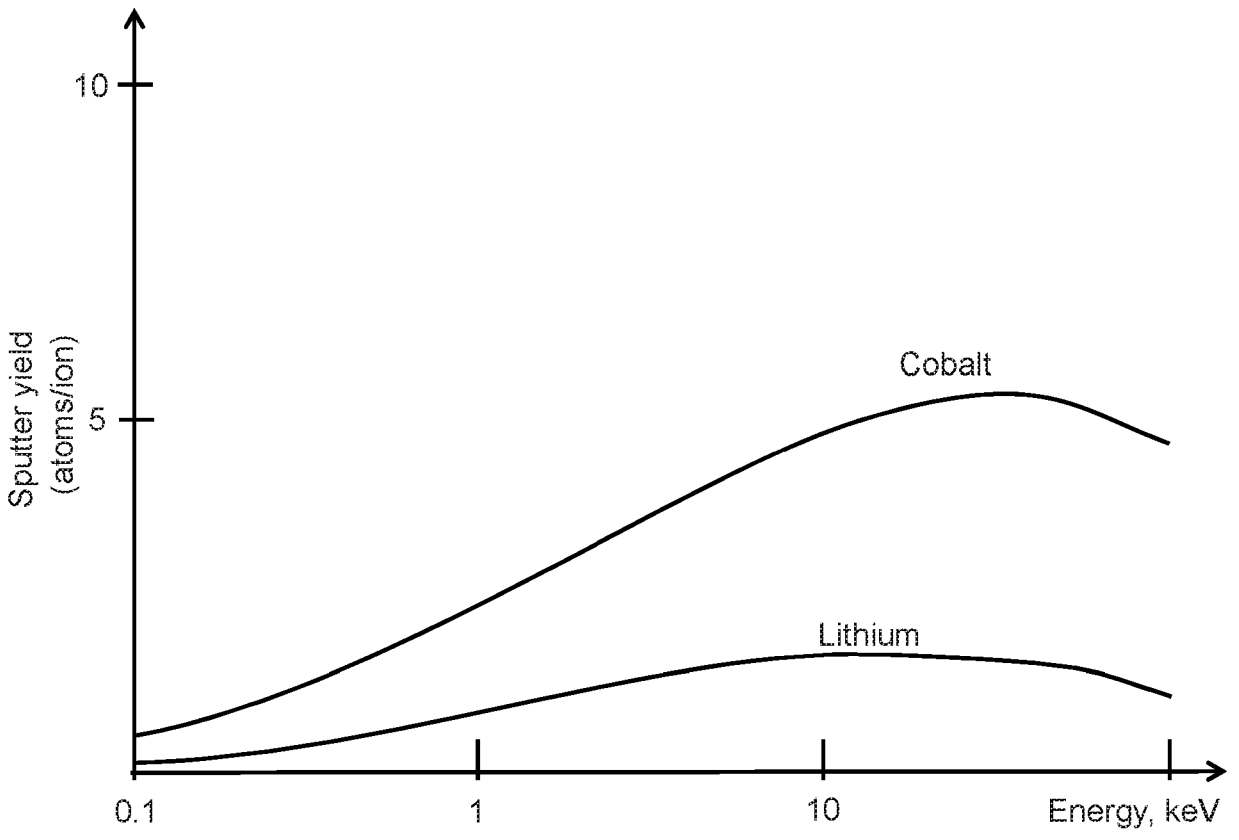


FIG. 3d

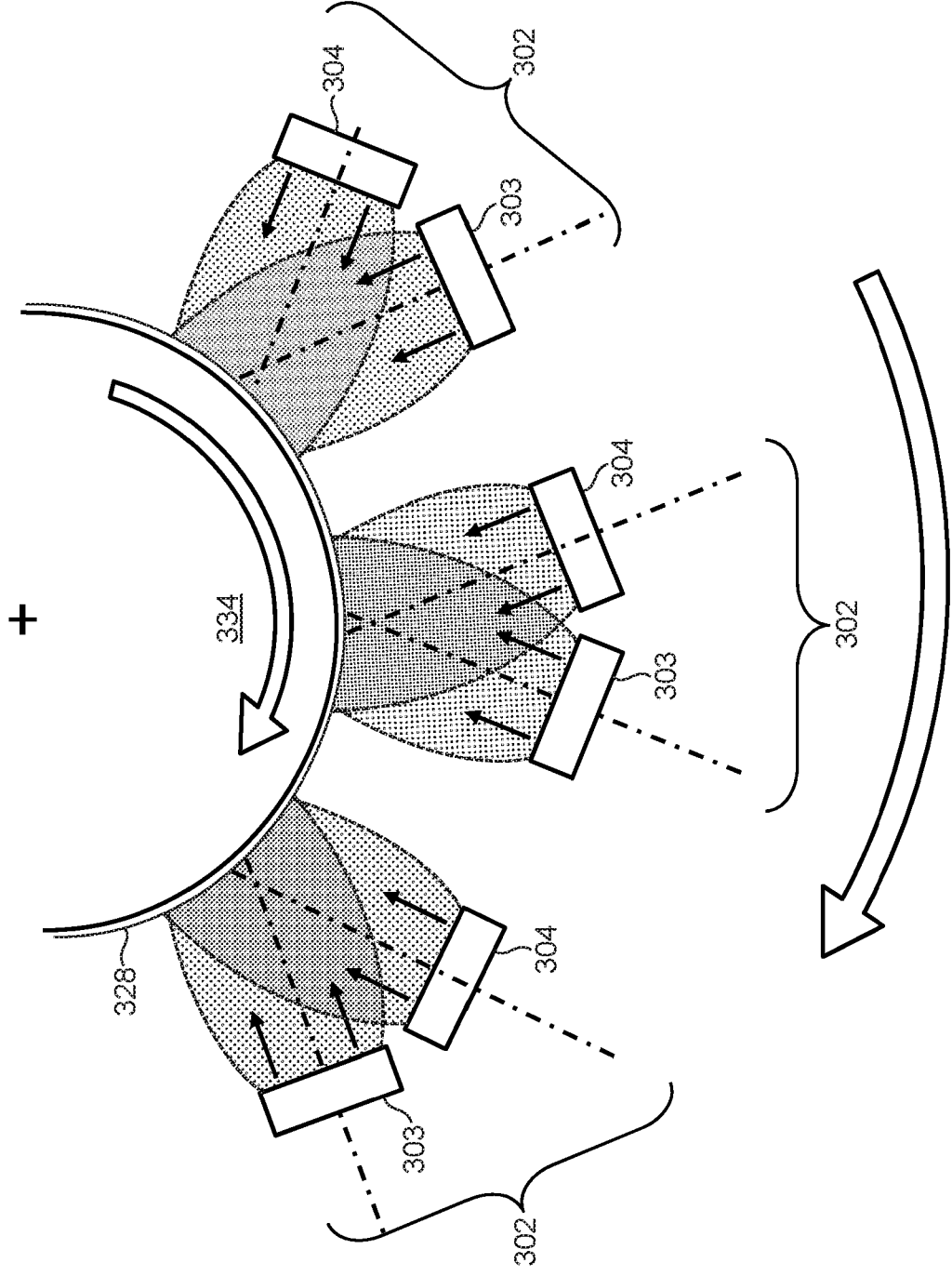


FIG. 3e

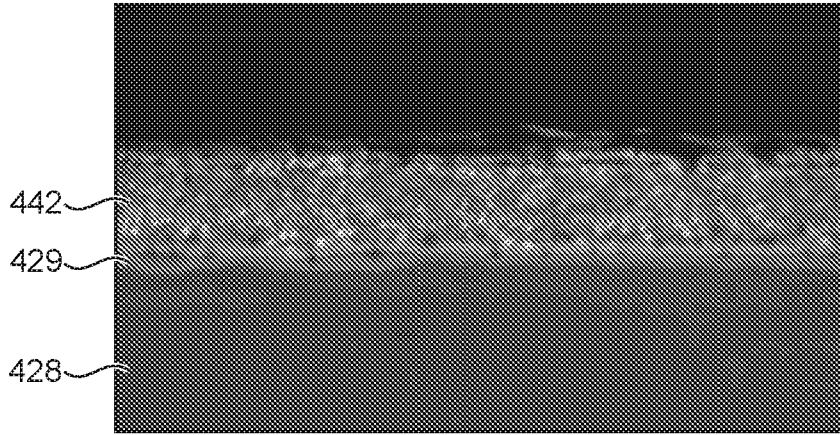


FIG. 4a

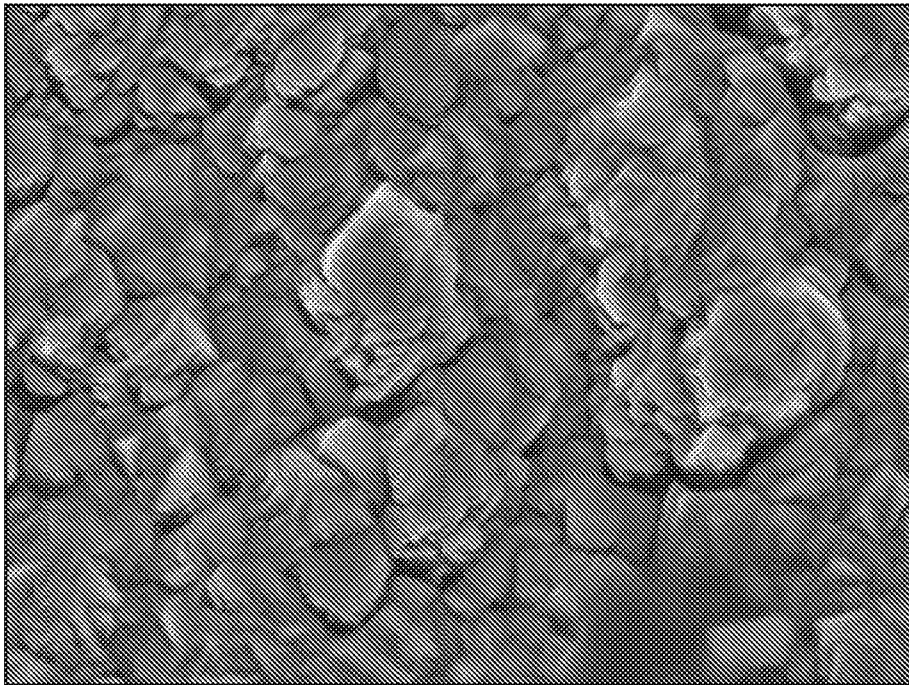


FIG. 4b

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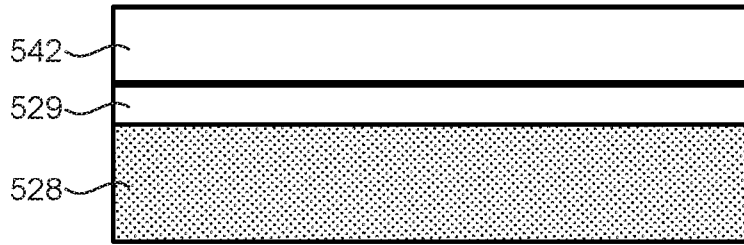


FIG. 5a

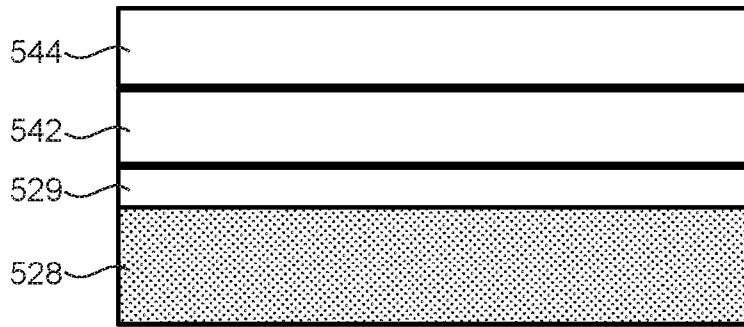


FIG. 5b

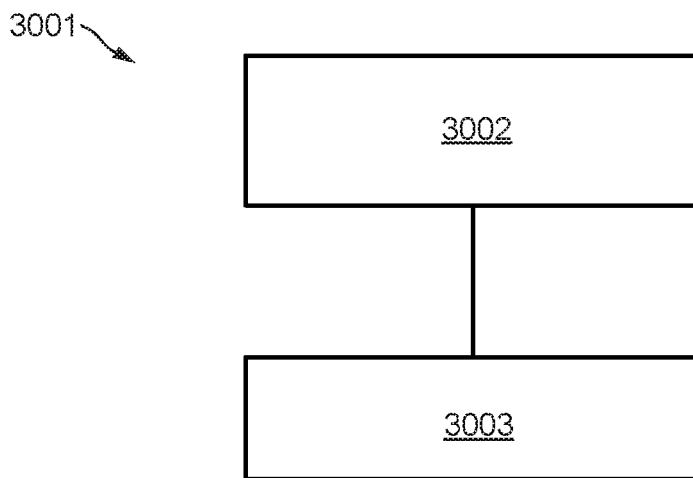


FIG. 5c

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5001 ↘

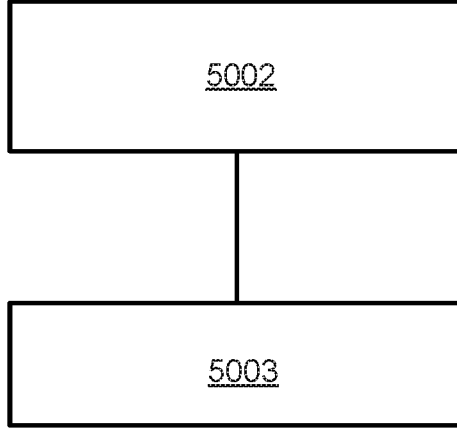


FIG. 6

6001 ↘

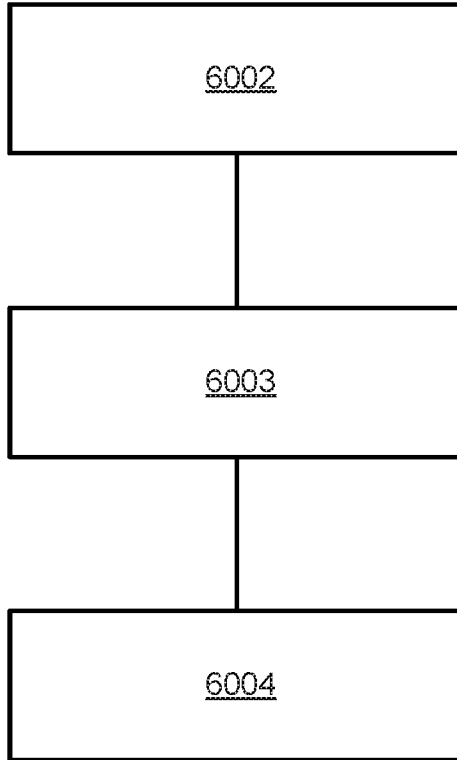


FIG. 7a

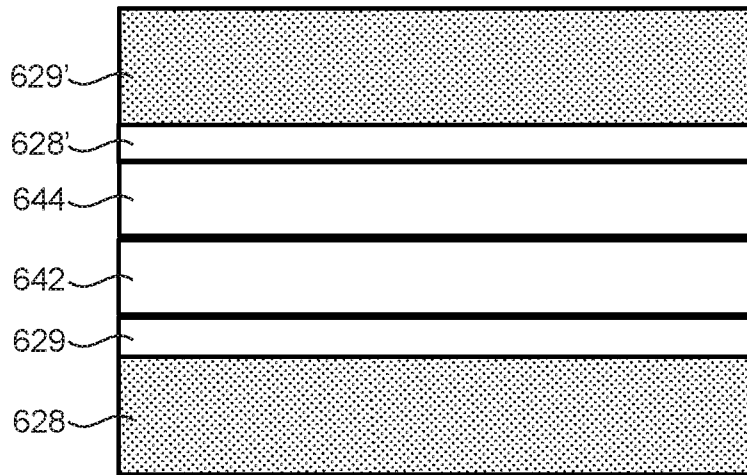


FIG. 7b

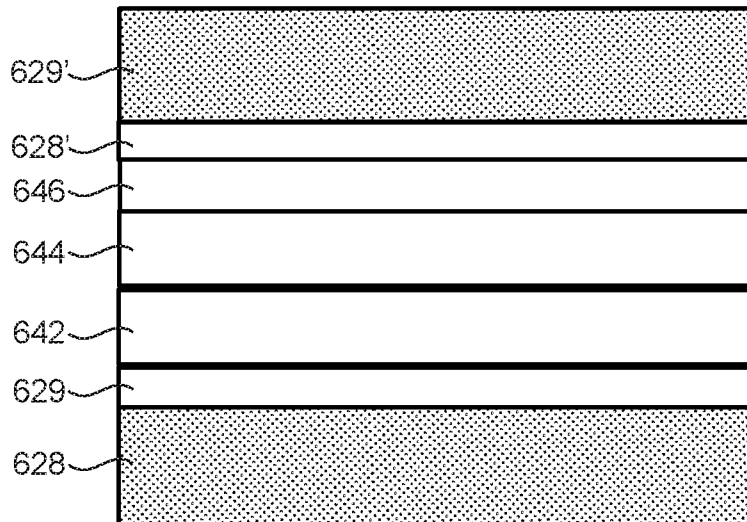


FIG. 7c

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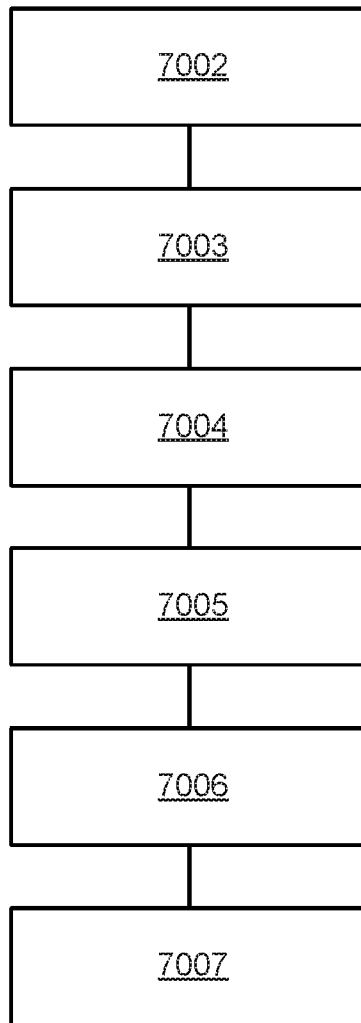


FIG. 8a

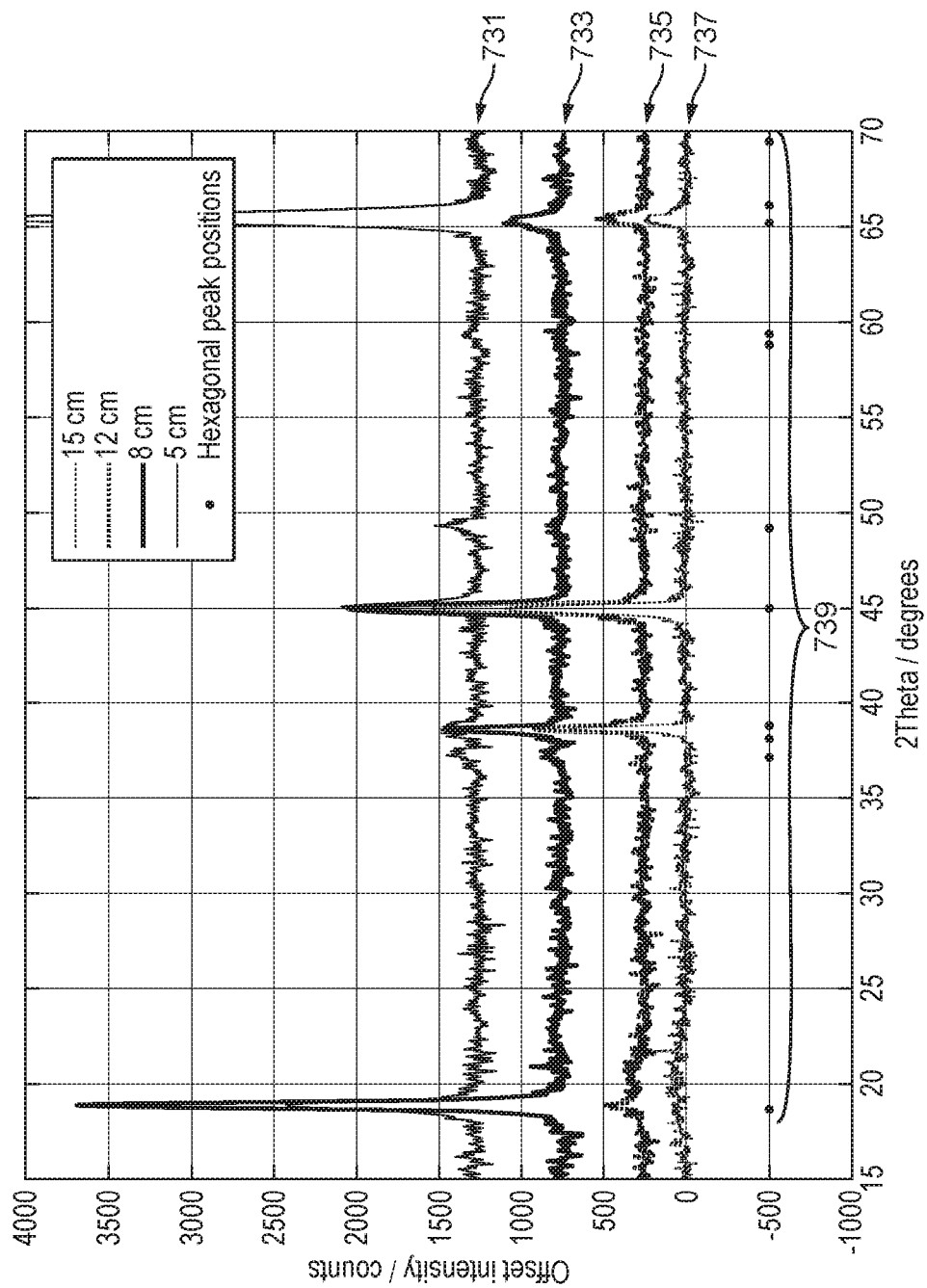


FIG. 8b

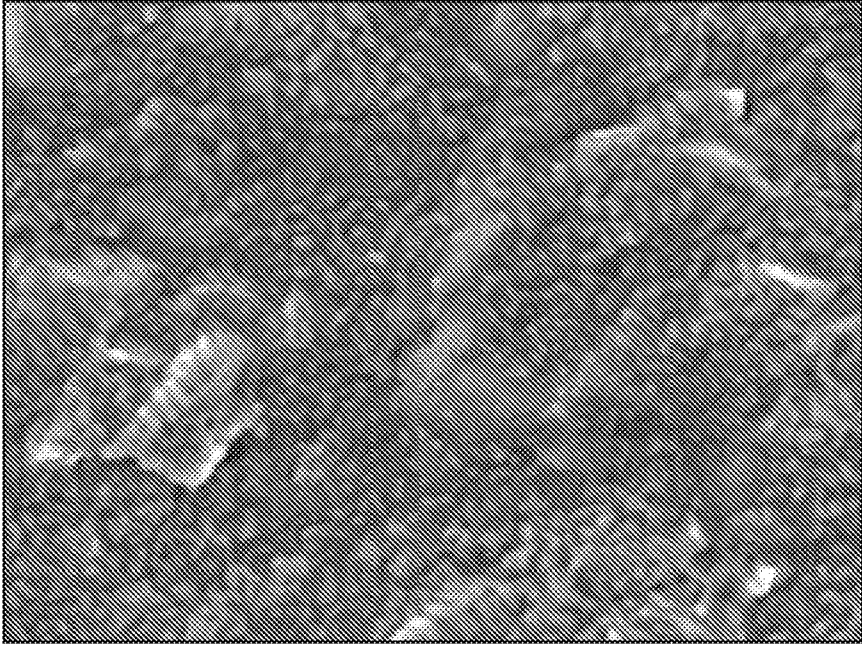


FIG. 9a

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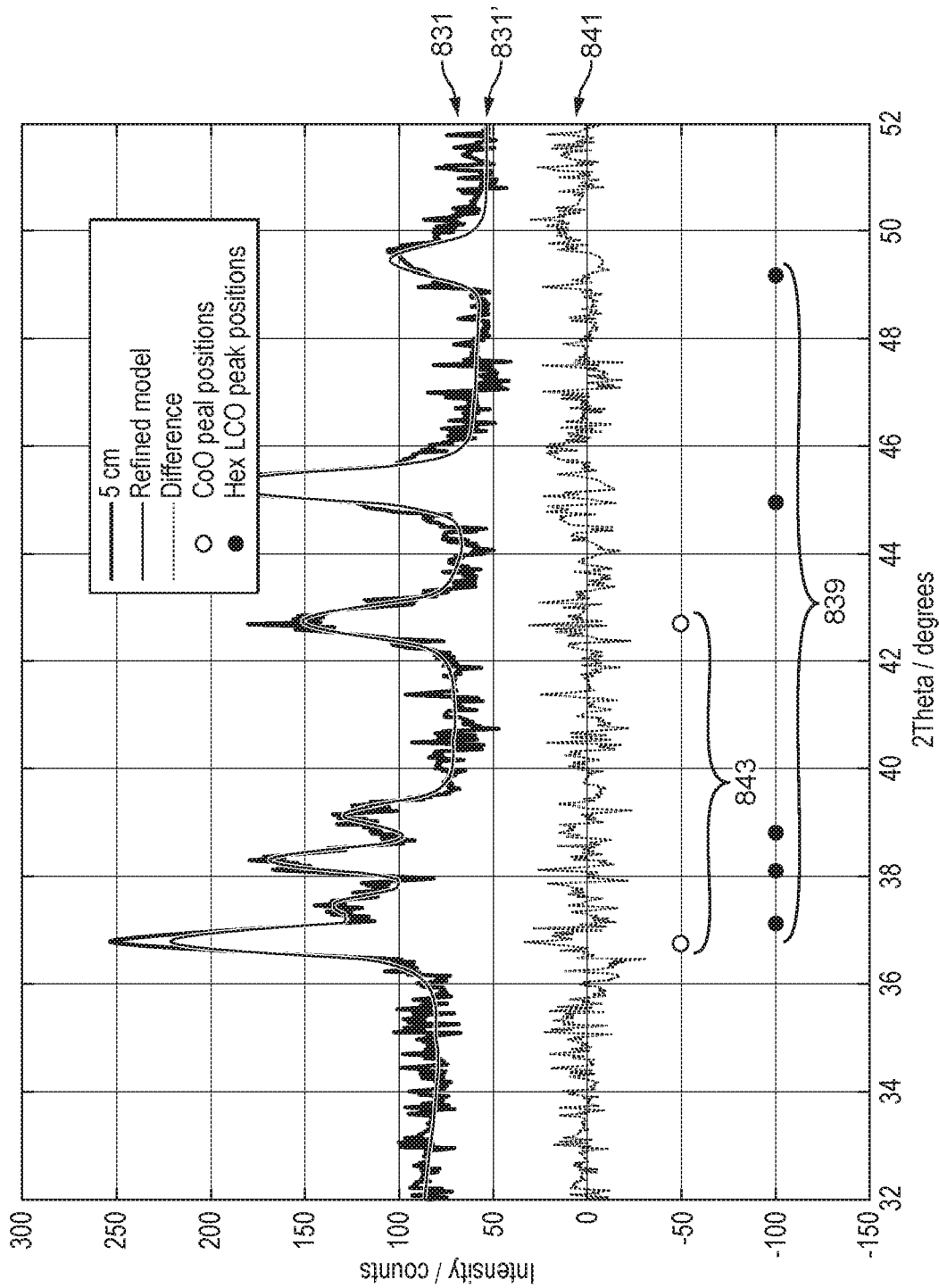


FIG. 9b

8001 ↘

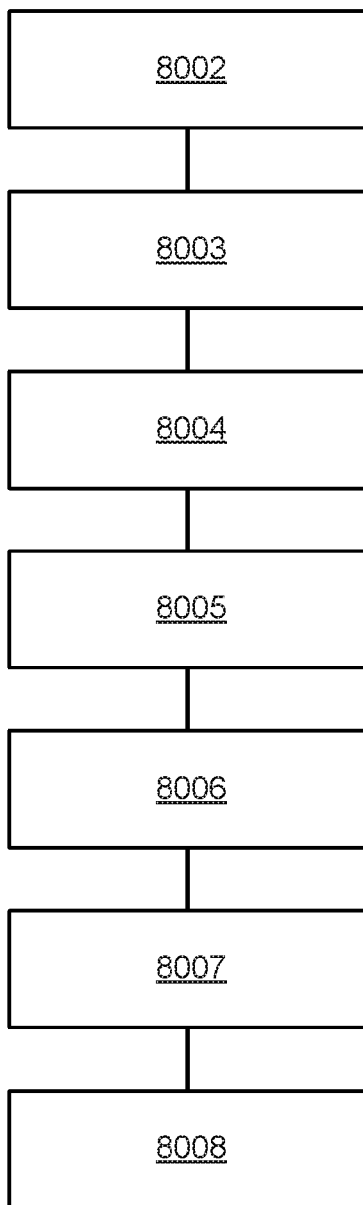


FIG. 10a

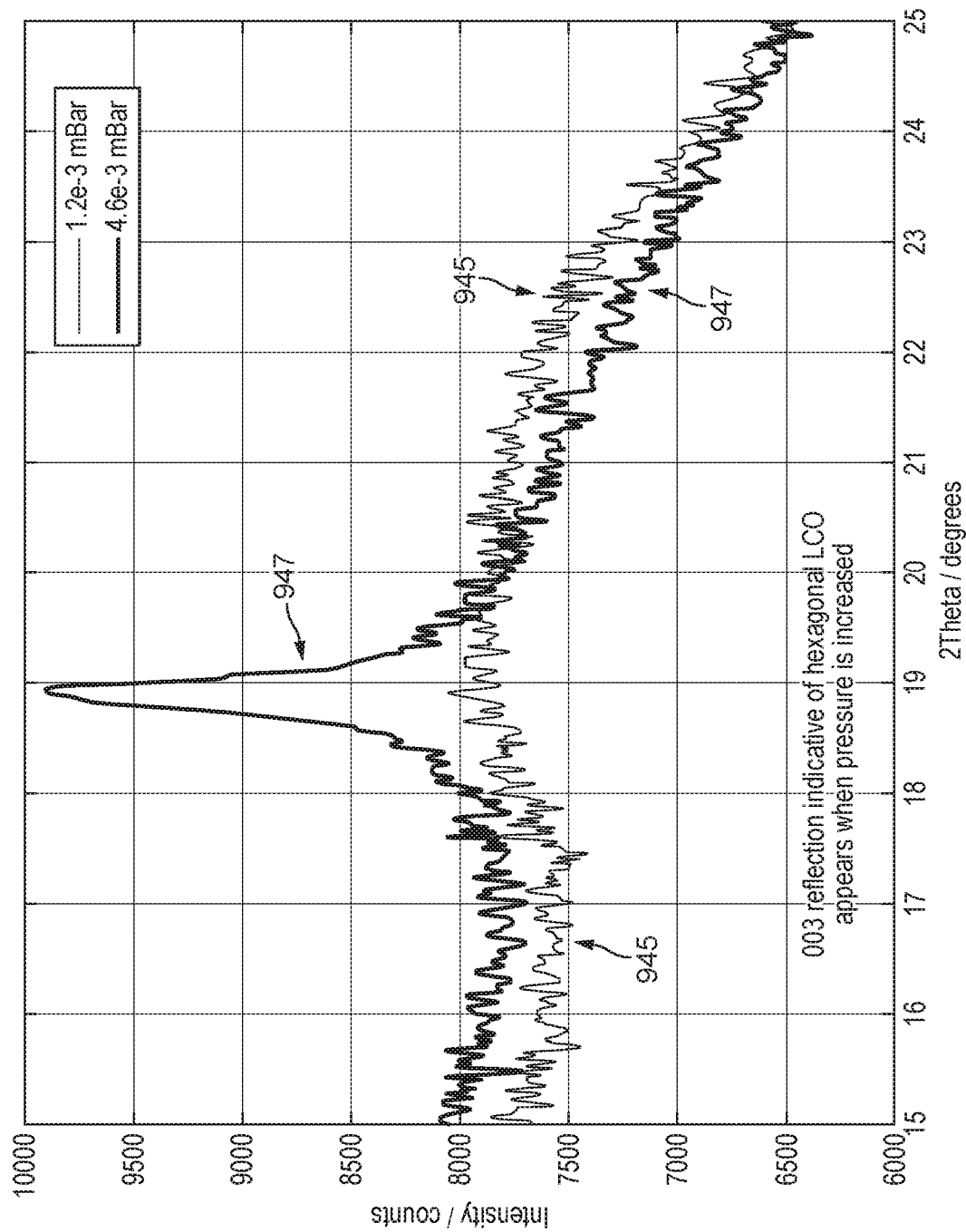


FIG. 10b

9001 ↘

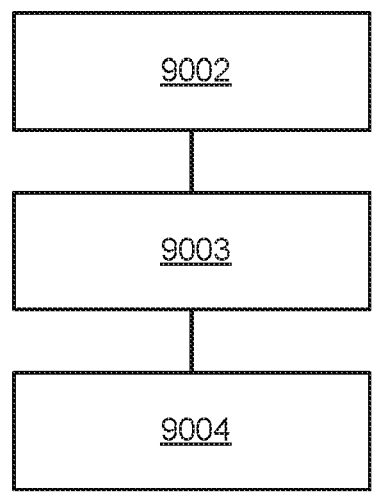


FIG. 11a

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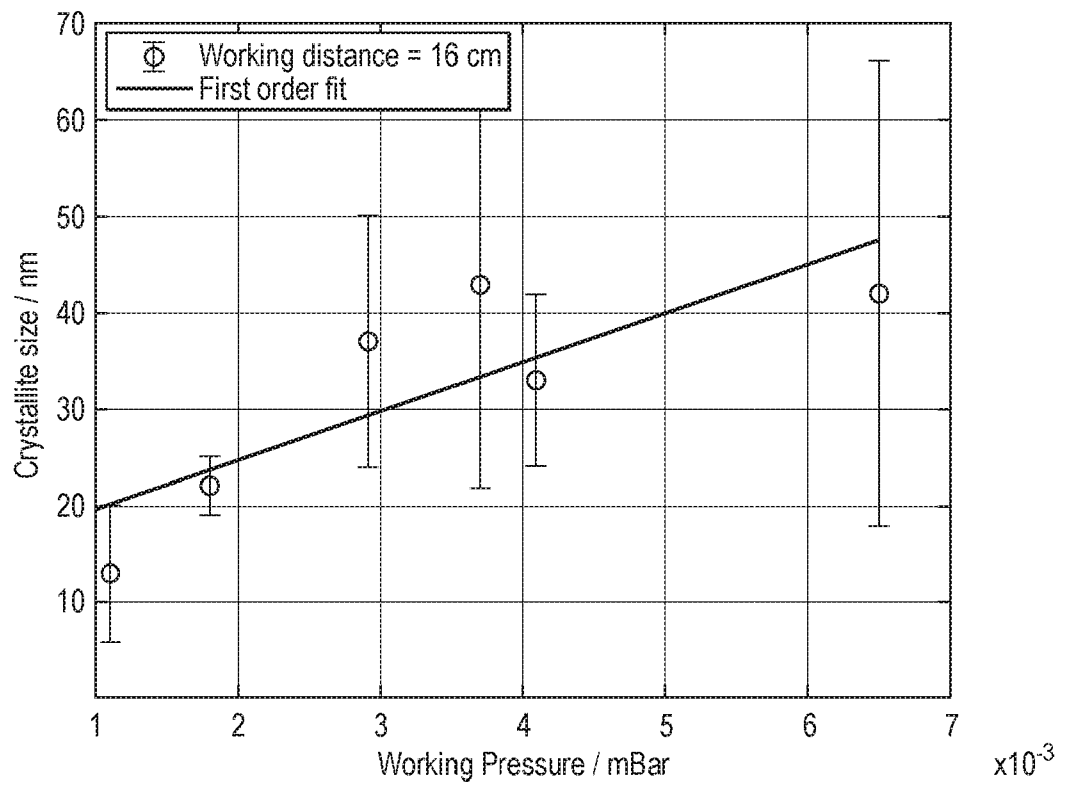


FIG. 11b

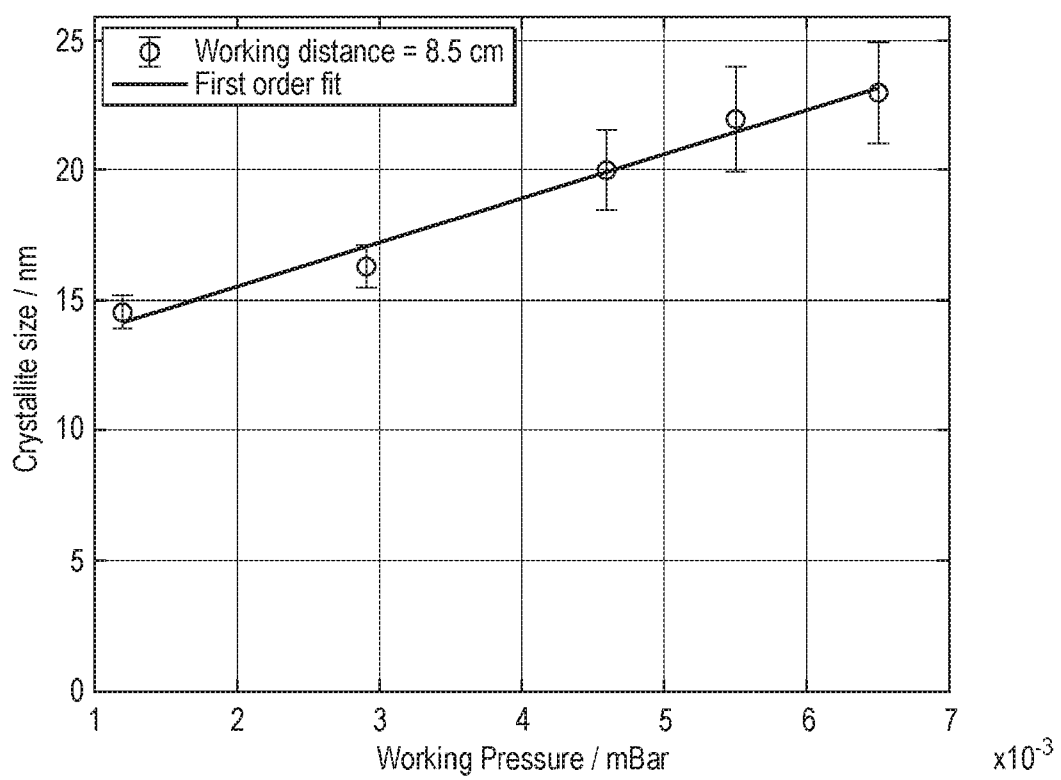


FIG. 11c

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1101 ↘

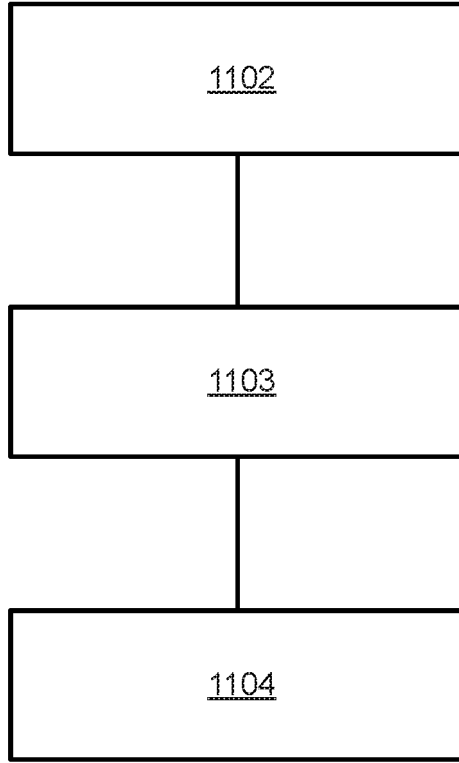


FIG. 12

1201 ↘

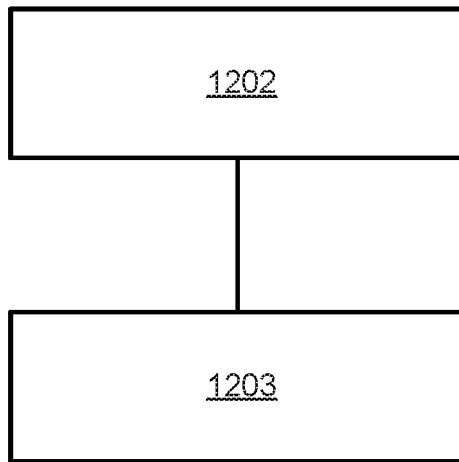


FIG. 13

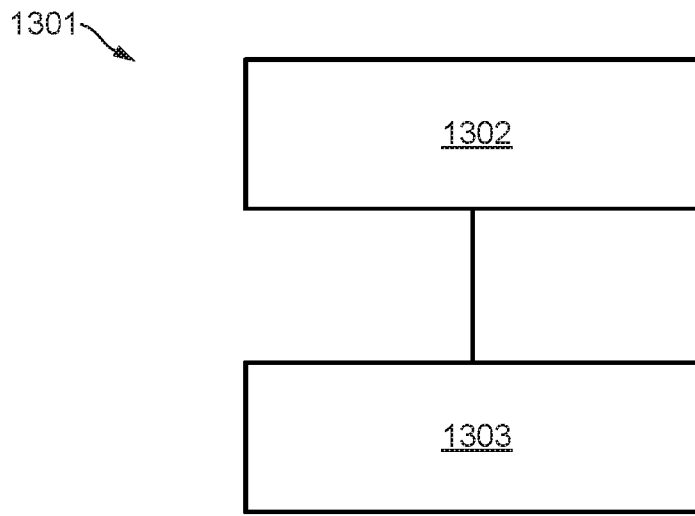


FIG. 14

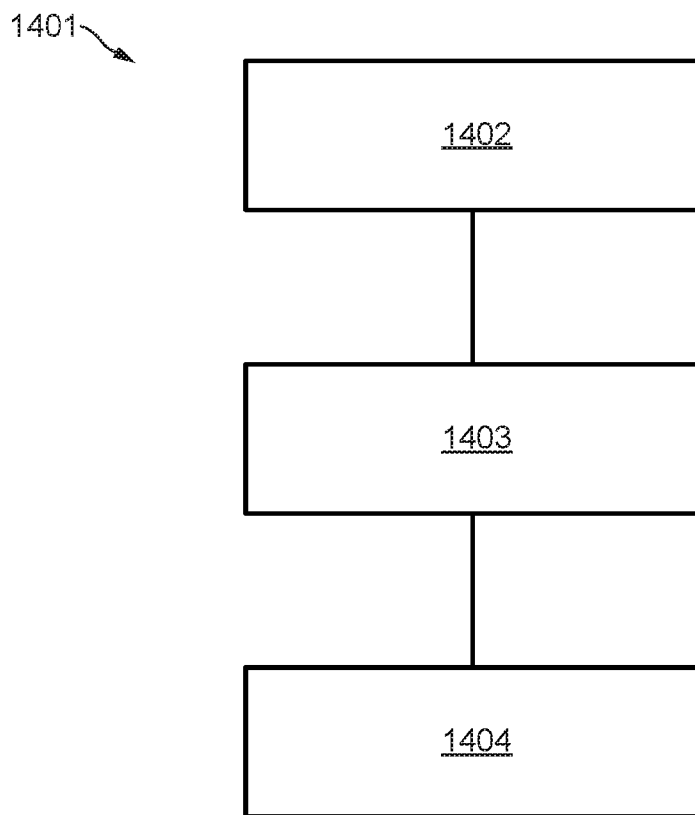


FIG. 15

1501 ↘

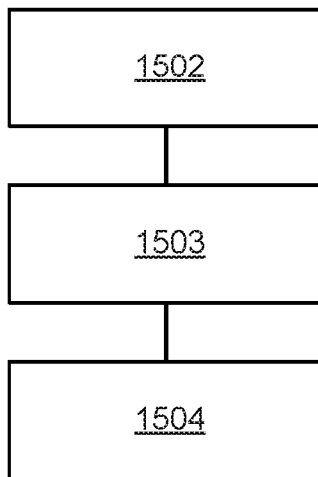


FIG. 16

1601 ↘

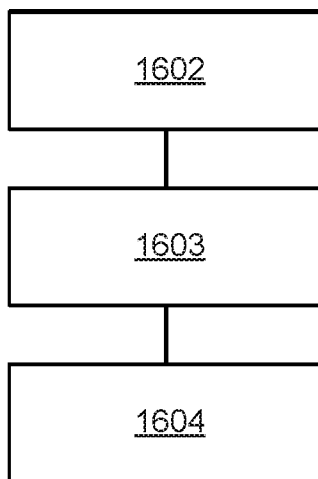


FIG. 17

Method of forming crystalline layer, method of forming a battery half cell

BACKGROUND OF THE INVENTION

[0001] The present disclosure relates to methods of forming crystalline layers, such as cathode layers of solid-state battery cells.

[0002] The present invention concerns methods of forming crystalline layers. More particularly, but not exclusively, this invention concerns a method of forming a crystalline layer on a substrate, a method of forming a crystalline cathode layer of a solid-state battery, a method of forming a solid state battery half-cell, a method of forming a solid state battery cell and a method of forming a solid state battery. The invention also concerns coated substrates, solid state battery half-cells, solid state battery cells and solid state batteries made in accordance with such methods.

[0003] Solid state batteries comprise a cathode material. Such materials are often lithium-ion containing materials, such as LiCoO_2 . They may be deposited using plasma, or sputter, deposition techniques, but typically require annealing in order to produce a high energy crystalline material which is used as a cathode material. The annealing process typically involves heating the lithium-containing material to temperatures of about 400°C after deposition onto a substrate. This requires a lot of energy and exposes any other materials associated with the lithium-containing material, such as underlying substrates to such temperatures which may not be desirable.

[0004] The present invention seeks to mitigate the above-mentioned problems. Alternatively or additionally, the present invention seeks to provide an improved method of forming a crystalline layer on a substrate.

SUMMARY OF THE INVENTION

[0005] There is provided a method of forming a crystalline layer on a substrate, the crystalline layer comprising an alkali metal or alkaline earth metal, at least one transition metal and a counter-ion, the method comprising: generating a plasma remote from one or more sputter targets for forming the cathode layer, generating sputtered material from the

one or more targets using the plasma, and depositing the sputtered material on the substrate, thereby forming the crystalline cathode layer.

[0006] The applicant has discovered that it is possible to deposit crystalline material comprising an alkali metal or an alkaline earth metal, at least one transition metal and a counter-ion on a substrate without having to anneal post-deposition.

[0007] Those skilled in the art will realise that the counter-ion is typically part of a compound, typically a crystalline compound, occupying lattice sites in the crystal structure.

[0008] In accordance with a first aspect of the present invention, there is provided a method of forming a crystalline cathode layer of a solid-state battery on a substrate, the method comprising: generating a plasma remote from one or more sputter targets for forming the cathode layer, generating sputtered material from the one or more targets using the plasma, and depositing the sputtered material on the substrate, thereby forming the crystalline cathode layer, wherein a bias is applied to the sputter target such that the ratio of the power used to generate the plasma to the power associated with the bias on the target is greater than 1:1.

[0009] The applicant has discovered that it is possible to deposit a cathode layer of a solid state battery in a high energy crystalline form onto a substrate without having to anneal the cathode layer post-deposition.

[0010] The cathode layer may comprise an alkali metal-based (optionally lithium-based) or alkaline earth metal based solid-state battery cathode material. The cathode layer optionally comprises at least one transition metal and a counter-ion.

[0011] For the avoidance of doubt, the statements below relate to both the methods of the first and second aspects of the present invention.

[0012] The plasma is generated remotely from the plasma target(s). In conventional plasma deposition, a target is required to produce and sustain the plasma.

[0013] In use, the alkali metal or alkaline earth metal is generally in an ionic state, and acts as a conductor in a solid-state battery. The transition metal optionally has at least two positive oxidation states and, in use as a solid-state battery, a proportion of the transition metal will be oxidised/reduced between the two oxidation states.

[0014] The alkali metal, if present, may optionally be one or more of Li, Na, K, Cs and Rb, optionally one or more of Li, Na or K, optionally Li or Na and optionally Li. Lithium ions are sometimes used as conductive species in cathodes of solid state batteries. The alkaline earth metal, if present, may optionally be one or more of magnesium, calcium, strontium or barium, optionally one or more of magnesium, calcium and barium and optionally one or both of magnesium and calcium.

[0015] The one or more transition metal may be in period 4 or period 5 of the Periodic Table. At least one, and optionally each, transition metal may optionally be selected from the group consisting of Fe, Co, Mn, Ni, Ti, Nb and V. The cathode material may comprise one or more alkali metal, one or more transition metal and (each of which is selected from the group consisting of Co, Ni, Mn, Fe, V, Nb and Ti, and optionally from the group consisting of Co, Ni and Mn), and optionally another metal not being an alkali metal or a transition metal (such as aluminium). The cathode layer or crystalline material may be an oxide or phosphate, and may comprise lithium and at least one transition metal, and optionally more than one transition metal, each transition metal being selected from the group consisting of Co, Ni, Mn, Fe, V, Nb and Ti, and optionally from the group consisting of Co, Ni and Mn. The cathode layer or crystalline material may be an oxide or phosphate, and may consist of oxygen (in the case of an oxide) or phosphate (in the case of a phosphate), in combination with lithium and at least one transition metal, and optionally more than one transition metal, each transition metal being selected from the group consisting of Co, Ni, Mn, Fe, V, Nb and Ti, and optionally from the group consisting of Co, Ni and Mn, and optionally aluminium.

[0016] The nature of the counter ion is not particularly important. The counter-ion optionally comprises one or more of PO₄, oxide, dioxide, borate and silicate.

[0017] The cathode layer or crystalline material may comprise a post-transition metal, such as aluminium.

[0018] The cathode layer or crystalline material is optionally an oxide, said oxide consisting essentially of oxygen, lithium, one or more of manganese, nickel and cobalt, and optionally aluminium.

[0019] The cathode layer or crystalline material may be of empirical formula $A_aM_1bM_2cO_2$, wherein A is an alkali metal (optionally lithium), M1 is one or more transition metal (optionally one or more of cobalt, nickel, niobium, vanadium and manganese) (b being the total of transition metal), M2 being aluminium, a being from 0.5 to 1.5 and z being from 0 to 0.5.

[0020] Optionally, a is 1, b is 1 and c is 0. Optionally, M1 is one of cobalt, nickel, vanadium, niobium and manganese.

[0021] Optionally, a is more than 1 and A is lithium. In the case, the materials are sometimes known as "lithium rich" materials. Such lithium-rich materials may be

$Li_{(1+\frac{z}{2})}Ni_xMn_{(1-z)}O_2$ with $x = 0, 0.06, 0.12, 0.2, 0.3$ and 0.4 , for example.

[0022] Another such material is $Li_{(1+\frac{z}{2})}Co_yMn_{(1-\frac{z}{2})}O_2$ wherein y has a value greater than 0.12 and equal to or less than 0.4.

[0023] Another such material is $Li_{(1+\frac{z}{2})}Ni_xCo_yMn_{(1-\frac{z}{2})}O_2$ wherein x has a value equal to or greater than 0.175 and equal to or less than 0.325; and y has a value equal to or greater than 0.05 and equal to or less than 0.35.

[0024] $Li_{(1+\frac{z}{2})}Ni_xCo_yAl_zMn_{(1-\frac{z}{2})}O_2$ is another such material, wherein x is equal to or greater than 0 and equal to or less than 0.4; y is equal to or greater than 0.1 and equal to or less than 0.4; and z is equal to or greater than 0.02 and equal to or less than 0.3.

[0025] The cathode layer or crystalline material is optionally selected from the group consisting of: lithium cobalt oxide, lithium manganese oxide, lithium nickel manganese cobalt oxide, lithium iron phosphate, lithium nickel cobalt aluminium oxide, lithium titanium oxide, lithium nickel oxide, lithium niobium oxide, lithium vanadium oxide.

[0026] The cathode layer or crystalline material is optionally selected from the group consisting of: $LiCoO_2$, $LiNiO_2$, $LiNbO_2$, $LiVO_2$, $LiMnO_2$, $LiMn_2O_4$, Li_2MnO_3 , $LiFePO_4$, $LiNiCoAlO_2$ and $Li_4Ti_5O_{12}$.

[0027] The ratio of the power used to generate the plasma to the power associated with the bias on the target is greater than 1:1, optionally less than or equal to 7:2 and is optionally less than or equal to 3:2. The applicant has discovered that such power ratios may be

beneficial in depositing crystalline materials without the need to anneal the material so deposited.

[0028] The actual power in the plasma may be less than the power used to generate the plasma. In this connection, the efficiency of the generation of the plasma ([actual power in the plasma/power used to generate the plasma] x 100) may typically be from 50% to 85%, typically about 50%.

[0029] During steady-state performance of the method (in which electrical energy supplied to the system is, within a margin of error, the same as the energy consumed by the system), it may be that the fraction of $(P_P * E_{PT}) / (P_T * E_{PP})$ is greater than 1, optionally in the range of 1 to 4, possibly in the range of 1 to 3, and in certain embodiments between 1 and 2, wherein P_P = the average use of plasma energy (in Watts), P_T = the power associated with the bias on the target, E_{PP} is a fraction (<1) being a measure of the efficiency of plasma generation and E_{PT} is a fraction (<1) being a measure of the efficiency of the supply of electrical energy to the target(s). The efficiency, E_{PP} , of the generation of the plasma may be calculated as [actual power in the plasma]/[electrical power used to generate the plasma].

[0030] The efficiency, E_{PT} , of the supply of electrical energy to the target may be calculated as [actual power delivered]/[electrical power used]. In typical set-ups it may be assumed that $E_{PT} = 1$. It is preferred that $E_{PT} > 0.9$.

[0031] During steady-state performance of the method, it may be that the normalised power ratio parameter, PRP_N (where $NPRP_N = N * P_P / P_T$ and where N is a normalising factor, which may satisfy $1.2 < N < 2$, or may simply be $N = 1.7$) is greater than 1, optionally in the range of 1 to 4, possibly in the range of 1 to 3, and in certain embodiments between 1 and 2. During steady-state performance of the method, it may be that the power ratio parameter, PRP (where $PRP = P_P / P_T$) is greater than 0.5, optionally in the range of 0.5 to 2, possibly in the range of 0.6 to 1.5, and in certain embodiments between 0.6 and 1.

[0032] The material sputtered from the target optionally passes through the remotely generated plasma before depositing on the substrate.

[0033] The remotely generated plasma may be of high energy.

[0034] The remotely generated plasma may be of high density. In this connection, the plasma may have an ion density of at least 10^{11}cm^{-3} .

[0035] The power density associated with the voltage bias of the target is optionally greater than 1 Wcm^{-2} and optionally up to 100 Wcm^{-2}

[0036] The crystalline layer or cathode layer may grow in a substantially epitaxial manner from the surface of the substrate.

[0037] The material deposited on the substrate is optionally layered, with the layers optionally being substantially parallel to the substrate.

[0038] The crystalline material deposited in the substrate optionally comprises a rhombohedral or hexagonal crystal structure. If the cathode layer or crystalline material comprises a lithium-containing material, for example, LiCoO_2 , the crystal structure of the LiCoO_2 which is deposited is optionally in the $R\bar{3}m$ space group.

[0039] The $R\bar{3}m$ space group structure is a layered oxide structure. This structure has a number of benefits, such as having a high usable capacity and high speed of charging and discharging compared to the low energy structure of LiCoO_2 , which has a structure in the $Fd\bar{3}m$ space group. The $R\bar{3}m$ space group is regarded as having better performance in typical battery applications due to enhanced reversibility and fewer structural changes on lithium intercalation and deintercalation. Therefore crystalline LiCoO_2 in the $R\bar{3}m$ space group is favoured for solid state battery applications.

[0040] During the deposition part of the method, the crystals may optionally grow substantially epitaxially from the surface of the substrate.

[0041] Epitaxial growth is favoured as it allows for lithium ions to intercalate and deintercalate more easily. The crystals are optionally aligned with the (101) and (110) planes substantially parallel to the substrate. At least a portion of and optionally all of the deposited material may have a hexagonal crystal structure.

[0042] The substrate may comprise a flexible substrate. The method of the present invention may advantageously be used with flexible substrates, such as substrates which comprise one or more polymers, such as PET or PEN.

[0043] The method may comprise depositing cathode material on a first portion of the substrate. The method may comprise moving the substrate, and depositing sputtered

material on a second portion of substrate, thereby forming cathode material on the second portion of the substrate.

[0044] This facilitates the reasonably rapid production of relatively large areas of cathode.

[0045] The substrate may comprise, or be in the form of, a sheet or web, optionally an elongate sheet or web. Such a sheet or web may be provided in the form of a roll or stack. Preferably, the substrate is provided as a roll. This facilitates simple and safe storage and handling of the substrate.

[0046] The substrate may be movably mounted to facilitate movement of the substrate (optionally in the form of a sheet). The substrate may be mounted in a roll-to-roll arrangement. Substrate upstream of the plasma deposition process may be held on roller or drum. Substrate downstream of the plasma deposition process may be held on a roller or drum. This facilitates simple and rapid handling of flexible sheets of substrate. A shutter may be provided to allow for a portion of the substrate to be exposed to the remotely generated plasma.

[0047] The use of a roll-to-roll arrangement has a number of advantages. It facilitates a high material throughput and allows a large cathode area to be deposited on one large substrate, though a series of depositions at a first portion of the substrate, followed by a second portion of the substrate, and so on. One of the main benefits of a roll-to-roll processing is that it allows for a number of depositions to occur without breaking vacuum. This saves both time and energy compared to systems in which the chamber needs to be taken to back up to atmospheric pressure from vacuum after deposition, in order to load a new substrate.

[0048] The plasma deposition process optionally takes place in a chamber. The upstream drum or roller for carrying the substrate may be located inside or outside the chamber. The downstream drum or roller for carrying the substrate may be located inside or outside the chamber.

[0049] The substrate may optionally not exceed its temperature corrected yield strength at any point as it passes between the upstream and downstream rollers or drums. This is important as roll-to-roll processing machines require the substrate to be in tension as the substrate is fed through various rolls, rollers and drums. If the substrate comprises a

polymer, then as the polymer heats up, its yield strength may begin to lower. If the polymer increases in temperature too much, the polymer may begin to deform as it passes through the roll-to-roll machine. This can lead to buckles, jams, and uneven deposition onto the substrate. Preferably, the temperature of the substrate does not exceed 200 degrees at any point during the plasma deposition process, or as it passes between the upstream and downstream rollers or drums.

[0050] The substrate may have a thickness of no more than 50 μm , optionally no more than 20 μm , optionally no more than 10 μm , optionally no more than 5 μm and optionally no more than 1.6 μm . The use of annealing typically exposes the substrate to relatively high temperatures. This can cause thermal damage to the substrate and/or may make the substrate difficult to handle. It is therefore beneficial to be able to deposit crystalline material onto thin substrates.

[0051] The substrate may comprise a polymer, such as an organic polymer, for example, polyethylene terephthalate (PET) or polyethylene naphthalate (PEN). The polymer may optionally provide support for the substrate.

[0052] Depositing the sputtered material on the substrate, thereby forming the crystalline cathode layer or the crystalline layer may comprise depositing sputtered material onto a first portion of the substrate. The method may optionally comprise depositing sputtered material onto a first portion of the substrate, moving the substrate and depositing sputtered material onto a second portion of the substrate. The substrate is optionally moved along a pre-defined path, optionally by one or more rollers.

[0053] The temperature of the substrate during the deposition of the cathode layer or the crystalline layer is optionally no more than 500°C, optionally no more than 300°C, optionally no more than 200°C, optionally no more than 150°C, optionally no more than 120°C and optionally no more than 100°C. The method of the present invention may take place at a low temperature, which facilitates the use of substrates and other materials which may not be usable at high temperatures. Furthermore, the handling of substrates at higher temperatures may be more difficult.

[0054] The maximum temperature reached at any given time by any given square of substrate material having an area of 1 cm^2 as measured on the surface opposite to said

surface on which the material is deposited and as averaged over a period of 1 second, may be no more than 500°C, optionally no more than 300°C, optionally no more than 200°C, optionally no more than 150°C, optionally no more than 120°C and optionally no more than 100°C.

[0055] The method may comprises providing first and second targets. The target material of the first and second targets may optionally be different. The orientation of the first and second targets relative to the substrate may be mutually different.

[0056] The method may comprise exposing the first target to the plasma, and exposing the second target to the plasma, thereby sputtering material from the first and second targets. The substrate may be exposed to material sputtered from the first and second targets. The sputtering of material from the first target may generate a first plume corresponding to the trajectories of particles from the first target assembly onto the substrate. The sputtering of material from the second target may generate a second plume corresponding to the trajectories of particles from the second target assembly onto the substrate. The first and second plumes may converge at the substrate, thereby forming the crystalline layer or the cathode layer. The first and second targets may be configured such that more plasma energy may be received at one of the first and second targets than at the other of the first and second targets. This may be beneficial if the energy required to sputter the material of the first or second target is greater than the energy requires to sputter the material of the other of the first or second target. For example, if the first target comprises elemental lithium and the second target comprises cobalt, then the first and second targets may be configured such that the second target received more plasma energy than the first target because cobalt requires more energy than lithium to sputter from the target.

[0057] The method may comprise containing and shaping the plasma using magnetic and/or electrostatic fields so that the shape of the electron density distribution of the plasma is the same for any given cross-section taken across the majority of the width of the plasma within a margin of error. The margin of error may optionally be up to 30%, optionally up to 20%, optionally up to 10% and optionally up to 5%.

[0058] The shape of the electron density distribution of the plasma is optionally the same within a margin of error. This may be tested by means of visual inspection, with the visible

glow being substantially the same along the width of the plasma. The plasma may be blanket-like. In this connection, the width and length of the visible plasma cloud may each be at least five times greater than the thickness.

[0059] The generation of the plasma may be performed by at least one antenna extending in a direction parallel to the width of the substrate. The generation of the plasma may be performed using a pair of antennae on opposing sides of plasma separated by distance L, each antenna having length, W. The thickness of plasma (defined either by maximum extent of glow in visible spectrum or the largest distance as measured in the direction perpendicular to both L and W which covers 90% of the free electrons in the plasma).

[0060] The first or second target may be closer to the plasma than the other of the first and second target. Such an arrangement may facilitate the first or second target receiving more plasma energy than the other of the first and second target.

[0061] The first or second target may, for any given cross-section section taken across the majority of the width of the plasma, be angled differently to the horizontal than the other of the first and second target. Such an arrangement may facilitate the first or second target receiving more plasma energy than the other of the first and second target.

[0062] One or both of the first and second target may be planar.

[0063] The target(s) of the second target assembly present, for any given cross-section section taken across the majority of the width of the plasma, present substantially the same amount of material to the plasma as the target(s) of the first target assembly.

[0064] The one or more targets is optionally opposite the substrate. Such an arrangement is effective when the plasma is generated remotely.

[0065] The substrate optionally comprises a current collecting layer. The current collecting layer may comprise an electrically-conductive material, such as an inert metal. The current collecting layer may be platinum. The current collecting layer may have a modified structure to increase its surface area. The current collecting layer may also act as an anode. The cathode material (such as LiCoO_2) may be deposited onto the current collecting layer. The substrate may be provided with an adhesion promoter layer immediately beneath the current collecting layer.

Working distances and pressures

[0066] The working distance between the target and the substrate may be within +/- 50% of the theoretical mean free path of the system.

[0067] Without wishing to be bound by theory, it is believed that the working distance has an influence on the “*ad atom*” energy of the sputtered material as it deposits onto the substrate. In a case where the working distance is greater than the mean free path of the system, it is thought that it is more likely that an ion in the sputter flux would be involved in a collision before reaching the substrate, resulting in relatively low *ad atom* energy. Conversely, if the working distance is shorter than the mean free path of the system, the *ad atom* energy is relatively high.

[0068] A definition of the mean free path is the average distance between collisions for an ion in the plasma. The mean free path is calculated based on the volume of interaction (varied by the working distance), and the number of molecules per unit volume (varied by the working pressure).

[0069] The working distance is optionally at least 3.0cm, optionally at least 4.0cm and optionally 5.0cm. The working distance is optionally no more than 20cm, optionally no more than 15cm and optionally no more than 13cm. The working distance may be from 4.0cm to 13cm, optionally from 6.0cm to 10cm, and optionally from 8.0cm to 9.0cm.

[0070] The working pressure may be from 0.00065 mBar to 0.01mBar, optionally from 0.001 to 0.007mBar. A higher working pressure in this range may result in a higher deposition rate. This is because a higher working pressure results in a larger number of process ion (usually Ar+) bombardments on the surface of the target, and hence material is sputtered from the target at a higher rate.

[0071] When the working distance is from 8.0 to 9.0 cm, the range of crystallite sizes available may be narrower, for example, if a working pressure of from 0.001 mBar to 0.0065 mBar is used. The crystallite size may be from 14 to 25 nm. This is evidence that within these parameter ranges, it is possible to form films with narrow and predictable thin film ranges.

Roughnesses

[0072] The surface onto which the layer of cathode is deposited may have a surface roughness X_S or less, where $X_S = 100$ nm, and the cathode layer may have a thickness of from 0.01 to 10 μ m and a surface roughness of no more than X_I , where X_I equals the product of F and X_S , where F is a factor in the range of 1 to 2.

[0073] X_S may be no more than 10% of the thickness of the substrate. The product of the thickness of the substrate and X_S may be no more than 10⁵ nm².

[0074] The substrate, optionally a polymer substrate, may be provided with embedded particles and of all of the embedded particles within or on the polymer material, the majority of those that contribute to surface roughness of the substrate have a median size from 10% to 125% of X_S .

[0075] Alternatively, the substrate, optionally a polymer substrate, may be provided with embedded particles and of all of the embedded particles within or on the polymer material, the majority of those that contribute to surface roughness of the substrate have a median size of no less than 150% of X_S .

[0076] The method may include a step of depositing material onto the surface using sputter deposition to form a further layer having a thickness of from 0.01 to 10 μ m and a surface roughness of no more than 150% of X_S , the material composition of the crystalline layer being different from the material composition of the further layer.

[0077] The method may comprise plasma sputtering material from a first target comprising an alkali metal or an alkaline earth metal onto a surface of or supported by a substrate, there being at least a first plume corresponding to trajectories of particles from the first target onto the surface, and plasma sputtering material from a second target comprising a transition metal (such as cobalt) onto the surface, there being at least a second plume corresponding to trajectories of particles from the second target onto the surface, and wherein the first target is positioned to be non-parallel with the second target, the first plume and the second plume converge at a region proximate to the surface of or supported by the substrate, and the crystalline layer is formed on the surface at said region.

[0078] More plasma energy may be received at the first target than at the second target.

[0079] The first target may face towards the substrate in a first direction, and the second target may face towards the substrate in a second direction, the first and second directions converging towards the substrate.

[0080] The notional line parallel to the first direction which extends from the centre of the surface of the first target may intersect, in the cross-section, the notional line parallel to the second direction which extends from the centre of the surface of the second target, at a location closer to the substrate than to either of the targets.

[0081] The location of the intersection may be closer to the substrate than half of the shortest distance from either of the targets to the substrate.

[0082] At least one of the substrate and the first and second targets may be moving as the crystalline layer is being formed on the surface.

[0083] The substrate may have a radius of curvature at the region at which the first plume and the second plume converge and the targets are arranged circumferentially around the centre of the radius of curvature.

[0084] In accordance with a third aspect of the present invention, there is provided a method of forming a solid state battery half-cell, the method comprising:

forming a crystalline layer in accordance with the method of the first aspect of the present invention or forming a cathode layer in accordance with the method of the second aspect of the present invention; and

depositing an electrolyte material suitable for a solid state battery cell on the cathode layer or the crystalline layer.

[0085] The electrolyte is optionally a ceramic material, such as LiPON (lithium phosphorous oxynitride). The method may comprise generating a plasma remote from one or more targets comprising target material (such as Li_3PO_4); exposing the plasma target or targets to the plasma, thereby generating sputtered material from the target or targets, optionally in a reactive atmosphere comprising a reactive gas (such as nitrogen), thereby forming ceramic material (such as LiPON) on the battery cathode.

[0086] Alternatively, the electrolyte comprises a polymer. In this case, the method may comprise depositing a polymer onto said battery cathode. Alternatively or additionally, the method may comprise depositing a precursor onto said battery cathode and forming a polymer from the precursor.

[0087] The method may comprise depositing a current collecting layer on the ceramic battery electrolyte material.

[0088] In accordance with a fourth aspect of the present invention, there is provided a method of forming a solid state battery cell, the method comprising:

forming a solid state battery half-cell in accordance with the third aspect of the present invention; and

contacting anode material suitable for a solid state battery cell on the electrolyte material.

[0089] The anode-forming material may comprise an electrically-conductive material. The anode-forming material may comprise a lithium alloy or a metal, such as lithium or copper.

[0090] There is provided a method of forming a solid-state battery, the method comprising:

Repeatedly:

Forming a cathode layer of a solid-state battery;

Depositing electrolyte material on the cathode layer or crystalline layer; and

Depositing anode material on the electrolyte material;

Wherein at least one step of forming a cathode layer of a solid-state battery comprises a method in accordance with the second aspect of the present invention.

[0091] There is provided a substrate provided with a layer made in accordance with the method of the first aspect of the present invention.

[0092] There is provided a substrate provided with a crystalline cathode layer of a solid-state battery, the cathode layer being made in accordance with the method of the second aspect of the present invention.

[0093] There is provided a solid-state battery half-cell made in accordance with a method of the third aspect of the present invention.

[0094] There is provided a solid-state battery cell made in accordance with a method of the fourth aspect of the present invention.

[0095] There is provided a solid-state battery made in accordance with a method of the fifth aspect of the present invention.

[0096] It will of course be appreciated that features described in relation to one aspect of the present invention may be incorporated into other aspects of the present invention. For example, the method of the invention may incorporate any of the features described with reference to the apparatus of the invention and vice versa.

Description of the Drawings

[0097] Embodiments of the present invention will now be described by way of example only with reference to the accompanying schematic drawings which can be briefly summarised as follows.

Figure 1a is a schematic side-on view of a plasma deposition chamber used in accordance with a first example;

Figure 1b shows the steps of a method of manufacturing a battery cathode in accordance with the first example;

Figures 1c to 1h are schematic illustrations of various polymer substrate materials in cross-section;

Figure 2a is a schematic side-on view of a plasma deposition chamber used in accordance with a second example method;

Figure 2b is an X-ray diffraction (XRD) spectra of a first sample of a battery cathode made in accordance with the method of the second example;

Figure 2c is a Raman spectra of a battery cathode from which the XRD data of Figure 2b are obtained;

Figure 2d is an XRD spectra of a second sample of a battery cathode made in accordance with a method of the second example;

Figure 2e is a Raman spectra of the battery cathode from which the XRD data of Figure 2d are obtained;

Figure 3a is a schematic side view of a plasma deposition chamber used in a method in accordance with a third example;

Figure 3b is a schematic plan view of the plasma deposition chamber shown in Figure 3a;

Figure 3c is a further schematic side view of the plasma deposition chamber shown in Figures 3a and 3b;

Figure 3d is a graph comparing sputter yields of cobalt and lithium as a function of energy;

Figure 3e is a schematic side view of a plasma deposition chamber used in a method in accordance with a fourth example;

Figure 4a is a cross-sectional scanning electron micrograph of a battery cathode relating to a first sample made using in accordance with the method of the second example;

Figure 4b is a birds-eye view of a scanning electron micrograph of a battery cathode relating to a second sample made in accordance with the method of the second example;

Figure 5a is a schematic cross-section through a battery cathode relating to a first sample made using a method of a fifth example;

Figure 5b is a schematic cross-section through a battery cathode relating to a second sample made using the method of the fifth example;

Figure 5c shows the steps of a method of manufacturing a battery cathodic half-cell in accordance with the fifth example;

Figure 6 is a schematic representation of an example of a method of making a battery cell in accordance with a sixth example;

Figure 7a is a schematic representation of an example of a method of manufacturing a solid-state thin film battery in accordance with a seventh example;

Figure 7b is a schematic cross-section through a solid-state thin film battery in accordance with a first sample of the seventh example;

Figure 7c is a schematic cross-section through a sample solid state thin film battery made in accordance with a second sample of the seventh example;

Figure 8a is a schematic representation of a method of determining an optimum working distance for a remote plasma deposition system configured for the deposition of layered oxide materials in accordance with an eighth example;

Figure 8b shows a number of X-Ray diffraction spectra collected as part of the method of Figure 8a, where the characterisation technique is X-Ray diffraction and the characteristic feature is a characteristic X-Ray diffraction peak associated with a layered oxide structure;

Figure 9a is a micrograph of a sample film formed in accordance with the first example of the invention,;

Figure 9b is an X-ray diffraction spectra obtained from the film shown in Figure 9a;

Figure 10a a schematic representation of an example of a method of determining an optimum working pressure for a remote plasma deposition system configured for the deposition of layered oxide materials in accordance with a ninth example;

Figure 10b shows two X-Ray diffraction spectra collected as part of the method as described with reference to Figure 10a, where the characterisation technique is X-Ray diffraction and the characteristic feature is a characteristic X-Ray diffraction peak associated with a layered oxide structure;

Figure 11a is an example of the steps of a method of determining the crystallite size of layered oxide materials in accordance with a tenth example;

Figure 11b is a graph showing how to determine the crystallite size at different working pressures in accordance with the tenth example, for a working distance of 16 cm, showing the crystallite size for a number of films deposited in accordance with the first example;

Figure 11c is a graph showing how to determine the crystallite size at different working pressures in accordance with the tenth example, for a working distance of 8.5 cm, the crystallite size for a number of films deposited in accordance with the first example;

Figure 12 is a schematic representation of a method of depositing a material on a substrate in accordance with an eleventh example of the invention;

Figure 13 is a schematic representation of an example of a method of manufacturing a component for an electronic device in accordance with a twelfth example;

Figure 14 is a schematic representation of an example of a method of manufacturing a component for an electronic device, in accordance with the thirteenth example of the invention;

Figure 15 is a schematic representation of an example of a method of manufacturing a Light Emitting Diode (LED) in accordance with a fourteenth example of the invention;

Figure 16 is a schematic representation of an example of a method of manufacturing a permanent magnet in accordance with a fifteenth example of the invention; and

Figure 17 is a schematic representation of an example of a method of manufacturing an electronic device comprising a layer of Indium Tin Oxide (ITO) in accordance with a sixteenth example of the invention.

Detailed Description

[0098] Figure 1a is a schematic side-on view of a plasma deposition process apparatus which is used in a method of depositing a (crystalline) material onto a substrate in accordance with a first example. The method is denoted generally by reference numeral 1001 and is shown schematically in Figure 1b, and comprises generating 1002 a plasma remote from one or more targets, exposing 1003 the plasma target or targets to the plasma such that target material is sputtered from one or more targets, and exposing 1004 a first portion of a substrate to sputtered material such that the sputtered material is deposited onto the first portion of the substrate, thereby forming crystalline material onto the first portion of the substrate. The method of depositing a (crystalline) material onto the substrate may be performed as a part of a method of manufacturing a battery cathode.

[0099] The crystalline material in this example takes the form ABO_2 . In the present example, the ABO_2 material takes a layered oxide structure. In the present example, the ABO_2 material is $LiCoO_2$. However, the method of the present example has been shown to work on a wide range of ABO_2 materials. In other examples, the ABO_2 material structure comprises at least one of the following compounds (described here with non-specific stoichiometry): $LiCoO$, $LiCoAlO$, $LiNiCoAlO$, $LiMnO$, $LiNiMnO$, $LiNiMnCoO$, $LiNiO$ and $LiNiCoO$. These materials are potential candidates for manufacturing a battery cathode. Those skilled in the art will realise that the stoichiometry may be varied.

[00100] In this example, the ABO_2 material is $LiCoO_2$ and is deposited as a layer that is approximately 1 micron thick. In other examples, the ABO_2 material is deposited as layer that is approximately 5 microns thick. In yet further examples, the ABO_2 material is deposited as a layer that is approximately 10 microns thick.

[00101] With reference to Figure 1a, the plasma deposition process apparatus is denoted generally by reference numeral 100 and comprises a plasma target assembly 102 comprising a target 104, a remote plasma generator 106, a series of electromagnets 108 for confining the plasma generated by the remote plasma generator 106, a target power supply 110, a remote plasma source power supply 112 and a housing 114. Remote plasma generator 106 comprises two pairs of radio frequency (RF) antennae 116. Housing 114 comprises a vacuum outlet 120 which is connected to a series of vacuum pumps located outside the chamber so that the chamber 122 defined by housing 114 can be evacuated.

Housing 114 is also provided with a gas inlet 124 which may be connected to a gas supply (not shown) for the introduction of one or more gases into the chamber 122. In other examples, the gas inlet 124 may be positioned over the surface of the target assembly 102. As can be seen from Figure 1a, the plasma is generated remote from the target 104.

[00102] In this example, the target 104 comprises material LiCoO_2 . Briefly, the chamber 122 is evacuated until a sufficiently low pressure is reached. Power provided by power supply 112 is used to power the remote plasma generator 106 to generate a plasma. Power is applied to the target 104 such that plasma interacts with target 104, causing LiCoO_2 to be sputtered from the target 104 and onto the substrate 128. In the present example, the substrate 128 comprises a polymer sheet which is introduced into the housing 114 via inlet 130 and out of the housing 114 via outlet 132. A powered roller 134 is used to help move the substrate 128. The LiCoO_2 is deposited onto the substrate 128 as a crystalline (non-amorphous) material.

[00103] The apparatus 100 also comprises a shutter 136, for restricting deposition of sputtered material onto the substrate 128, and an input 138 for cooling the drum. Shutter 136 allows a portion of the substrate 128 to be exposed to the sputtered material.

[00104] As mentioned above, a powered roller 134 is used to help move the substrate 128 into and out of the plasma deposition apparatus 100. Powered roller 134 is part of a roll-to-roll substrate handling apparatus (not shown) which comprises at least a first storage roller upstream of the plasma deposition apparatus 100 and a second storage roller downstream of the plasma deposition apparatus 100. The roll-to-roll substrate handling apparatus is a convenient way of handling, storing and moving thin, flexible substrates such as the polymer substrate used in this example. Such a roll-to-roll system has a number of other advantages. It allows for a high material throughput and allows a large cathode area to be deposited on one substrate, throughout a series of depositions at a first portion of the substrate, followed by a second portion of the substrate, and so on. Furthermore, such roll-to-roll processing allows for a number of depositions to occur without breaking vacuum. This saves both time and energy compared to systems in which the chamber needs to be taken back up to atmospheric pressure from vacuum after deposition in order to load a new substrate. In other examples, sheet-to-sheet processing is used instead of roll-to-roll

processing, wherein the substrate is provided with a support. Alternatively, the substrate may be supplied in discrete sheets that are handled and stored in relatively flat sheets. The substrate may be planar in shape as the material is deposited thereon. This may be the case, when the substrate is provided in the form of discrete sheets, not being transferred to or from a roll. The sheets may each be mounted on a carrier, having greater structural rigidity. This may allow for thinner substrates to be used than in the case of substrate film held on a roller. It may be that the substrate is a sacrificial substrate. It may be that the substrate is removed before the layer(s) of material. Part or all of the substrate may be removed before integrating the crystalline layer or a part thereof in an electronic product package, component or other end product. For example, the layer of crystalline material may be lifted off from the substrate. There may be a layer of other intervening material between the base substrate and the crystalline material. This layer may lift off with the crystalline material or assist in the separation of the crystalline material from the base substrate. A laser-based lift-off technique may be used. The substrate may be removed by a process that utilises laser ablation.

[00105] Similar techniques are described in the prior art. For example, KR20130029488 describes a method of making a battery including using a sacrificial substrate and laser radiation to harvest a battery layer. In other examples, another suitable processing regime is used, provided it is capable of sufficiently high production throughput.

[00106] The polymer substrate 128 is under tension when moving through the system, for example withstanding a tension of at least 0.001N during at least part of the processing. The polymer is robust enough such that when the polymer is fed through the roll-to-roll machine, it does not experience deformation under tensile stress. In this example, the polymer is Polyethylene terephthalate (PET), and the substrate 128 has a thickness of 1 micron or less, in examples the thickness is 0.9 microns. The substrate 128 is pre-coated with a current collecting layer, which is made of an inert metal. In this example, the inert metal used as the current collecting layer is platinum. The yield strength of the PET film is sufficiently strong that the substrate does not yield or plastically deform under the stresses of the roll-to-roll handling apparatus. The inert metal used in other examples can alternatively be gold, iridium, copper, aluminium or nickel.

[00107] The use of such thin polymer substrates is beneficial because this facilitates batteries with a higher energy density to be manufactured. In other examples, a material, which is not polymeric, is used, providing that it can be manufactured in a sufficiently thin and flexible manner to allow for a high battery density and ease of handling post-deposition.

[00108] The plasma deposition process and subsequent manufacturing processes are however subject to the technical challenges that working with such thin layers impose.

[00109] Before the substrate 128 is so pre-coated, it has a surface roughness that is carefully engineered so as (a) to be great enough to mitigate the undesirable effects that would otherwise result from electrostatic forces (such as increasing the force required to unwind the polymer film from the drum on which it is held) and (b) to be small enough that the roughness does not cause problems when depositing material onto the substrate. In this example, the surface roughness is engineered to be about 50 nm. It will be noted that the product of the thickness of the substrate (0.9 microns) and the surface roughness is $4.5 \times 10^4 \text{ nm}^2$ and is therefore less than 10^5 nm^2 and less than $5 \times 10^4 \text{ nm}^2$ in this example. It has been found that that the roughness needed for easing handling of thin films rises with decreasing thickness. Generally, it has been found that the roughness required to improve handling of thinner substrates (i.e. less than 10 microns, particularly less than 1 micron) increases as the substrate thickness decreases.

[00110] Figure 1c shows (not to scale) a typical thin-film polymer being about 1 micron thick and having embedded particles providing roughness. The roughness of the surface features provided by the particles is at least 90 nm and possibly higher. This is too rough for the particular example envisaged (although may be acceptable for other examples).

[00111] Figure 1d shows (not to scale) one way in which the desired roughness can be achieved. Spherical particles of polystyrene are embedded in the substrate material such that at least 90% of those which contribute to the roughness of the substrate protrude from the local substrate surface by no more than half the volume of the particle. The particles have a diameter of about 90 nm. Thus, a majority of the embedded particles that contribute to surface roughness of the substrate have a median size of about 180% of the surface

roughness of the substrate. In other examples, the embedded spherical particles are made of different material, such as silicon oxide.

[00112] Figure 1e shows (not to scale) an alternative way in which a desired roughness can be achieved. Spherical embedded particles of polystyrene are present on the surface of the substrate material such that at least 90% of those which contribute to the roughness of the substrate protrude from the local substrate surface by more than half the volume of the particle. The particles used in the example of Fig. 1e are smaller than those used in the example of Fig. 1d.

[00113] Examples such as those of Fig. 1d and 1e enable good quality films to be deposited, as crystalline material, on thin substrates in a manufacturing environment. The advantages of the presence of embedded particles are retained, but by careful control of the location and size distribution of such particles, the potential disadvantages can be avoided or reduced. Figures 1f to 1h show schematically a cross-section corresponding to the substrate shown in Figures 1c to 1e after a layer of crystalline material has been formed on the substrate surface. The intermediate layer of metal current collector is omitted from Figures 1f to 1h. The roughness of the substrate shown in Figures 1c and 1f is such that problems arise. The dominating protrusions caused by certain embedded particles 152 cause shadowing and competing crystal growth, which are illustrated schematically by means of the contrasting shading 154 in Figure 1f. This competing crystal growth which is aligned in a conflicting direction gives rise to discontinuities in the layer that affects performance of the final product. Also, there is a surprisingly profound effect on the likelihood of delamination of the layer of deposited material from the substrate. This may be as a result of poor contact between the deposited layer and the underlying substrate in the region near to any embedded particles that protrude far from the median plane of the surface (illustrated schematically by the voids 156 in Figure 1f), where the local asperity radius is small. In contrast, it can be seen from Figure 1g and 1h that no such problems arise. The roughness of the surface of the material deposited on the substrate is approximately 50 nm.

[00114] The roughness of the substrate can be measured with a profilometer. This instrument has a stationary stylus. The surface to be measured is translated under the stylus,

and the deflections of the stylus measure the surface profile, from which various roughness parameters are calculated.

[00115] Roughness can also be measured using “non-contact” methods. A suitable machine for measuring roughness is the “Omniscan MicroXAM 5000B 3d” which uses optical phase shift interference to measure the surface profile.

[00116] The roughness, Ra, can be calculated using the formula

$$Ra = \frac{1}{n} \sum_{i=1}^n |y_i|$$

where the deviation y from a smooth surface is measured for n data points.

[00117] The surface roughness, Sa, of an area A extending in the x- and y- directions can be calculated using the formula:

$$Sa = \frac{1}{A} \iint_A |Z(x,y)| dx dy$$

where Z is the deviation from a mathematically perfectly smooth surface.

[00118] In the present example, the average surface roughness is measured with a non-contact method.

[00119] The remotely generated plasma is created by the power supplied to the antennae 116 by power supply 112. There is therefore a measurable power associated with that used to generate the plasma. The plasma is accelerated to the target by means of electrically biasing the target 104, there being an associated electrical current as a result. There is thus a power associated with the bias on the target 104. The ratio of the power used to generate the plasma to the power associated with the bias on the target is greater than 1:1, and optionally greater than 1.0:1.0. Note that in this example, the ratio is calculated on the assumption that the power efficiency of the plasma-generating source is taken to be 50%. The power associated with the bias on the target is at least 1 Wcm^{-2} .

[00120] In further examples, the ratio of the power used to generate the plasma to the power associated with the bias on the target is greater than 1:1, and no more than 7:2, optionally 7.0:2.0. In yet further examples, the power associated with the bias on the target is greater than 1:1 and no more than 3:2, optionally 3.0:2.0. In some examples, the power efficiency of the plasma generating source is taken to be 80%. In some examples, the power associated with the bias on the target is 10 Wcm^{-2} . In yet further examples, the power associated with the bias on the target is 100 Wcm^{-2} . In yet further examples, the power associated with the bias on the target is 800 Wcm^{-2} . In other examples, the efficiency of the plasma generating source may be different, and the power ratio may also be different.

[00121] When the LiCoO_2 film is deposited onto the substrate, it forms a crystalline film of LiCoO_2 . The crystalline structure which forms onto the substrate is in the $R\bar{3}m$ space group. This structure is a layered oxide structure. This structure has a number of benefits, such as having a high accessible capacity and high rate of charge and discharge compared to the low energy structure of LiCoO_2 , which has a structure in the $Fd\bar{3}m$ space group. Crystalline LiCoO_2 in the $R\bar{3}m$ space group is often favoured for solid state battery applications.

[00122] Throughout the plasma deposition process, the temperature of the substrate 128 does not exceed the degradation point of the polymer substrate 128. Moreover, the temperature of the substrate is sufficiently low throughout the deposition process such that the temperature adjusted yield stress of the polymer substrate remains sufficiently high such that the polymer substrate does not deform under the stresses exerted by the roll-to-roll processing machine.

[00123] The general shape of the confined plasma made from the remote plasma generator 106 is shown by the dashed lines B in Figure 1a. The series of electromagnets 108 is used to and confine the plasma to a desired shape/volume.

[00124] It should be noted that, whilst in this first example, substrate 128 is fed into the chamber at inlet 130, and exits the chamber at outlet 132, alternative arrangements are possible. For example, the roll or other store upstream of shutter 136 may be inside the

process chamber 122. The roll or other store downstream of shutter 136 may be inside or could be stored inside the process chamber 122.

[00125] In addition the means 112 of powering the plasma source, may be of RF, (Direct Current) DC, or pulsed-DC type.

[00126] In this first example, the target assembly 102 comprises only one target 104. This target is made of LiCoO_2 . It should be appreciated that alternative and/or multiple target assemblies may be used, for example, comprising a distinct region of elemental lithium, a distinct region of elemental cobalt, a distinct region of lithium oxide, a distinct region of cobalt oxide, a distinct region of a LiCo alloy, a distinct region of LiCoO_2 , or any combination thereof. In other examples, the ABO_2 material may not be LiCoO_2 . In these examples, the target assembly or assemblies contain distinct regions of A, distinct regions of B, distinct regions of a compound containing A and/or B, and/or distinct regions containing ABO_2 .

[00127] For the avoidance of doubt, the target 104 of the target assembly 103 acts as a source of material alone and does not function as a cathode when power is applied to it from the RF, DC or pulsed DC power supply.

[00128] In this example, the working pressure of the system is 0.0050 mBar. The theoretical mean free path of the system is approximately 10 cm. The theoretical mean free path is the average distance between collisions for an ion in the plasma. The working distance between the target 104 and substrate 128 is approximately 8.5 cm. This working distance is therefore approximately 85% of the theoretical mean free path of the system.

[00129] In this example, the working pressure is above a lower bound below which crystalline material in the layered oxide structure does not form, but below an upper bound above which observable damage is caused to the substrate. The working distance is shorter than an upper bound above which crystalline material in the layered oxide structure does not form, and longer than a lower bound below which the energy of the deposition causes observable damage to the substrate, or unfavourable oxide states to form.

[00130] The average crystallite size of the crystallites which form on the film in this example is around 20 nm. In other examples, the average crystallite size of the crystallites which form on the film is around 50 nm.

[00131] In an alternative example, the working pressure of the system is 0.0020 mBar. The theoretical mean free path of the system is approximately 12 cm. The working distance between the target 104 and substrate 128 is approximately 9 cm. This working distance is therefore approximately 75% of the theoretical mean free path of the system.

[00132] In an alternative example, the working pressure of the system is 0.0065 mBar. The theoretical mean free path of the system is approximately 15 cm. The working distance between the target 104 and substrate 128 is approximately 7.5 cm. This working distance is therefore approximately 50% of the theoretical mean free path of the system.

[00133] A second example method uses the apparatus shown in Figure 2a. The main differences between the apparatus of Figure 1a and the apparatus of Figure 2a will now be described. Figure 2a shows that instead of the flexible substrate 128 presented in the first example, an inflexible planar glass substrate 228 is used. Furthermore, no drum is present in this example. The thickness of the glass substrate is in the order of millimetres. A single target 204 is used in this example. A thermal indicator sticker was attached to the face of the glass slide opposite to that on which the cathode material was deposited. The thermal indicator sticker is configured to indicate whether or not the substrate 228 experienced a temperature of 270°C or more during the plasma deposition process. After deposition, the sticker indicated that the substrate did not experience a temperature of 270°C or more during the deposition process. The general shape of the plasma is indicated by the area enclosed by the broken line B' in Figure 2a.

[00134] Table 1 shows the properties of the resultant exemplary battery cathodes produced in accordance with the second example:

Example identifier	Target composition	Measured film Composition (At%)			Plasma source power (W)	Sputtering Power (W)	Process pressure (mBar)	Ar process flow rate (SCCM)	Film thickness (nm)	Film Roughness Sa (nm)	Dep time (min)
		O	Co	Li							
Sample 1	LiCoO ₂	56	21	23	1800	500	3.90e-03	52	910	51.8	100
Sample 2	LiCoO ₂	55	21	24	1800	800	3.90e-03	52	915	106	100

Table 1 – properties of LiCoO₂ cathode films as a function of deposition parameters

[00135] In Table 1 above, the elemental film composition was determined by x-ray photoelectron spectroscopy using a Thermo Fisher K-alpha spectrometer with a MAGCIS ion gun. Quoted compositions were taken from depth profiling measuring at about 10 levels with a film. Plasma source power is the electrical power supplied to generate the plasma. Sputtering power is the electrical power applied to the target 204. Process pressure is the pressure in the chamber. Film thickness and roughness measurements were taken after deposition, using an Omniscan MicroXAM 5000b 3d optical profiler. Film thicknesses were measured after deposition, as step-heights at masked edges and roughness measurements were taken from sample areas of about 400microns x 500microns.

[00136] Figure 2b shows an X-ray diffraction (XRD) spectra of the battery cathode of Sample 1. The structure of the film was characterised by X-ray diffraction using a diffractometer (Rigaku-Smartlab) with nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5406\text{\AA}$). The diffraction pattern was taken at room temperature in the range $10^\circ < 2\theta < 80^\circ$ using a fixed incident angle of $< 5^\circ$. Data were collected using step scans with a resolution of $0.04^\circ/\text{step}$ and a count time of $0.5\text{s}/\text{step}$. The peak at approximately 37° is associated with the (101) plane of the crystals being substantially orientated parallel to the substrate surface. The peak at approximately 66° is associated with the crystals being substantially oriented such that the (110) plane is parallel to the substrate. The peak at approximately 55° is associated with the glass substrate, and for the purposes of determining the crystal structure of the LiCoO_2 , should be ignored.

[00137] The absence of extra reflections associated with the $Fd3m$ space group is an initial indicator that the LiCoO_2 deposited is in the $R\bar{3}m$ space group.

[00138] Also notably absent is the peak associated with the (003) plane. This implies that very few crystals are orientated in such a way that the (003) plane is parallel to the substrate surface. It is beneficial that very few crystals are orientated in this way. A detailed explanation is beyond the scope of the present application, but briefly, the accessible capacity of a cathode increases when a higher proportion of the crystals are aligned such that the (101) and (110) planes are parallel to the substrate, as opposed to being aligned such that the (003) plane is parallel to the substrate as the apparent resistance to ion

migration is lower. The crystals have formed such that the longitudinal axis of the crystals is normal to the substrate. In other words, the crystals have formed in an epitaxial manner.

[00139] The applicant has discovered that if the ratio of the power used to generate the plasma to the power associated with the biasing of the target is more than 1:1, then generally a crystalline material is deposited. In Sample 1, the ratio is 1800:500 (3.6:1) and in Sample 2, the ratio is 1800:800 (9:4). Note that in this example, the ratio is calculated on the assumption that the power efficiency of the plasma-generating source is taken to be 50%.

[00140] In a comparative example, the experiment was repeated with a plasma source power of 1kW and a power associated with bias to the target of 1kW. The material deposited was substantially amorphous. The performance of the film of the comparative example as a cathode was investigated by depositing an electrolyte (in this case, LiPON) and an anode metal on top of the cathode layer, thereby making a solid state battery. The charge-discharge characteristics of the battery were investigated and were found to be poor, with a cathode specific capacity of about 10mAh/g. When analogous batteries were made using crystalline LiCoO₂ such as that formed in Sample 1 and Sample 2, the charge-discharge characteristics were far superior, with typical cathode specific capacities of about 120mAh/g.

[00141] Figure 2c shows a Raman spectra of the battery cathode of Sample 1. The bonding environment of the films was characterised by Raman Spectroscopy. Raman spectra were collected using a JY Horiba LabRAM ARAMIS imaging confocal Raman microscope using 532 nm excitation. Note that the strong sharp peak at 600 cm⁻¹ can be considered as anomalous due to the unphysical nature of the sharpness of the peak. The strong, characteristic peak observed at 487 cm⁻¹ is well known in the art to be associated with the $R\bar{3}m$ space group crystal structure of LiCoO₂.

[00142] Figure 2d shows an XRD spectra (collected in the same way as that for Sample 1) of the cathode of Sample 2. The spectra shown is similar to that shown in Figure 2b. However, in Figure 2d, the relative intensity of the peak at approximately 66° is far stronger than that of the peak at 37°. This indicates that the number of crystals with their (110) planes parallel to the substrate is higher than the number of crystals with their (101)

planes parallel to the substrate for Sample 2. This is beneficial as it means that the ion channels of the thin film are orientated perpendicular to the substrate, making for easier for intercalation and de-intercalation of the ions from their interstitial sites from within the crystal structure of the cathode. This improves the accessible capacity and the rate of charge of the cathode. Figure 2e is a Raman spectra of the cathode of Sample 2; the same comments apply to Figure 2e that apply to Figure 2c.

[00143] Figures 3a to 3c show an alternative example of an apparatus for use in another example of a method of manufacturing a layer of crystalline material on a surface using plasma sputtering according to a third example. The apparatus and method of manufacture employed is similar to that described with reference to the first example. Only the significant differences will now be described. The same parts are labelled with reference numerals sharing the same last two digits. For example, rotating drum 334 in Fig. 3a is the same as rotating drum 134 in Fig. 1a. The apparatus of Fig. 3a comprises a rotating drum 334 on which a polymer substrate 328 is supported within a region defined by a process chamber 322 (the walls of the chamber being omitted for the sake of clarity). The target assembly 302 comprises a plurality of targets. There is provided a first target 304 consisting of elemental lithium and a plurality of targets 303 consisting of elemental cobalt (referred to now as the second targets). The targets are all positioned at a working distance of about 10 cm from the substrate 328 (the working distance being shortest separation therebetween). The surface of each target 303, 304 facing the drum 334 is flat (and planar). The radius of the drum 334 is significantly greater than the working distance (the size of the drum 334 being shown in the Figures as being relatively smaller than it is in reality for the sake of the illustration). The targets 303, 304 are arranged circumferentially around the circumference of the drum 334. The apparatus also comprises a shutter 336, for restricting deposition of sputtered material onto the substrate 328.

[00144] A plasma of argon ions and electrons is generated by means of two electrically powered spaced apart antennae 316. The plasma is confined and focussed by a magnetic field controlled by two pairs of electromagnets 308, each pair being positioned proximate to one of the antennae 316 and the electric field generated by the system. The overall shape of the plasma (the 90% highest concentration of which being illustrated in

highly schematic fashion in Figure 3c by the plasma cloud B'') is that of a blanket, in that the length and width of the plasma cloud are much greater than the thickness. The width of the plasma is controlled in part by the length of the antennae 316. The two pairs of antennae 316 are separated by a distance that is comparable to the length of the plasma. The length and width of the plasma are in the same general direction as the length and width, respectively, of the substrate.

[00145] The plasma source is spaced apart from the targets, and may thus be considered as a remotely generated plasma. The theoretical mean free path of the system (that is, the average distance between collisions for an ion in the plasma) is about 12 cm, meaning that the majority of particles travel from the target to the substrate without colliding with any argon ions in the plasma.

[00146] Figure 3a is a partial schematic cross-sectional view showing part of the substrate travelling on the drum 334 and also shows schematically the trajectories of particles that travel from the targets 303, 304 to the substrate. Thus, there is a first plume corresponding to the trajectories of particles from the first target 304 to the surface of the substrate 328 and a second plume corresponding to the trajectories of particles from the second target 303 to the surface of the substrate 328. The first plume is shown as a spotted region and each second plume is shown as a solid grey region. It will be seen from Figure 3a that the first plume and the second plume converge at a region proximate to the substrate. It will also be seen in Figure 3a that the first target 304 faces towards the substrate in a first direction (defined in this example by the notional line extending from the centre of the surface of the target 304) and the adjacent second target 303 to the left as shown in Figure 3a, faces towards the substrate in a second direction (defined in this example by the notional line extending from the centre of the surface of the target 303). The first and second directions converge towards the substrate and intersect at a location just beyond the substrate (the location being about 3 cm beyond the substrate). Oxygen gas is supplied at a controlled rate into the process chamber 322 through inlets 325. The targets are stationary as the substrate moves with rotation of the drum. In other examples, the inert sputtering gas is introduced through the gas inlet (not shown here, but substantially the same configuration as that shown in Figure 1a).

[00147] The amount of oxygen introduced into the chamber may be reduced in some other examples if distinct regions of lithium oxide and cobalt oxide are present in targets 304, 303, and the oxygen content in such targets may be sufficiently high in some examples such that no additional oxygen gas need be introduced into the chamber 322 at all.

[00148] Figure 3b is a view looking from the drum towards the targets. Figure 3c is a cross-sectional view that includes sections of the first target 304, the second targets 303 and the substrate 328 on the drum 334.

[00149] It will be seen that in Figure 3c (the view of the cross-section) the first target 304 is angled relative to each of the second targets 303.

[00150] In performance of the method, the plasma generated is used to sputter material from the first target and from the second targets onto the substrate.

[00151] As shown in Figure 3d, elemental lithium material has a lower sputter yield than cobalt as measured in atoms yielded per ion received at the surface at a given energy (less than half at 10keV). As such, the (negative) potential applied to the first target has a magnitude greater than the potential applied to the second targets. The first target also has a slightly larger surface area exposed to the plasma than the sum area of the second targets. As such, the number of ionised Li atoms arriving at the substrate per unit is substantially the same as the number of ionised Co atoms arriving at the substrate per unit. Ionised oxygen atoms are also present as are electrons from the plasma. The high energy particles made possible by the remote plasma allows for crystalline LiCoO_2 material, having a hexagonal crystal structure, to be formed in situ on the surface of the substrate.

[00152] A greater number of high energy particles from the plasma are received at the first target 304 (over the whole surface area of the target) than at the second targets 303 (summed over the whole surface area of both second targets).

[00153] Figure 3e shows a schematic cross-section through a further example of an apparatus in accordance with a fourth example, similar to that shown in Figures 3a to 3c, but in which the targets move and are arranged in pairs, circumferentially around the drum 334. Each pair of targets (i.e. each assembly 302) is arranged to be angled to face towards a location very near to the substrate on the drum. Each pair 302 comprises a first target 304 of elemental lithium and a second target of elemental cobalt 303. The targets are all

positioned at a working distance of about 15 cm from the substrate, the working distance being the shortest separation therebetween. The theoretical mean free path of the system (that is, the average distance between collisions for an ion in the plasma) is about 20 cm. For each pair of targets (302), in use there is a first plume of particles from the first target (304) and a second plume of particles from the second target (303) which converge at a region proximate to the substrate. The centre of rotation of the main drum 334 is also the centre of rotation of the targets. The targets move with an angular velocity about the centre of rotation slower than the drum. Targets may be replaced when they have moved out of the plasma on a rotating basis, thus allowing for constant deposition of material on the moving substrate.

[00154] An example of a battery cathode made in accordance with the second example will now be described with reference to Figures 4a, 4b and 5a. The substrate 428, 528 comprises a current collecting layer 429, 529, in this case, a layer of platinum, on which a layer of LiCoO_2 442, 542 is deposited. In other examples, another inert metal is used as a current collecting layer, for example gold, iridium, copper, aluminium or nickel. In yet further examples, the current collecting layer may be carbon based. In some examples, the current collecting layer is surface modified, and in some examples, the current collecting layer comprises rod-like structures.

[00155] As shown on the Scanning Electron Microscope (SEM) image of Figure 4a (cross sectional view of a first sample deposited film) and Figure 4b (bird's-eye view a second sample deposited film), the LiCoO_2 film layer 442, 542 of both samples is polycrystalline in nature. The battery cathodes of Figures 4a, 4b and 5a can also be made in accordance with the methods of the third or fourth example.

[00156] A method of making a cathodic half-cell in accordance with a fifth example will now be described with reference to Figure 5a (a first sample), Figure 5b (a second sample), and Figure 5c. The method, generally described by reference numeral 3001, comprises depositing 3002 a battery cathode material 542 onto a substrate (which in this example comprises a current collecting layer 529), and depositing 3003 onto said battery cathode material 542 battery electrolyte material 544. In this example, the material deposited for the electrolyte 544 is lithium phosphorous oxy-nitride (LiPON). In other

examples, the material deposited is another suitable electrolyte material. In some samples of the fifth example of the invention (such as the second sample), the half-cell may comprise an electrode material 544, and in other samples of the fifth example, the half-cell may not comprise an electrode material 544 (such as the first sample).

[00157] In this example, the LiPON is deposited in substantially the same way as the ABO_2 materials in the first, second, third or fourth examples, using a remotely-generated plasma. However, in this example, the target material used is Li_3PO_4 , with deposition occurring in a reactive nitrogen atmosphere. In other examples, the target assembly may include a number of targets, with distinct regions of lithium and/or phosphorous containing compounds, elemental lithium, or lithium oxide. In other examples, the deposition additionally occurs in a reactive oxygen atmosphere.

[00158] An example of a method of making a solid-state battery cell in accordance with a sixth example will now be described with reference to Figure 6. The method is denoted generally by reference numeral 5001 and comprises making 5002 a cathodic half-cell in accordance with the fifth example (for example, as described above with reference to Figure 5b and 5c) and contacting 5003 said cathodic half-cell with an anode. In this example, the anode is deposited by a convenient method, including remote plasma sputtering, magnetron sputtering, CVD etc. In other examples, the anode is deposited by thermal evaporation, e-beam evaporation, pulsed laser deposition, or simple DC-sputtering.

[00159] An example of a method of making a solid-state battery in accordance with a seventh example will now be described with reference to Figure 7a. The method is denoted generally by reference numeral 6001 and comprises making 6002 a plurality of cathodic half-cells of a solid state thin film battery, making 6003 a plurality of anodic half cells of a solid state thin film battery and bringing 6004 said cathodic and anodic half cells into contact with one another, thereby forming at least one battery. A battery so made according to a first sample of the seventh example of the present invention is shown schematically in Figure 7b. Referring to Figure 7b, 628 and 628' are substrate materials, 629 and 629' are current collecting layers, 642 is the cathode material, in this case, $LiCoO_2$, and 644 is LiPON, which acts as both electrolyte and anode.

[00160] Alternatively, in other examples the current collector material acts as an anode material. Alternatively, in a second sample of the seventh example of the invention a further anode material may be deposited. This is shown schematically in Figure 7c. Referring to Figure 7c, 628 and 628' are substrate materials, 629 and 629' are current collecting layers, 642 is the cathode material, in this case, LiCoO_2 , 644 is LiPON, which acts as electrolyte, and 646 is a suitable anode material.

[00161] An example of a method of determining an optimum working distance for a remote plasma deposition system configured for the deposition of layered oxide materials in accordance with an eighth example will now be described with reference to Figure 8a. The method is generally described by numeral 7001 and comprises:

- Selecting 7002 a range of working distances, wherein a working distance within said range is +/- 50% of the theoretical mean free path of the system,
- for a number of test specimens, for each respective specimen, performing 7003 the method of depositing material according to the first example at different working distances within the selected range,
- performing 7004 a characterisation technique capable of determining a characteristic feature of a layered oxide structure on each of the test specimens after deposition has occurred,
- identifying 7005 specimens where said characteristic property is present;
- from those specimens, selecting 7006 the specimen wherein the (normalised) intensity of said characteristic peak is highest, and subsequently selecting 7007 the working distance for the system to that which was used during deposition of said test specimen.

[00162] In this eighth example, the characterisation technique used is X-ray diffraction, and the characteristic property is a diffraction peak or series of diffraction peaks. Figure 8b shows a number of X-Ray diffraction patterns recorded of films deposited at different working distances. From the top diffraction pattern to the bottom diffraction pattern the working distances were 5 cm (ref. no. 731), 8 cm (733), 12 cm (735) and 15 cm

(737), respectively. As can be seen from the figure, a working distance of 8 cm shows the highest intensity peak 733 at 19 degrees 2theta (which is one of the required peak positions 739 for hexagonal LiCoO_2 , this particular peak not being present in cubic or spinel structures of LiCoO_2). Therefore, in this example, 8 cm is chosen as the working distance. In other examples, a different characterisation technique may be used other than X-Ray diffraction. The intensity of the diffraction pattern 731 measured for a working distance of 5cm is less intense at 19 degrees 2theta than the diffraction pattern 733 at a working distance of 8cm. The diffraction patterns collected for a working distance of 12 cm 735 and 15 cm 737 do not show the characteristic peak for hexagonal LiCoO_2 at 19 degrees 2theta at all.

[00163] In some examples, the test specimens of the method are replaced with an average value for a number of test specimens, comprising a number of test specimens, wherein the method of the first example has been performed a number of times at the same working distance, and an average taken. In some examples the method may be performed a number of times such that a range of optimal working distances can be found for operating the system.

[00164] Figure 9a shows a sample formed in accordance with the first example, during performing the method of the eighth example, and shows a damaged substrate surface (with undesirable oxides) which forms due to the deposition when the working distance is too short. In this example, the working distance was 5 cm, and the material deposited was LiCoO_2 . As can be seen from the figure, crystallites have not formed over the whole substrate surface, and deformation of the substrate can be seen. In addition, regions of Co(II)O , an undesirable phase of cobalt oxide, can be seen forming on the substrate at this working distance. This is confirmed by the spectra as shown in Figure 9b, which shows peaks relating to Co(II)O phases (identified at two values 843 of 2theta) being detected in a diffraction pattern 831 obtained for a sample at which the working distance was 5 cm, in addition to hexagonal LCO, peaks (identified at 5 values 839 of 2theta). A structural refinement model 831' containing both hexagonal LiCoO_2 and Co(II)O phases, was obtained from the collected diffraction pattern of 831. The difference between the diffraction pattern 831 and the refinement model 831' is illustrated by the difference line

841. Thus, during the method of the eighth example, overly short working distances cannot be selected as the optimum working distance.

[00165] An example of a method of determining an optimum range of working pressures for a remote plasma deposition system configured for the deposition of layered oxide materials in accordance with a ninth example will now be described with reference to Figure 10a. The method is generally described by numeral 8001 wherein the method comprises:

- Selecting 8002 an initial range of working pressures, from 0.00065 mBar to 0.01 mBar (and optionally from 0.001 to 0.007mBar),
- for a number of test specimens, for each respective specimen, performing 8003 the method of depositing material according to the first example at different working pressures within the selected range,
- performing 8004 a characterisation technique capable of determining a characteristic property of a layered oxide structure on each of the test specimens after deposition has occurred,
- selecting 8005 the test specimen which was deposited at the lowest working pressure from the group of test specimens which display a characteristic feature of a layered oxide material, and setting 8006 this working pressure as the lower bound of the range,
- selecting 8007 the test specimen which was deposited at the highest working pressure from the group of test specimens which do not show observable signs of damage to the substrate, and setting 8008 this working pressure as the higher bound of the range.

[00166] In this ninth example, the characterisation technique used is X-ray diffraction, and the characteristic feature is a feature comprises a characteristic X-Ray diffraction peak of a layered oxide material. Figure 10b shows an example X-Ray spectra showing how below a certain working pressure, this characteristic feature is not present. In this example, the presence of a peak at 19 degrees 2theta in the pattern 947 for the sample

deposited at 0.0046mBar resulted in the formation of a hexagonal crystalline phase, whereas the pattern 945 for the sample deposited at 0.0012mBar did not lead to the formation of a hexagonal crystalline phase, as shown by the absence of the peak. In other examples, a characterisation technique may be used other than X-Ray diffraction.

[00167] In further examples, the test specimens of the method are replaced with an average value for a number of test specimens, comprising a number of test specimens wherein the method of the first example has been performed a number of times at the same working pressure, and an average taken.

[00168] In some examples, the method also comprises selecting the optimum working pressure of the system within the desired range. In this example, the optimum working pressure is the working pressure within the range that results in the highest deposition rate.

[00169] An example of a method of determining the crystallite size for deposition of layered oxide materials in accordance with a tenth example will now be described with reference to Figure 11a. The method is generally described by numeral 9001 wherein the method comprises:

- selecting 9002 an initial range of working pressures, from 0.00065 mBar and 0.01 mBar,
- for a number of test specimens, for each respective specimen, performing 9003 the method of depositing material according to the first example at different working pressures within the selected range,
- performing 9004 a characterisation technique capable of determining the crystallite size of each film for each of the test specimens after deposition has occurred,

[00170] The selected range of working pressures may be from 0.001 to 0.007 mBar, for example.

[00171] Figure 11b is a graph showing, after performing the method of the tenth example over a given range of working pressures, for a working distance of 16 cm, that the range of crystallite size that forms for a number of films deposited in accordance with the

first example at different working pressures between 0.001 mBar and 0.0065 mBar, is relatively broad in comparison to Figure 11c.

[00172] Figure 11c is a graph showing, after performing the method of the tenth example over a given range of working pressures, for a working distance of 8.5 cm, that the range of crystallite size that forms for a number of films deposited in accordance with the first example at different working pressures between 0.001 mBar and 0.0065 mBar is relatively narrow in comparison to Figure 11b.

[00173] It is beneficial to have a narrow distribution of crystallite sizes, as this makes the crystallite size of films deposited on an industrial scale both predictable and repeatable.

[00174] An example of a method of depositing a material on a substrate in accordance with an eleventh example of an example will now be described with reference to Figure 12. The method is generally described by numeral 1101 and comprises:

- generating 1102 a plasma remote from a plasma target or targets suitable for plasma sputtering,
- exposing 1103 the plasma target or targets to the plasma, thereby generating sputtered material from the target or targets,
- depositing 1104 the sputtered material on a first portion of the substrate.

[00175] The method of depositing material on a substrate as described by the eleventh example comprises all of the features of the deposition of the first example, although in this example, the target material may be any material. In this example, the target material is crystalline, however in other examples the deposited material may take a semi-crystalline form, or be amorphous.

[00176] Also presented is a twelfth example, which relates to a method of manufacturing a component for an electronic device comprising a substrate, which will now be described with reference to Figure 13. The method is generally described by numeral 1201 and comprises depositing 1202 a material onto the substrate using a method of the as described in the eleventh example. The method of the eleventh example in this example is performed a plurality of times 1203 in order to deposit multiple layers. In this

example, at least some of the multiple layers may be semi-conducting layers. In this example, the method is therefore a method of manufacturing a semi-conducting device or part thereof. In this example adjacent layers are deposited with differing parameters and/or target materials used for the deposition of each layer, in order to produce an electronic device. In other examples, multiple layers of a plurality of layers of material are deposited with substantially the same target materials and parameters.

[00177] In this example, the substrate comprises one intermediate layer, which may optionally act as a current collecting layer. In other examples, there are more intermediate layers, which help with adhesion during deposition steps. In some other examples, there is no intermediate layer. The deposition of the intermediate layer onto the substrate is performed in accordance with the method as described in the eleventh example. In other examples, deposition of the intermediate layer onto the substrate is performed by another appropriate deposition technology such as sputtering, thermal evaporation, electron beam evaporation, pulsed laser deposition, or other thin film deposition technology.

[00178] In this example, the method comprises depositing a first semiconducting layer of material. In this example, the first semiconducting layer is deposited onto an intermediate layer of material. In other examples, the first semiconducting layer is deposited directly onto the substrate. In this example, the first semiconducting layer comprises silicon. In other examples, the first semiconducting layer comprises aluminium, and in some further examples, gallium nitride. In examples where the semiconducting layer of material is gallium nitride, the deposition occurs under a reactive nitrogen atmosphere. In this example, the first semiconducting layer of material is doped n-type. This is achieved in this example by sputtering of a target comprising a compound containing phosphorous. In other examples, this is achieved by use of a different dopant such as arsenic, antimony, bismuth or lithium. In some further examples, the semiconducting layer of material is doped p-type, with dopants such as boron, aluminium, gallium or indium. In further examples, the semiconducting layer of material is not doped, and is an intrinsic semiconductor. In some of these examples, the dopant material is not introduced as a target which can be sputtered, and is instead introduced as a gas after deposition, such that the dopant diffuses into the surface of the semiconducting layer.

[00179] In this example, the method comprises depositing a second semiconducting layer of material, onto the first semiconducting layer of material. In other examples, the second semi-conducting layer of material is deposited directly onto the substrate or the intermediate layer (if present). In this example, the second semiconducting layer of material is an intrinsic semiconductor. In this example, the second semiconducting layer of material is gallium nitride. In further examples, the second semiconducting layer of material is doped n-type with dopants such as phosphorous, arsenic, antimony, bismuth or lithium. In some further examples, the second semiconducting layer of material is doped p-type, with dopants such as boron, aluminium, gallium or indium. In some of these examples, the dopant material is not introduced as a target that can be sputtered, and is instead introduced as a gas after deposition, such that the dopant diffuses into the surface of the semiconducting layer.

[00180] In this example, the method comprises depositing a third semiconducting layer of material. In this example, the third semiconducting layer is deposited onto the second semi-conducting layer of material. In other examples, the third semiconducting layer is deposited directly onto the first semiconducting layer, second semiconducting layer, the intermediate layer or the substrate. In this example, the third semiconducting layer comprises silicon. In other examples, the third semiconducting layer comprises aluminium, and in some further examples, gallium nitride. In some examples where the semiconducting layer of material is gallium nitride, the deposition occurs under a reactive nitrogen atmosphere. In this example, the third semiconducting layer of material is doped p-type. This is achieved in this example by sputtering of a target comprising a compound containing boron. In other examples, this is achieved by use of a different dopant such as aluminium, gallium or indium. In some further examples, the third semiconducting layer of material is doped n-type, with dopants such as phosphorus, arsenic, antimony, bismuth or lithium. In further examples, the third semiconducting layer of material is not doped, and is an intrinsic semi-conductor. In some of these examples, the dopant material is not introduced as a target, which can be sputtered, and is instead introduced as a gas after deposition, such that the dopant diffuses into the surface of the semiconducting layer.

[00181] The method of this example may therefore be used to form a p-n or p-i-n junction.

[00182] In this example, no further dopants are introduced into some of the semiconducting layers hitherto described. In some examples, germanium is introduced as a dopant in the first, second and/or third layers. Germanium alters the band gap of the electronic device, and improves the mechanical properties of each semiconducting layer of material. In some examples, nitrogen is introduced as a dopant in the first, second and/or third layers of material. Nitrogen is used to improve the mechanical properties of the semiconducting layers formed.

[00183] Also presented is a thirteenth example, which relates to a method of manufacturing a crystalline layer of Yttrium Aluminium Garnet (YAG), which will now be described with reference to Figure 14. The method is generally described by numeral 1301 and comprises using the method as described in the eleventh example 1302, wherein the YAG is doped 1303 with at least one f-block transition metal.

[00184] In this example, the dopant material is a lanthanide.

[00185] In this example, the dopant material comprises neodymium. In other examples, the dopant material comprises chromium or cerium in addition to neodymium. In this example, the crystalline layer of material comprises 1.0 molar percent neodymium. In some examples, the material also comprises 0.5 molar percent cerium.

[00186] In yet further examples, the dopant material comprises erbium. In this example, the dopant material is provided as a target, and sputtered as described in the eleventh example. The crystalline layer of material in this further example comprises 40 molar percent erbium. In one example, the crystalline layer of material comprises 55 percent erbium.

[00187] In yet further examples, the dopant material comprises ytterbium. In one of these examples, the crystalline layer of material comprises 15 molar percent ytterbium.

[00188] In yet further examples, the dopant material comprises thulium. In further examples, the dopant material comprises dysprosium. In further examples, the dopant material comprises samarium. In further examples, the dopant material comprises terbium.

[00189] In yet further examples, the dopant material comprises cerium. In some examples where the dopant material comprises cerium, the dopant material also comprises gadolinium.

[00190] In some examples, instead of the dopant material being provided as a distinct region of a target or targets, the dopant material is, at least in part, introduced after the deposition of the layer of crystalline material, by providing the dopant material as a gas, such that it diffuses into the layer of crystalline material.

[00191] According to a fourteenth example, a method of manufacturing a light emitting diode is presented, which will now be described with reference to Figure 15. The method is generally described by numeral 1401 and comprises performing the method according to the twelfth example 1402, and thereafter or therein performing the method according to the thirteenth example 1403, in the case where the dopant used during the method of the thirteenth example comprises cerium 1404. The layer of cerium-doped YAG is used as a scintillator in an LED in this example.

[00192] The methods according to the twelfth and thirteenth examples may be performed inside the same process chamber.

[00193] According to a fifteenth example, a method of manufacturing a permanent magnet is presented, which will now be described with reference to Figure 16. The method is generally described by numeral 1501 and comprises comprising performing the method according to the eleventh example 1502, wherein the distinct regions of the target or targets provided comprise neodymium, iron, boron and dysprosium 1503, and the method comprises processing the film 1504 such that the layer of material becomes a permanent magnet.

[00194] In this example, the final layer of material comprises 6.0 molar percent dysprosium. In further examples, the molar percentage of dysprosium is less than 6.0.

[00195] The high target utilisation that the current method provides is beneficial when constructing electronic devices from rare elements such as dysprosium. Dysprosium is available in limited Earth abundancy, and so a deposition system with a high target utilisation results in less material waste.

[00196] According to a sixteenth example, a method of manufacturing a layer of Indium Tin Oxide (ITO) is presented, which will now be described with reference to Figure 17. The method is generally described by numeral 1601 and comprises performing the method according to the eleventh example 1602, wherein the distinct regions of the targets provided comprise indium and tin 1603. The layer of ITO is deposited in such a way that it directly forms a transparent crystalline layer of material on deposition 1604 onto the substrate. In other examples, a composite target is used, which comprises both indium and tin. In yet further examples, the composite target comprises an oxide of indium and tin. The number of targets used thus may differ in further examples, and a single target may be used.

[00197] In yet further examples the targets may comprise an oxide of indium, or an oxide of tin. The deposition process in further examples comprises providing oxygen, such that the sputtered material from the targets reacts with the oxygen in order to form Indium Tin Oxide on the substrate.

[00198] According to a seventeenth example, not separately illustrated, a method of manufacturing a photovoltaic cell is presented. In this example, the method further comprises the deposition of an ITO, as described in the fifteenth example. In further examples, no layer of ITO is deposited. In this example, the method also comprises the deposition of a layer of perovskite material in between a n-type doped layer of semiconducting material and a p-type doped layer of semiconducting material. The perovskite layer of material is in this case deposited as described by the method of the eleventh example. In further examples, it is deposited by another suitable means such as physical vapour deposition, or wet chemistry techniques. In further examples, no perovskite layer of material is deposited.

[00199] In alternative examples, the method comprises the deposition of a layer of copper indium gallium selenide in accordance with the eleventh example. The copper, indium, gallium, and selenide is provided as distinct regions of the target or targets. In this example the copper is provided as an elemental target, and the indium, gallium, and selenide are provided as oxide targets. Other combinations of oxide, elemental, compound

or composite targets are used in further examples. The number of targets used thus may differ in further examples, and a single target may be used.

[00200] In some examples, the method comprises the deposition of a layer of cadmium sulphide in accordance with the eleventh example. In this example, the cadmium and sulphide are provided as distinct regions of the targets in oxide form. Other combinations of oxide, elemental, compound or composite targets are used in further examples. The number of targets used thus may differ in further examples, and a single target may be used.

[00201] In some examples, the method comprises deposition of a layer of cadmium telluride in accordance with the eleventh example. The cadmium and telluride is provided as distinct regions of elemental targets in tis example. In other examples, the cadmium and telluride is provided as distinct regions of the target or targets in elemental, an oxide, a composite or any combination thereof. The number of targets used thus may differ in further examples, and a single target may be used.

[00202] Whilst the forgoing description has been described and illustrated with reference to particular examples, it will be appreciated by those of ordinary skill in the art that the invention lends itself to many different variations not specifically illustrated herein. By way of example only, certain possible variations will now be described.

[00203] Where in the foregoing description, integers or elements are mentioned which have known, obvious or foreseeable equivalents, then such equivalents are herein incorporated as if individually set forth. Reference should be made to the claims for determining the true scope of the example, which should be construed so as to encompass any such equivalents. It will also be appreciated by the reader that integers or features of the invention that are described as preferable, advantageous, convenient or the like are optional and do not limit the scope of the independent claims. Moreover, it is to be understood that such optional integers or features, whilst of possible benefit in some embodiments of the invention, may not be desirable, and may therefore be absent, in other embodiments.

Claims

1. A method of forming a crystalline cathode layer of a solid-state battery on a substrate, the method comprising:
generating a plasma remote from one or more sputter targets for forming the cathode layer,
generating sputtered material from the one or more targets using the plasma, and
depositing the sputtered material on the substrate, thereby forming the crystalline cathode layer,
wherein a bias is applied to the sputter target such that the ratio of the power used to generate the plasma to the power associated with the bias on the target is greater than 1:1.
2. A method according to claim 1 wherein the cathode layer comprises an alkali metal-based (optionally lithium-based) or alkaline earth metal based solid-state battery cathode material.
3. A method according to claim 2 wherein the cathode layer comprises at least one transition metal and a counter-ion.
4. A method according to any preceding claim wherein the cathode layer is selected from the group consisting of: LiCoO_2 , LiNiO_2 , LiNbO_2 , LiVO_2 , LiMnO_2 , LiMn_2O_4 , Li_2MnO_3 , LiFePO_4 , LiNiCoAlO_2 and $\text{Li}_4\text{T}_{15}\text{O}_{12}$.
5. A method according to any preceding claim wherein said ratio is less than or equal to 7:2.
6. A method according to any preceding claim wherein said ratio is less than or equal to 3:2.

7. A method according to any preceding claim wherein the power density associated with the voltage bias of the target is greater than 1 Wcm^{-2} .
8. A method according to any preceding claim wherein the cathode layer comprises a rhombohedral or hexagonal crystal structure.
9. A method according to any preceding claim wherein the substrate comprises a flexible substrate.
10. A method according to any preceding claim wherein the substrate comprises, or is in the form of, a sheet or web.
11. A method according to any preceding claim wherein the substrate is movably mounted to facilitate movement of the substrate.
12. A method according to claim 11 wherein the substrate is mounted in a roll-to-roll arrangement.
13. A method according to any preceding claim wherein the temperature of the substrate during the deposition of the cathode layer is no more than 300°C .
14. A method according to claim 13 wherein said temperature is no more than 200°C .
15. A method according to any preceding claim wherein the maximum temperature reached at any given time by any given square of substrate material having an area of 1 cm^2 as measured on the surface opposite to said surface on which the material is deposited and as averaged over a period of 1 second, is no more than 300°C .
16. A method according to claim 15 wherein said temperature is no more than 200°C .

17. A method of forming a solid state battery half-cell, the method comprising:
forming a cathode layer in accordance with the method of any preceding claim; and
depositing an electrolyte material suitable for a solid state battery cell on the
cathode layer.

18. A method of forming a solid state battery cell, the method comprising:
forming a solid state battery half-cell in accordance with claim 17; and
contacting anode material suitable for a solid state battery cell on the electrolyte
material.