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(19) **United States**(12) **Patent Application Publication****Fuchita et al.**(10) **Pub. No.: US 2007/0048170 A1**(43) **Pub. Date: Mar. 1, 2007**(54) **METHOD FOR FORMING A FILM OF LITHIUM METAL OR LITHIUM ALLOYS AND AN APPARATUS FOR THE SAME****Publication Classification**(51) **Int. Cl.**
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C22C 33/02 (2006.01)(52) **U.S. Cl.** **419/28; 419/55**(76) Inventors: **Eiji Fuchita**, Narita (JP); **Yoshiyuki Honjo**, Osaka (JP); **Yukio Yamakawa**, Osaka (JP)

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Pittsburgh, PA 15219 (US)(21) Appl. No.: **11/510,860**(22) Filed: **Aug. 28, 2006**(30) **Foreign Application Priority Data**Aug. 31, 2005 (JP) 2005-250686
Aug. 31, 2005 (JP) 2005-250687(57) **ABSTRACT**

A lithium or lithium alloy film forming method comprises: the step of heating and evaporating lithium or lithium alloy under an atmosphere of inert gas in an ultra fine particle producing chamber to produce ultra fine particles of lithium or lithium alloy therein; the step of transporting the ultra fine particles through a transfer pipe with the inert gas into a film forming chamber under vacuum atmosphere; the step of jetting the ultra fine particles onto a substrate arranged in the film forming chamber from a nozzle; the step of moving a substrate holder holding the substrate in the X-direction and/or Y-direction; the step of preheating the substrate at a predetermined temperature within the range of 100 to the melting point of lithium or lithium alloy; and the step of forming a film of lithium or lithium alloy on the substrate being moved with the substrate holder.

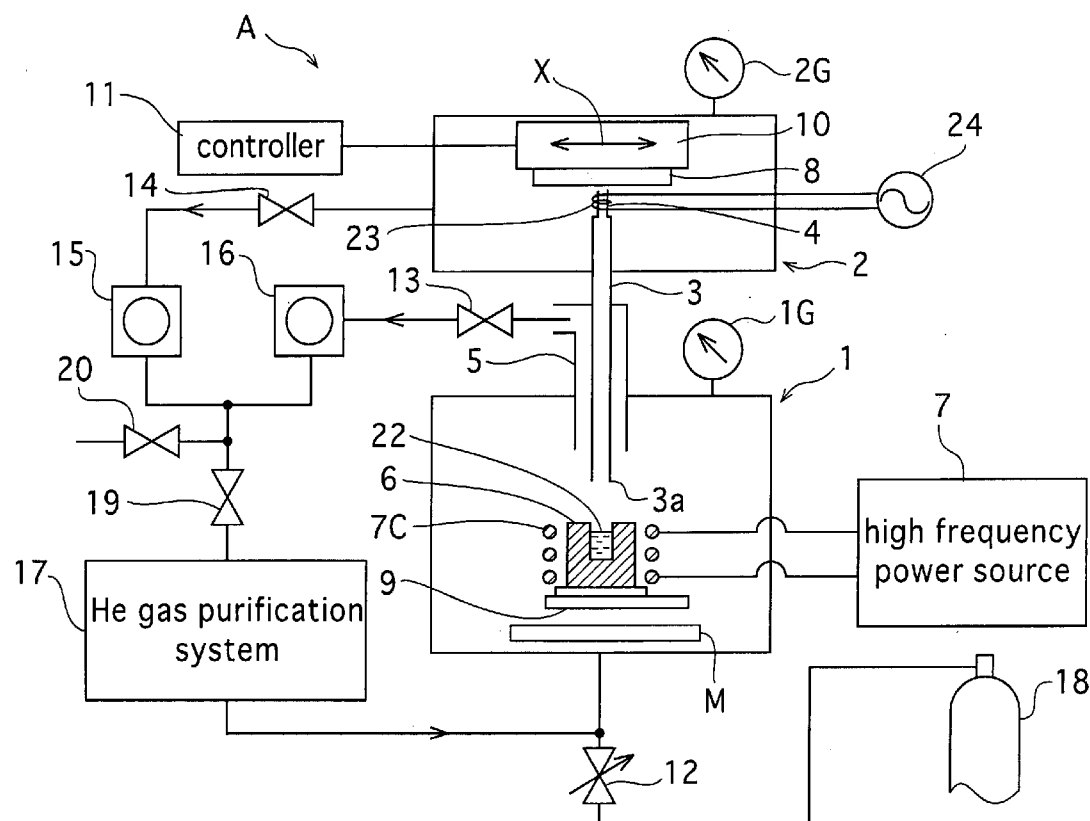


FIG.2A

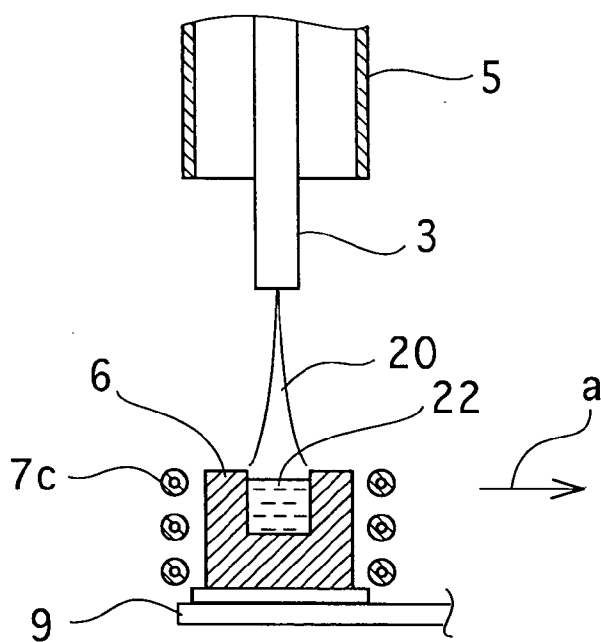


FIG.2B

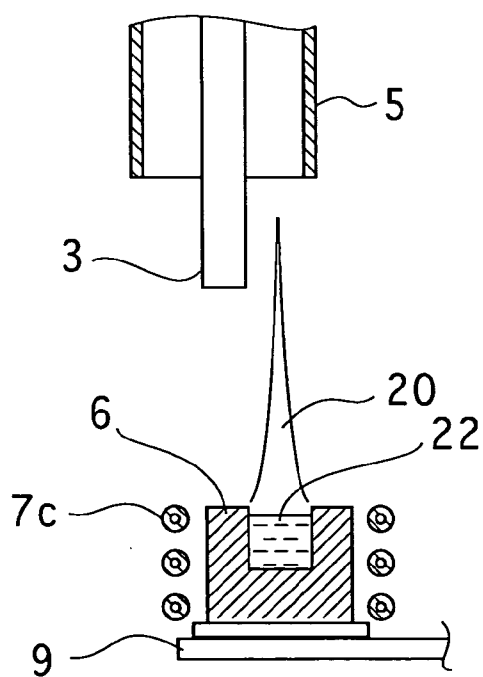


FIG. 3

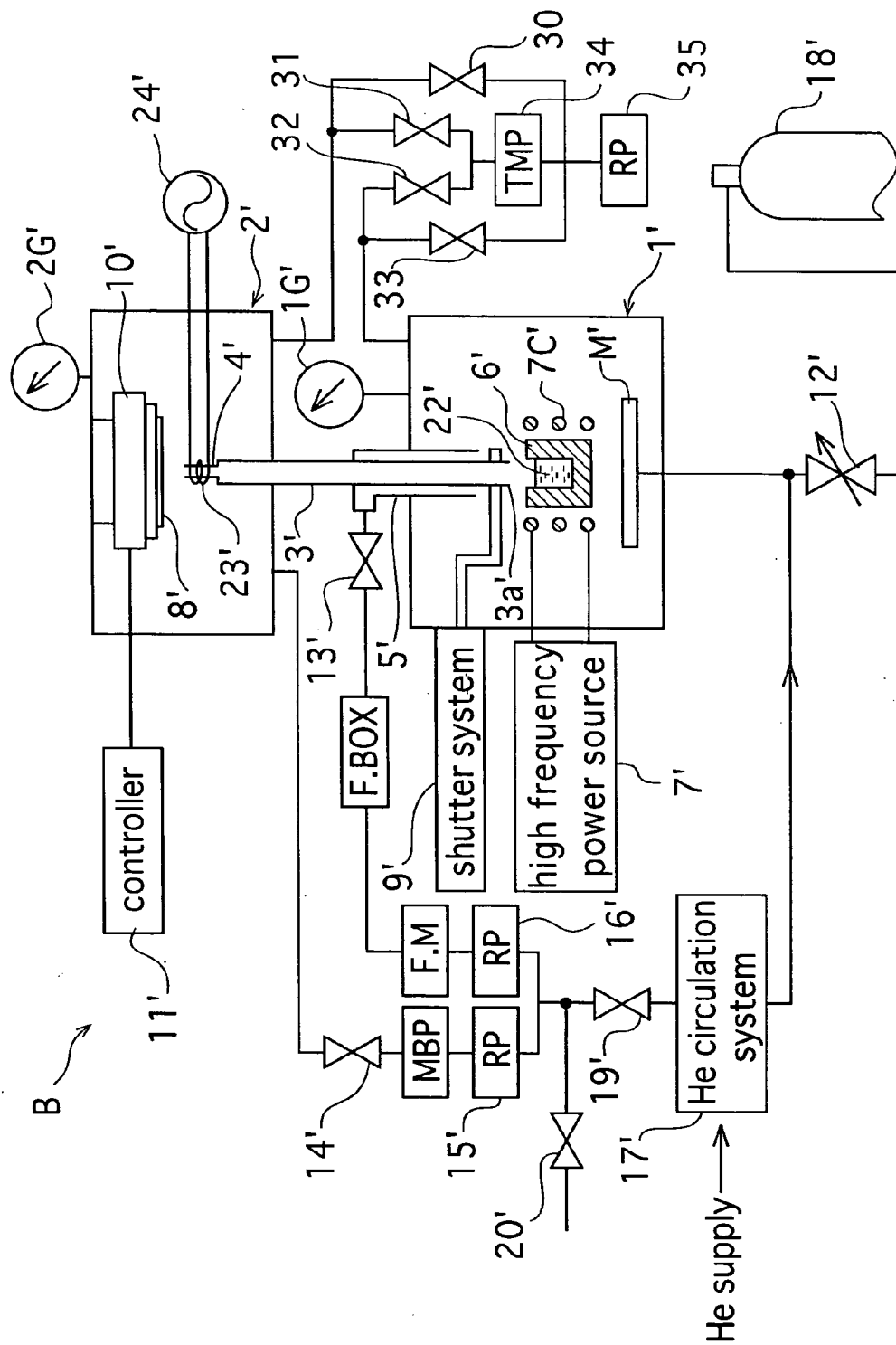


FIG. 4A

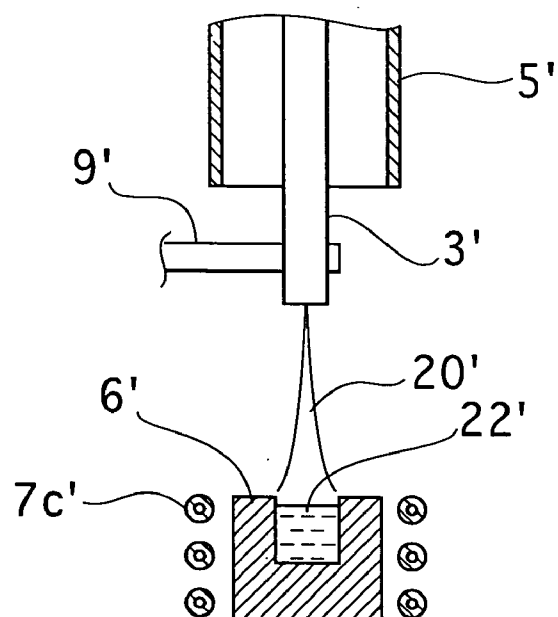
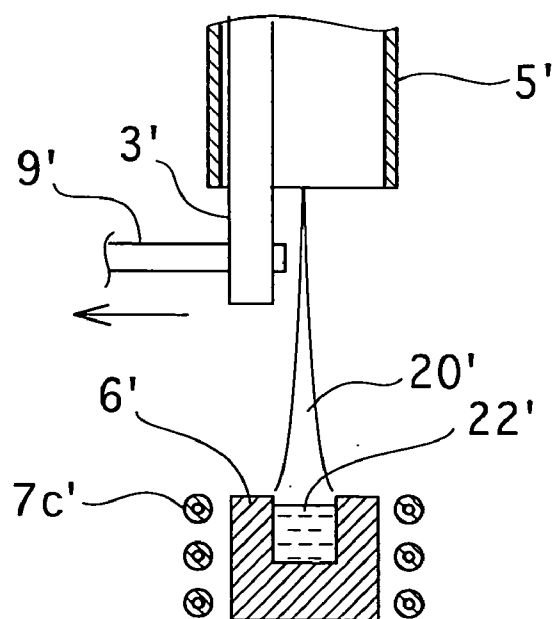


FIG. 4B



METHOD FOR FORMING A FILM OF LITHIUM METAL OR LITHIUM ALLOYS AND AN APPARATUS FOR THE SAME

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to a method for forming a film of lithium metal or lithium alloy and an apparatus for the same.

[0003] 2. Description of the Prior Art

[0004] Publication J8-209330A discloses a pattern forming method for a conductive metal thick film in which a conductive metal material is heated and evaporated with high frequency induction heat under an inert gas atmosphere, in an ultra fine particle evaporation chamber, and produced ultra fine particles are transported in a pipe, with the inert gas, into a film forming chamber in a vacuum. The fine particles are jetted onto a substrate, arranged in the film forming chamber, from a nozzle heated at a temperature under the melting point of the ultra fine particles, with the applied pressure of the inert gas. The nozzle or the substrate is moved at an arbitrary speed and the thick film of conductive metal is formed with a desired thickness in a desired pattern.

[0005] However, in the above gazette publication, the conductive metal is aluminum or an aluminum alloy. The aluminum alloys are Al—Si, Al—Cu, Al—Si—Cu, Al—Si—Ti or Al—Cu—Ti.

[0006] On the other hand, JP2002-100346 discloses:

[0007] a method of producing a negative electrode for a lithium secondary cell having a thin film made of an inorganic solid electrolyte, comprising the steps of:

[0008] placing a closed container containing a negative electrode base material and a closed container containing a source material for an inorganic solid electrolyte, into a chamber space, which is substantially inactivate to lithium and which is insulated from air and provided adjacent to an apparatus for forming the thin film, the base material having a surface made of a material selected from the group consisting of lithium metal and lithium alloys;

[0009] taking out the base material and the source material from each container in the chamber space;

[0010] transferring the base material and the source material into the apparatus without exposing them to air;

[0011] using the source material and forming a thin film made of an inorganic solid electrolyte on the base material in the apparatus;

[0012] transferring the base material having the thin film formed thereon, without exposing it to air, from the apparatus into a chamber space, which is substantially inactivate to lithium and which is insulated from air and positioned adjacent to the apparatus; and

[0013] placing the base material into a closed container in the chamber space.

[0014] In the above mentioned method, the film of the material selected from the group consisting of lithium metal

and lithium alloys is formed on the substrate by the gas phase deposition method. Thus, the negative electrode is adjusted. The gas phase deposition method is selected from the typical group consisting of sputtering, vacuum deposition, laser abrasion and ion plating. The film is heated, and the film has a relatively high ion conductivity.

SUMMARY OF THE INVENTION

[0015] However, ultra fine particles are not used for forming a film in the gas phase deposition method of the above JP2002-100346A reference, although they are used in the JP8-209330A reference. The film forming principles are different between the above two patent opening gazettes. Further the purity of the film of lithium is low in the method of the JP2002-100346 publication. Thus, discharge capacity is small. Thus, an ideal lithium electrode, which has high discharging capacity, cannot be manufactured.

[0016] This invention has been conceived in consideration of the above mentioned problem. The object of the invention is to provide a method for forming lithium or lithium alloy film which can form a lithium or lithium alloy film always having a high purity and an apparatus for forming lithium or lithium alloy film which can form a lithium or lithium alloy film always having high purity.

[0017] In accordance with an aspect of this invention: a lithium or lithium alloy film forming method comprises:

[0018] (a) the step of heating and evaporating a lithium or lithium alloy under an atmosphere of inert gas in an ultra fine particle producing chamber to produce ultra fine particles of lithium or lithium alloy therein;

[0019] (b) the step of transporting the ultra fine particles through a transfer pipe with the inert gas into a film forming chamber under vacuum atmosphere;

[0020] (c) the step of jetting the ultra fine particles onto a substrate arranged in the film forming chamber from a nozzle;

[0021] (d) the step of moving a substrate holder holding the substrate in the X-direction and/or Y-direction;

[0022] (e) the step of heating the substrate at a predetermined temperature within the range of 100° C. to the melting point of lithium or lithium alloy; and

[0023] (f) the step of forming a film of lithium or lithium alloy on the substrate being moved with the substrate holder.

[0024] In accordance with another aspect of this invention: an apparatus is provided for forming a lithium or lithium alloy film which comprises:

[0025] (a) an ultra fine particle producing chamber including a crucible containing lithium or lithium alloy;

[0026] (b) a transfer pipe vertically arranged directly above the crucible;

[0027] (c) a nozzle attached to a top end of the transfer pipe;

[0028] (d) a film-forming chamber including a substrate and a substrate holder holding the substrate, the nozzle being arranged directly under the substrate, and the

holder being movable in the X-direction and/or the Y-direction, in the plane of the substrate;

[0029] (e) evacuating means for evacuating the ultra fine particle producing chamber, the transfer pipe and the film forming chamber; and

[0030] (f) means for introducing inert gas and circulating it into and through the ultra fine particle producing chamber, the transfer pipe and the film forming chamber, whereby, after the ultra fine particle producing chamber, the transfer pipe and the film forming chamber have been evacuated to a predetermined pressure, lithium or lithium alloy in the crucible is heated and evaporated in the ultra fine particle producing chamber to produce ultra fine particles and the inert gas is introduced into the ultra fine particle producing chamber, produced ultra fine particles are transported through the transport pipe with the inert gas, and are jetted onto the substrate from the nozzle, and a lithium or lithium alloy film is formed onto the substrate being moved with the holder, and wherein the predetermined pressure is lower than 5×10^{-4} Pa.

[0031] The foregoing and other objects, features and advantages of the present invention will be more readily understood upon consideration of the following detailed description of the preferred embodiments of the invention, taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] FIG. 1 is a schematic view of an apparatus for forming a film of lithium according to a first embodiment of this invention.

[0033] FIG. 2 is a schematic view for explaining operation of a shutter system, FIG. 2A showing transport of ultra fine particles and FIG. 2B showing cessation of transport.

[0034] FIG. 3 is a schematic view of an apparatus for forming a lithium film according to a second embodiment of this invention.

[0035] FIG. 4 is a schematic view for explaining operation of a shutter system, FIG. 4A showing the situation during the transport of the ultra fine particles and FIG. 4B showing the situation during the cessation of the transport.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0036] Next, a gas deposition apparatus according to a first embodiment of this invention will be described with reference to the drawings.

First Embodiment

[0037] FIG. 1 shows a gas deposition apparatus A of the first embodiment. Generally, it consists of an ultra fine particle evaporation chamber 1, a transfer pipe 3, and a film forming chamber 2, which are arranged in a vertical direction. A crucible 6 which is made of, for example, tantalum, the inner diameter and the outer diameter of which are equal to 38mm(ϕ) and 40mm(ϕ), respectively, is arranged in the ultra fine particle evaporation chamber 1. The height of the crucible 6 is equal to 40 mm. Evaporation material 22 (Li) is contained in the crucible 6. An electromagnetic coil 7C for heating inductively lithium 22 is wound around the crucible

6. The coil 7C is connected to a radio (high) frequency (150 kHz) electric power source 7 which is arranged outside of the ultra fine particle evaporation chamber 1.

[0038] A helium (He) gas is introduced into the ultra fine particle evaporation chamber 1 through a mesh-filter type introducing port M, so that the ultra fine particle evaporation chamber 1 is maintained at a predetermined pressure. The helium gas is used for transporting the produced ultra fine particles. The mesh-filter type introducing port M is of the type in which the area of the filter and the aperture ratio can be changed. The helium gas flows through a variable flow valve 12 from a helium gas source 18. The gas flow is introduced into the ultra fine particle evaporation chamber 1 through the mesh-filter type introducing port M that adjusts the gas flow speed around the crucible 6. A pressure gauge 1G is installed on the ultra fine particle evaporation chamber 1.

[0039] The transfer pipe 3 is straight in the vertical direction. The outer diameter of the transfer pipe 3 is equal to $\frac{1}{4}$ inch. The lower end portion of the transfer pipe 3 is inserted into the ultra fine particle evaporation chamber 1. An inlet port 3a of the transfer pipe 3 is located directly above the crucible 6, and an inner diameter of the inlet port 3a of the transfer pipe 3 is equal to 30 mm. The top portion of the transfer pipe 3 is inserted into the film forming chamber 2. A nozzle 4, which ejects out ultra fine particles, is connected to an outlet port 4 of the transfer pipe 3.

[0040] The nozzle 4 has a throat or narrow hole portion, the inner diameter of which is equal to 1.0 mm. The transfer pipe 3 is straight without bends. Accordingly, turbulence does not occur in the transfer flow of the ultra fine particles through the transfer pipe 3. Further, a nozzle heater 23, wound on the nozzle 4, is heated with an AC power source 24.

[0041] Referring to FIG. 1, an inhalant or evacuation intake pipe 5, which is concentric with the transfer pipe 3, is located above the inlet 3a of the transfer pipe 3, in the ultra fine particles evaporation chamber 1, so that an annular space is formed between the transfer pipe 3 and the intake pipe 5. The intake pipe 5 is so arranged that it sucks in ultra fine particles drifting around the crucible 6 in the ultra fine particle evaporation chamber 1. The intake pipe 5 is directed separately from the transfer pipe 31 outside of the ultra fine particle evaporation chamber 1. It is connected to a vacuum pump 16 through a vacuum valve 13.

[0042] A substrate 8 is arranged in the film forming chamber 2, and is positioned at a right angle with respect to the nozzle 4. The distance between the nozzle 4 and the substrate 8 is equal to 3 mm. The substrate 8 is supported on an operating plate or holding plate 10 which is movable in the X-direction, the Y-direction and the Z direction, which are at right angles with respect to each other. The operating plate or holding plate 10 has a heating mechanism (which is not shown) for heating the substrate 8. The film forming chamber 2 is connected to a vacuum pump 15 through a vacuum valve 14. Further, a vacuum gauge 2G is attached to the film forming chamber 2.

[0043] A shutter system 9 supports the crucible 6 at the bottom. The shutter system 9 locates the crucible 6 at a position directly under the transfer pipe 3 as shown in FIG. 2A, or locates the crucible 6 at another position directly under the annular space between the transport pipe 3 and the intake pipe 5 as shown in FIG. 2B. The distance between the one position and the other position is equal to 50 mm in the direction as shown by the arrow a. Metal vapor from the crucible 6 is cooled by the atmosphere of the transport gas (helium gas) to thereby become ultra fine particles, which are sucked into the transfer pipe 3, at the one position, and the intake pipe 5 at the other position as shown in FIG. 2B. The shutter system 9 is moved between the one position and the other position in accordance with a program of a controller which is not shown. Transport or non-transport of the ultra fine particles through the transport pipe 3 is thus controlled.

[0044] The nozzle 4 of 1.0 mm in inner diameter is inserted through the top and the upper end portion of the transfer pipe 3. A nozzle heater 23 is wound around the nozzle 4 and is electrically connected to the outward alternative power source 24. The substrate 8 is arranged directly over the nozzle 4. It is held by the holder 10. The distance between the substrate 8 and the nozzle 4 is variable within the range of 3 to 30 mm. The movement of the holder or operating plate 10 is programmatically controlled by a controller 11. The substrate 8 is moved in the plane of the X-direction and Y-direction at the speed of 0.5 to 6 mm per second.

[0045] According to this invention, the holder 10 includes a heating mechanism which is controlled to heat the substrate 8 at a predetermined temperature within the range of 100° to 180.5° C. (melting point of lithium metal) by a temperature control portion of the controller 11. In this embodiment, the substrate 8 is heated at the predetermined temperature of 100° C. through the heating mechanism in the holder 10 with the temperature control portion of the controller 11.

[0046] The discharge conduits of the vacuum pumps 15 and 16 are combined to form one conduit and connected through a valve 19 to a He gas purification recycle system 17. Output gas of the helium gas purification system 17 is transported into the bottom of the ultra fine particle producing chamber 1, which is further connected through the valve 12 to the helium gas source 18. It contains helium gas of a purity of 99.9999% or more. Discharge conduits of the vacuum valves 15, 16 are combined with the conduit which is further connected through a valve 20 to a divided conduit.

[0047] Next, there will be described the method of forming a lithium metal film on the substrate 8 by using the above described apparatus. In this embodiment, a copper foil is used as the substrate 8, the thickness of which is exaggeratedly shown. The thickness is equal to 10 mm.

[0048] Referring to FIG. 1, the ultra fine particle producing chamber 1 and the film forming chamber 2 are evacuated to a pressure of 10^{-4} Pa by the vacuum pumps 15, 16. The valves 13, 14 and 20 are opened and the valves 12 and 19 are closed. The vacuum pumps 15 and 16 are continuously driven. The valve 20 is closed. The valves 12 and 19 are

opened. Helium gas of a purity of 99.9999% or more is introduced at a predetermined rate into the ultra fine particle producing chamber 1 from the helium gas source 18. The opening of the valve 13 is so adjusted so as to maintain the pressure of the ultra fine particle producing chamber 1 at 100 kPa. The introduced helium is sucked into the intake pipe 5 at the rate of 30 SLM (number of liters per minute under standard conditions). Helium gas is flowed through the transfer pipe 3 at the rate of 10 SLM, into the film forming chamber 2. The helium gas is introduced into the film forming chamber 2 and evacuated through the valve 14. The pressure of the film forming chamber 2 is maintained at about 300 Pa. The pressure difference between the film forming chamber 2 and the ultra fine particle producing chamber 1 becomes about 100 kPa. At that time, the valve 12 is closed.

[0049] The reason why the flow amount into the intake pipe 5 is larger, is as follows: when the ultra fine particles stay in the ultra fine particle producing chamber 1 for some time, ultra fine particles are apt to coagulate together and the coagulations might be transferred in the transfer pipe 3. The coagulations have an undesirable influence on the film being formed on the substrate. The larger flow amount into the intake pipe 5 prevents the formation of coagulation of the ultra fine particles.

[0050] When the above condition exists for longer than 30 minutes, the helium gas discharged from the helium gas purification recycle system 17 becomes purified at a purification of 99.9999% or more. Helium gas of a purification of 99.9999% is circulated in the direction as shown by the arrows.

[0051] After the above condition, the crucible 6 containing lithium metal 22 is inductively heated with the high frequency power source 7. The metal 22 is heated at a temperature of 480° C. and it is evaporated from the crucible 6 and therefore ultra fine particles are formed. Almost all of the formed ultra fine particles are sucked into the transfer pipe 3 and they are jetted onto the substrate 8 from the nozzle 4, which is heated at the temperature of 100° C. by the nozzle heater 23. The substrate 8 is heated at the temperature of 100° C. According to this invention, it is preheated at the temperature of 100° C. with the heater unit included in the substrate holder 10 before introducing the ultra fine particles into the film forming chamber 2. Thus, a lithium film is formed on the substrate 8.

[0052] The substrate 8 is moved in the X-direction and the Y-direction in the plane of the substrate 8. The stop and start of the transfer of the ultra fine particles is freely controlled with the shutter system 9. An arbitrary pattern can be formed from one arbitrary point to another arbitrary point.

[0053] The content of lithium in the film was measured electrochemically.

[0054] The method of calculation of the content is shown in formula 3. Lithium amount obtained from the electrolysis (discharge) is shown in formula 1. Lithium amount (theoretical capacity) obtained from the weight (film thickness) is shown in formula 2. Formula 1/Formula 2×100=content [%]

[0055] [Formula 1]

Lithium amount obtained from the electrolysis

[0056] (Discharge time: t [sec], Constant current value: 0.001 [A/cm²])

$$G = \frac{t[\text{sec}] \times 0.001 [\text{A/cm}^2]}{96487 [\text{C/mol}]} [\text{mol/cm}^2]$$

[0057] [Formula 2]

Lithium amount obtained from the weight

[0058] (Lithium weight: W [g], Dimension: S [cm²])

$$M = \frac{W[\text{g}]}{6.941 [\text{g/mol}] \times S[\text{cm}^2]} [\text{mol/cm}^2]$$

[0059] [Formula 3]

$$\frac{G}{M} \times 100 = \text{rate of content } [\%]$$

[0060] In this embodiment, the substrate **8** is heated to the predetermined temperature within the range of 100 to 180.5° C. by the substrate holder **10**. When the substrate **8** is not heated, the content is equal to 87%. However, when the substrate **8** is heated to the temperature of 100° C., it is equal to 96%, according to this invention. The content of lithium or purity of lithium is greatly raised. Accordingly, the electrical capacity of the lithium can be widely improved.

[0061] The reason why the content or purity of lithium is greatly raised, is considered to be that the surface of the substrate is cleaned, or particularly that water is removed from the surface of the substrate, or that various contaminants from the walls of the vacuum chamber are eliminated from the surface of the substrate **8** by the heat.

[0062] Next, a gas deposition apparatus according to a second embodiment of this invention will be described with reference of FIG. 3 and FIG. 4.

Second Embodiment

[0063] FIG. 3 shows a gas deposition apparatus B of the second embodiment. The parts which correspond to those in FIG. 1, are denoted by the same, but primed, reference numerals. Generally, it consists of an ultra fine particle evaporation chamber **1'**, a transfer pipe **3'**, and a film forming chamber **2'**, which are arranged in a vertical direction. A crucible **6'**, the inner diameter of which is equal to 5.0 mm, is arranged in the ultra fine particle evaporation chamber **1'**. Evaporation material **22'** (Li) is contained in the crucible **6'**. An electromagnetic coil **7C'** for inductively heating lithium in the crucible **6'** is wound around the crucible **6'**. The coil **7C'** is connected to a radio (high) frequency electric power source **7'** which is arranged outside of the ultra fine particle evaporation chamber **1'**.

[0064] A helium (He) gas is introduced into the ultra fine particle evaporation chamber **1'** through a mesh-filter type introducing port **M'**, so that the ultra fine particle evaporation chamber **1'** is maintained at a predetermined pressure. The helium gas is used for transporting the produced ultra fine particles. The mesh-filter type introducing port **M'** is of the type in which the area of the filter and the aperture ratio can be changed. The helium gas flows through a variable flow valve **12'** from a source **18'**. The gas flow is introduced into the ultra fine particle evaporation chamber **1'** through the mesh-filter type introducing port **M'** that adjusts the gas flow speed around the crucible **6'**. A pressure gauge **1G'** is installed on the ultra fine particle evaporation chamber **1'**.

[0065] The transfer pipe **3'** is straight in the vertical direction. The inner diameter of the transfer pipe **3'** is equal to 4.3 mm. The lower end portion of the transfer pipe **3a'** is inserted into the ultra fine particle evaporation chamber **1'**. An inlet port **3a'** of the transfer pipe **3'** is located directly above the crucible **6'** and the inlet port **3a'** of the transfer pipe **3'** is equal to 30 mm. The top portion of the transfer pipe **3'** is inserted into the film forming chamber **2'**. A nozzle **4'**, which ejects ultra fine particles, is connected to an outlet port **4'** of the transfer pipe **3'**.

[0066] The nozzle **4'** has a throat or narrow passage portion, the inner diameter of which is equal to 0.6 mm. The transfer pipe **3'** is straight without bends. Accordingly, turbulence does not occur in the transfer flow of the ultra fine particles through the transfer pipe **3'**. Further, the nozzle **4'** is heated with an alternating power source **24'**. A nozzle heater **23'** wound on the nozzle **4'** is connected to the alternating power source **24'**.

[0067] Referring to FIG. 3, an inhalant or evacuation intake pipe **5'**, which is concentric with the transfer pipe **3'**, is located above the inlet **3a'** of the transfer pipe **3'**, in the ultra fine particle evaporation chamber **1'**, so that an annular space is formed between the transfer pipe **3'** and the intake pipe **5'**. The intake pipe **5'** is so arranged that it sucks in ultra fine particles drifting around the crucible **6'** from the ultra fine particle evaporation chamber **1'**. The intake pipe **5'** is directed separately from the transfer pipe **3'** outside of the ultra fine particle evaporation chamber **1'**. It is connected through a vacuum valve **13'**, an F.Box and an FM to a vacuum pump **16'**.

[0068] A substrate **8'** is arranged in the film forming chamber **2'**, and makes a right angle with the nozzle **4'**. The distance between the nozzle **4** and the substrate **8'** is equal to 3 mm. The substrate **8'** is supported on an operating plate or a holder **10'** which is movable in the X-direction, the Y-direction and the Z direction, which are at right angles with each other. The operating plate **10'** has a heating mechanism (which is not shown) for heating the substrate **8'**. The film forming chamber **2'** is connected to a vacuum pump **15'** through a vacuum valve **14'**. Further, a vacuum gauge **2G'** is attached to the film forming chamber **2'**.

[0069] A shutter system **9'** is connected to the lower end of the transfer pipe **3'**. The shutter system **9'** locates the transfer pipe **3'** at a position directly above the crucible **6'** as shown in FIG. 4A or locates the transfer pipe **3'** at another position shifted from the crucible **6'** in FIG. 4B. The distance between the one position and the other position is equal to 50 mm in the direction as shown by the arrow. Metal vapor from the crucible **6'** is cooled by the atmosphere of the transport gas

(helium gas) to become ultra fine particles and is sucked into the transfer pipe 3' at the one position and the intake pipe 5' at the other position as shown in FIG. 4B. The shutter system 9' is moved between the one position and the other position in accordance with a program of a controller which is not shown. Transport or non-transport of the ultra fine particles through the transfer pipe 3' is thus controlled.

[0070] The nozzle 4' of 1.0 mm inner diameter is inserted through the top and the upper end portion of the transfer pipe 3'. A nozzle heater 23' is wound around the nozzle 4' and is electrically connected to the outward alternative power source 24'. A substrate 8' is arranged directly over the nozzle 4'. It is held by the holder 10'. The distance between the substrate 8' and the nozzle 4' is variable within the range of 3 to 30 mm. The holder 10' is programmatically controlled by a controller 11'. The substrate 8' is moved in the plane of the X-direction and the Y-direction at a speed of 0.5 to 6 mm per sec.

[0071] The discharge conduits of the vacuum pumps 15' and 16' are combined to one conduit and connected through a valve 19' to an He gas circulation system 17'. Output gas of helium gas circulation system 17' is transported into the bottom of the ultra fine particle producing chamber 1', which is further connected through a valve 12' to a helium gas source 18'. It contains helium gas of purity 99.9999% or more. Discharge conduits of the vacuum pumps 15', 16' are combined to the conduit which is connected through a valve 20' to a divided conduit.

[0072] Further, in this embodiment, a turbo molecular pump (TMP) 34 and a rotary pump 35 are connected through valves 30 and 31 to the film forming chamber 2' and through valves 32 and 33 to the ultra fine particle producing chamber 1'.

[0073] In this embodiment, a shutter system 9' is fixed to the lower end of the transfer pipe 3' as shown in FIG. 4. FIG. 4A shows one position at which the crucible 6' is direct under the transfer pipe 3'. The evaporation 20' is almost sucked into the transfer pipe 3'. In FIG. 4B, the transfer pipe 3' is shifted leftwards by the shutter system 9'. The evaporation 20' is always sucked into the intake pipe 5'.

[0074] Next, there will be described the method of forming a lithium metal film on the substrate 8' by using the above described apparatus. In this embodiment, a copper foil is used as the substrate 8', the thickness of which is exaggeratedly shown. The thickness is equal to 10 m.

[0075] The ultra fine particle producing chamber 1' and the film forming chamber 2' are evacuated to high vacuum with the turbo molecular pump (TMP) 34 and the rotary pump 35. According to this invention, the film forming chamber 2' is evacuated to lower than 5×10^{-4} Pa, which is measured with pressure gauge 2G'. In other words, the ultimate vacuum is lower than 5×10^{-4} Pa.

[0076] Next, the valves 31 and 32 are closed, and the rotary vacuum pumps 15 and 16 and the mechanical booster pump (MBP) are driven. The valves 14 and 13 are opened and also the valves 12' and 19' are opened. The helium gas of purity higher than 99.9995% is introduced into the ultra fine particle producing chamber 1' at a predetermined rate. The pressure of the ultra fine particle producing chamber 1' is maintained at the pressure of 100 kPa. The introduced helium gas is flowed into the intake pipe 5' at the rate of 5

to 30 SLM (Standard liters per minute), and it is flowed thorough the transfer pipe 3' at the rate of 2 to 10 SLM into the film forming chamber 2'. The helium gas is discharged through the valve 14'. The pressure of the film forming chamber 2' is maintained at a pressure of about 300 Pa. The pressure difference between the ultra fine particle producing chamber 1' and the film forming chamber 2' is equal to about 100 kPa. At that time, the valve 12' is closed. "F.M" is a helium gas flow meter which is operated at the same time as the MBP. "F.BOX" represents a particle trap.

[0077] The reason why the flow amount into the intake pipe 5' is larger, is as follows. When the ultra fine particles stay in the ultra fine particle producing chamber 1' for some time, the ultra fine particles are apt to coagulate together and the coagulations might be transferred in the transfer pipe 3'. The coagulations have an undesirable influence on the film being formed on the substrate. The larger flow amount into the intake pipe 5' prevents the formation of coagulations of the ultra fine particles.

[0078] When the above condition continues for longer than 30 minutes, the helium gas discharged from the helium gas purification recycle system 17' becomes purified at a purification of 99.9999% or more. Helium gas of purification of 99.9999% is circulated in the direction as shown by the arrows.

[0079] After the above condition is attained, the crucible 6' containing lithium metal 22' is inductively heated with the high frequency power source 7'. The metal 22' is heated at a temperature of 480° C. and it is evaporated from the crucible 6', thereby forming ultra fine particles. Almost all of the formed ultra fine particles are sucked into the transfer pipe 3' and they are jetted onto the substrate 8' from the nozzle 4', which is heated to a temperature of 100° C. by the nozzle heater 23'. The substrate 8' is heated to a temperature of 100° C. It is preheated to a temperature of 100° C. with the heater unit included in the substrate holder 10. Thus, a lithium film is formed on the substrate 8'.

[0080] The substrate 8' is moved in the X-direction and the Y-direction in the plane of the substrate 8'. The stop and start of the transfer of the ultra fine particles is freely controlled with the shutter system 9'. An arbitrary pattern can be formed from one arbitrary point to another arbitrary point.

[0081] The content of lithium in the film was measured electrochemically.

[0082] The calculation method of the content is shown in formula 3. Lithium amount obtained from the electrolysis (discharge) is shown in formula 1. Lithium amount (theoretical capacity) obtained from the weight (film thickness) is shown in formula 2. Formula 1/Formula 2 $\times$ 100=content [%]

[0083] [Formula 1]

Lithium amount obtained from the electrolysis

[0084] (Discharge time: t [sec], Constant current value: 0.001 [A/cm²])

$$G = \frac{t[\text{sec}] \times 0.001 [\text{A/cm}^2]}{96487 [\text{C/mol}]} [\text{mol/cm}^2]$$

[0085] [Formula 2]

Lithium amount obtained from the weight

[0086] (Lithium weight: W [g], Dimension: S [cm²])

$$M = \frac{W[\text{g}]}{6.941 [\text{g/mol}] \times S[\text{cm}^2]} [\text{mol/cm}^2]$$

[0087] [Formula 3]

$$\frac{G}{M} \times 100 = \text{rate of content } [\%]$$

[0088] Also in this embodiment, it has been proved that the purification of the lithium is greatly raised, and that it is more than 95% of the theoretical electric capacity. Thus, the electrical capacity of the lithium is greatly raised.

[0089] The reason why the theoretical electrical capacity is greatly raised, is considered to be that, before a lithium film is formed, the surface of the substrates 8' is cleaned with the lowering of the ultimate vacuum, and particularly that the water content is removed and contaminants from the walls of vacuum chamber are eliminated from the surface of the substrate.

[0090] While the preferred embodiments of the Invention have been described, without being limited to this, variations thereto will occur to those skilled in the art within the scope of the present inventive concepts that are delineated by the following claims.

[0091] For example, in the above embodiments, helium gas of purity of 99.9999% or more is used as the inert gas, however argon, neon or xenon may be used as the inert gas.

[0092] Furthermore, in the first embodiment, the predetermined heating temperature is 100° C. It may be higher than 100° C., but lower than the melting point of lithium or lithium alloy.

[0093] Furthermore, in the above embodiments, the shutter system is used. However, it is not always necessary. The ON/OFF of the transport of the ultra fine particles may be effected by any other means.

[0094] Further, in the above embodiment, lithium or lithium alloy in the crucible, is heated inductively with the coil. Instead, the crucible may be heated by a resistance heating method, wherein the crucible is directly heated by Joule heat.

[0095] Furthermore, the heating mechanism may be included in the substrate 8.

What is claimed is:

1. A lithium or lithium alloy film-forming method comprising:

- (a) the step of heating and evaporating lithium or lithium alloy under the atmosphere of an inert gas in an ultra fine particle producing chamber to produce ultra fine particles of lithium or lithium alloy therein;
- (b) the step of transporting said ultra fine particles through a transfer pipe with said inert gas into a film forming chamber under vacuum atmosphere;

- (c) the step of jetting said ultra fine particles onto a substrate arranged in said film forming chamber from a nozzle;

- (d) the step of moving a substrate holder holding said substrate in the X-direction and/or the Y-direction;

- (e) the step of heating said substrate at a predetermined temperature within the range of 100° C. to the melting point of lithium or lithium alloy; and

- (f) the step of forming a film of lithium or lithium alloy on said substrate while being moved with said substrate holder.

2. A lithium or lithium alloy film forming method according to claim 1 in which said inert gas is selected from the group consisting of helium, neon, xenon and argon.

3. A lithium or lithium alloy film forming method according to claim 1 in which a heating mechanism is included in said substrate holder to heat said substrate.

4. A lithium or lithium alloy film forming method according to claim 1 in which a thermocouple is attached to said substrate and the output of said thermocouple is supplied to a control portion of said substrate holder.

5. An apparatus for forming a lithium or lithium alloy film comprising:

- (a) an ultra fine particle producing chamber including a crucible containing lithium or lithium alloy;

- (b) a transfer pipe vertically arranged directly above said crucible;

- (c) a nozzle attached to a top end of said transfer pipe;

- (d) a film-forming chamber including a substrate and a substrate holder holding said substrate, said nozzle being arranged directly under said substrate, and said holder being movable in the X-direction and/or the Y-direction, in the plane of said substrate;

- (e) evacuating means for evacuating said ultra fine particle producing chamber, said transfer pipe and said film forming chamber;

- (f) means for inductively heating and evaporating the lithium or lithium alloy in said ultra fine particle producing chamber to produce ultra fine particles; and

- (g) means for introducing and circulating inert gas into and through said ultra fine particle producing chamber, said transfer pipe and said film-forming chamber, whereby, after said ultra fine particle producing chamber, said transfer pipe and said film-forming chamber have been evacuated to a predetermined pressure, and said inert gas is introduced into said ultra fine particle producing chamber, said produced ultra fine particles are transported through said transfer pipe with said inert gas, and are jetted onto said substrate from said nozzle whereby a lithium or lithium alloy film is formed onto said substrate being moved with said holder, said predetermined pressure being lower than 5×10^{-4} Pa.

6. An apparatus according to claim 5 in which said inert gas is of purity of 99.9995% or more.

7. An apparatus according to claim 5 in which said evacuating means includes a turbo-molecular pump.

8. An apparatus according to any one of claims 5 in which said inert gas is selected from the group consisting of helium, argon, xenon and argon.

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