

## **Gas Phase Co-Deposition of Hydrogen/Deuterium Loaded Metallic Structures**

### **Technical field**

**[001]** The present invention relates generally to deposition methods for making a metallic film, and more specifically, to deposition methods in the presence of a partial hydrogen/deuterium pressure.

### **Background**

**[002]** Deposition methods are widely used to make metallic coatings or films. Well-known deposition methods include physical vapor deposition (PVD), chemical vapor deposition (CVD), etc. In PVD, a piece of metal wire or plate is turned into vapor through a physical process, such as sputtering. In a sputter deposition process, an atom of an inert gas, such as argon, is accelerated toward a metal plate with sufficient energy to dislodge metal atoms from the plate. The dislodged metal atoms or ions are accelerated under a force field to reach a substrate and are deposited onto the substrate. In CVD, metal atoms are part of a molecule. Energy, such as a plasma or heat, acts to break up the molecule so that individual metal atoms may deposit on a substrate.

**[003]** In either PVD or CVD, the deposition process takes place in a deposition chamber. The deposition chamber is under a vacuum and filled with one or more inert gases. Alternatively, the deposition chamber can also be filled with reactive gasses, e.g., oxygen, for creating a metallic compound, such as a metal oxide. The metallic compound is formed when the reactive gasses interact with the gas phase metal.

**[004]** In PVD or CVD, a co-deposition process can be used to deposit metallic atoms and one or more other atoms onto the substrate. An example of existing co-deposition technologies include liquid phase co-deposition by electrolysis. Another example of a co-deposition technique is cyclically exposing the reaction material or deposition material to a gas in between deposition processes.

### **Summary**

**[005]** The present disclosure relates to methods and apparatus for fabricating a metallic or alloy structure in the presence of a partial hydrogen/deuterium gas pressure such that the metallic or alloy structure is loaded with hydrogen/deuterium upon creation.

Moreover, due to the presence of the hydrogen/deuterium gas, the number of vacancies in the fabricated metallic or alloy structure is increased.

**[006]** In the present disclosure, a method of fabricating a hydrogen loaded metallic structure in a deposition chamber is disclosed. The deposition chamber comprises a substrate holder and the deposition chamber is evacuated to create a vacuum. The substrate holder holds a substrate. The method comprises introducing a deuterium gas to the deposition chamber to build a partial gas pressure. The method further comprises depositing a metallic material onto the substrate in the partial gas pressure to form a hydrogen loaded metallic structure. In some embodiments, two or more gases may be introduced into the deposition chamber. The two or more gases include a hydrogen/deuterium gas and the metallic material is deposited on the substrate in the presence of both a hydrogen/deuterium gas and a second gas. In one embodiment, the second gas is fluorine. In another embodiment, the second gas is chlorine. In some

embodiments, the metallic material is deposited onto the substrate via a vapor deposition method, for example, physical vapor deposition or chemical vapor deposition.

**[007]** A deposition chamber for fabricating a hydrogen loaded metallic structure in the presence of a partial hydrogen/deuterium gas pressure is also disclosed. The deposition chamber comprises a substrate holder, a vacuum pump, a gas valve, and a target. The substrate holder is configured for holding a substrate onto which the metallic structure is deposited. The vacuum pump is configured for evacuating the deposition chamber. The gas valve is configured for introducing one or more gases into the deposition chamber, wherein the one or more gases include a hydrogen gas. The target is configured to sputter the metallic material onto the substrate. In some embodiments, a first power supply is applied to provide a voltage bias between the substrate holder and the ground, and a second power supply is applied to provide a voltage bias between the target and the ground. The substrate is in physical contact with the substrate holder. The substrate may or may not be in electrical contact with the substrate holder.

### **Brief Description of Figures**

**[008]** Figure 1 illustrates an exemplary deposition chamber.

**[009]** Figure 2 illustrates an exemplary cyclical deposition process.

**[010]** Figure 3 is a flow chart illustrating a first exemplary gas-phase co-deposition process.

**[011]** Figure 4 is a flow chart illustrating a second exemplary gas-phase co-deposition process.

**[012]** Figure 5 illustrates an exemplary packaging process of a hydrogen loaded metallic structure.

### **Detailed Description**

**[013]** The present disclosure teaches advantageous methods and apparatus for fabricating a hydrogen loaded metallic structure using gas phase co-deposition techniques.

**[014]** Figure 1 illustrates an exemplary apparatus 100 configured for gas phase co-deposition of a hydrogen loaded metallic structure. The exemplary apparatus 100 comprises a deposition chamber 102, a vacuum pump 116, a pressure gauge 112, and a process gas supply 114. The deposition chamber 102 comprises a target 104 and a substrate holder 106, which holds a substrate 118. The target 104 is made of a metallic material and can be used to produce free metal atoms/ions when a voltage bias is applied to the target. When a bias is applied to the substrate holder 106, the metal ions are accelerated from the target 104 to the substrate holder 106 and deposited onto the substrate 118. The substrate 118 is configured for deposition of the metallic material. The target 104 and the substrate holder 106 are each connected to power supplies 108 and 110 respectively. The voltage bias applied to the substrate holder 106 creates an electric field that accelerates metal ions that are dislodged from the target 104 toward the substrate holder 106 to form a metallic structure on the substrate 118.

**[015]** In Figure 1, the vacuum pump 116 is connected to the deposition chamber 102. The vacuum pump 116 is configured to evacuate any undesirable or residual gas from the deposition chamber 102 to create a high vacuum in the chamber 102. The deposition

chamber 102 is also connected to a pressure gauge 112 and one or more gas supplies 114. The pressure gauge 112 is configured to measure the pressure of the deposition chamber 102. The one or more gas supplies 114 are configured to supply one or more process gases to the deposition chamber 102. In some embodiments, one of the process gases is hydrogen/deuterium gas. In some embodiments, two or more process gases may be introduced into the reaction chamber. The two or more process gases include a hydrogen/deuterium gas and a second gas. In some embodiments, the second gas is fluorine. In some embodiments, the second gas is chlorine.

**[016]** The apparatus 100 shown in Figure 1 is configured to deposit some of the metallic material dislodged from the target 104 onto the substrate 118. The deposition process can be a physical vapor deposition (PVD) or a chemical vapor deposition (CVD) process. An exemplary PVD process is sputtering deposition, which is illustrated in Figure 2.

**[017]** Figure 2 depicts a deposition chamber 100 that comprises the target 104 and the substrate holder 106. The deposition chamber 100 is filled with argon gas. The argon gas is of a pressure less than the atmospheric pressure and is in a plasma state due to a voltage bias created between the substrate holder 106 and the ground. Argon ions (Ar) 202 in a plasma state possess high kinetic energies. When argon ions (Ar) 202 bombard the target 104, their kinetic energies are transferred to the metallic material in the target 104. Metal ions ( $M^+$ ) are dislodged from the target 104. The process of dislodging material from a target is known as sputtering. As shown in Figure 1, the target 104 and the substrate holder 106 are connected to different power supplies. The target power supply 108 can be used to enhance the sputtering of metallic material by creating a voltage bias between the target 104 and the ground. The voltage bias created by the

power supply 110 induces an electric field that accelerates the metal ions ( $M^+$ ) towards the substrate holder 106 and the substrate 118. Some portion of the metal ions ( $M^+$ ) which hit the substrate 118, are deposited on the substrate 118 to form a metallic coating 210. After the metallic coating 210 has reached a desired thickness, the power supplies may be turned off for a period of time.

**[018]** During power off, the metallic coating 210 does not grow substantially, or not at all. In one embodiment, deuterium gas is introduced into the deposition chamber 100 via the gas supply 114. Plasma argon ions collide with deuterium gas molecules and break the molecules into deuterium ions ( $D^+$ ). Deuterium ions ( $D^+$ ) created by plasma argon ions will adsorb onto the metallic coating 210 to form a layer of deuterium 212. Some portion of the deuterium ions will diffuse into the metallic coating. When enough deuterium ions 212 have accumulated on and/or absorbed into the metallic coating 212, the vacuum pump 116 may be turned on and the deposition chamber 100 is evacuated. After both the deuterium and argon gases are evacuated, argon is reintroduced into the deposition chamber 100. The power supplies to the target 104 and the substrate holder 106 are turned on. The sputtering process is resumed and another layer of metallic coating 214 is deposited on the substrate 118. When the second layer of metallic coating 214 has reached a desired thickness, the sputtering process may be suspended and the deuterium gas may be introduced to the deposition chamber 100 once again. A second layer of deuterium is then adsorbed by and/or absorbed into the metallic coating 214. This gas-phase co-deposition process can be repeated for a number of times as needed. The final product deposited on the substrate 118 is a metallic structure loaded with hydrogen.

**[019]** In some embodiments, the target 104 comprises palladium and the final product deposited on the substrate 118 is a deuterium loaded palladium. Hydrogen/deuterium loaded palladium has many industrial applications. However, in several of the industrial applications, it is desirable to achieve a high hydrogen loading ratio. Under normal conditions, the hydrogen loading ratio in palladium often cannot exceed 0.7 or 0.8. To attain a high hydrogen loading ratio, extraordinary conditions are often required. For example, ultra-high pressure ( $> 10,000$  Pascal) or ultra-high temperature ( $> 1000$  °C) are often needed to achieve a hydrogen loading ratio exceeding 1.0.

**[020]** The gas phase co-deposition process depicted in Figure 2 is a cyclical deposition process, which can be used to manufacture a hydrogen loaded metallic structure having a high hydrogen loading ratio. It is noted that in the metallic structure deposited on the substrate comprising the layers 210, 212, and 214, the amount of hydrogen/deuterium ions or atoms which absorb into the metallic structure can be varied by controlling the hydrogen/deuterium gas pressure inside the deposition chamber 100, and by controlling the time period between two consecutive sputtering processes. Increasing the time period between two sputtering processes allows more hydrogen/deuterium atoms to be absorbed by the metallic structure, thus attaining a higher hydrogen loading ratio in the final deposition product.

**[021]** Figure 3 is a flow-chart illustrating an exemplary gas phase co-deposition process 300. The gas phase co-deposition process 300 takes place in the deposition chamber 100. The deposition chamber 100 comprises a (metal) target 104 and a substrate holder 106. In step 302 of the gas-phase co-deposition process 300, the deposition chamber 100 is evacuated to remove any undesirable gas, and an argon gas is then introduced to the

deposition chamber 100. A voltage bias created between the substrate holder 106 and the ground is used to produce argon plasma. The deposition chamber 100 is now ready for gas phase co-deposition.

**[022]** In step 304 of the gas phase co-deposition process 300, the sputtering process starts when the argon plasma is created. During the sputtering process, a metallic structure is deposited onto the substrate 118 held by the holder 106. After the metallic structure has reached a desirable thickness, the sputtering process is turned off by removing the voltage bias between the substrate 106 and the ground (step 306). A hydrogen/deuterium gas is then introduced into the deposition chamber 100 (step 306). During the time period when the sputtering process is turned off, hydrogen/deuterium ions or atoms adsorb and, after some time, absorb into the metallic layer 212. After a desirable amount of hydrogen/deuterium has been adsorbed and/or absorbed into the metallic layer 212, the hydrogen/deuterium gas is evacuated from the deposition chamber 100 and an argon gas is re-introduced into the deposition chamber 100 (step 308). Afterwards, the sputtering process is turned on to deposit a second metallic layer 214 onto the substrate 118 (step 310).

**[023]** In the gas phase co-deposition process 300 shown in Figure 3, deposition of the metallic layers 210, 214 and that of the hydrogen/deuterium layer 212 onto the substrate 118 are performed sequentially. In some embodiments, deposition of the metallic material may be performed in the presence of a partial hydrogen gas pressure, as illustrated in the gas phase co-deposition process 400 in Figure 4.

**[024]** In the gas phase co-deposition process 400, a deuterium gas is introduced into the deposition chamber 100 to build a partial deuterium gas pressure (step 402). In the



presence of the partial deuterium gas pressure, a metallic material is deposited onto the substrate 118 to form a hydrogen loaded metallic structure (step 404). The metallic structure fabricated in the gas phase co-deposition process 400 comprises hydrogen/deuterium atoms/ions loaded within the metallic structure and a number of vacancies that are left in the metallic structure by escaped hydrogen/deuterium atoms/ions.

**[025]** Figure 5 illustrates an exemplary packaging process 500 of the substrate 118 created in the gas co-deposition process 300 or 400. The substrate 118 is transferred into a glove box filled with a hydrogen gas of a pressure greater than one atmospheric pressure (step 502). The substrate 118 is packaged in the presence of the pressurized hydrogen gas (step 504) so that the hydrogen/deuterium atoms/ions adsorbed or absorbed in the substrate 118 are retained.

**[026]** The present invention may be carried out in other specific ways than those herein set forth without departing from the scope and essential characteristics of the invention. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive, and all changes coming within the meaning and equivalency range of the appended claims are intended to be embraced therein.

**Claims**

1. A method of fabricating a hydrogen loaded metallic structure in a deposition chamber, wherein the deposition chamber comprises a substrate and the deposition chamber is evacuated to form a vacuum, said method comprising:  
  
    introducing a deuterium gas to the deposition chamber to build a partial gas pressure; and  
  
    depositing a metallic material onto the substrate in the presence of the partial gas pressure to form the hydrogen loaded metallic structure.
2. The method of claim 1, further comprising introducing a second gas into the deposition chamber.
3. The method of claim 2, wherein the second gas is fluorine.
4. The method of claim 2, wherein the second gas is chlorine.
5. The method of claim 2, wherein the metallic material is deposited on the substrate in the presence of both the deuterium gas and the second gas.
6. The method of claim 1, wherein the metallic material is deposited onto the substrate via a vapor deposition process.
7. The method of claim 6, wherein the vapor deposition process is a chemical vapor deposition process.

8. The method of claim 6, wherein the vapor deposition process is a physical vapor deposition process.
9. The method of claim 1, wherein the metallic material is deposited onto the substrate via an electrolysis process.
10. The method of claim 1, wherein the metallic material is deposited onto the substrate via an evaporation process.
11. The method of claim 8, wherein the metallic material is deposited onto the substrate via a sputtering process.
12. The method of claim 1, further comprising:
  - transferring the substrate into a glove box filled with a hydrogen gas of a pressure greater than an atmospheric pressure; and
  - packaging the substrate in the presence of the pressurized hydrogen gas.
13. A deposition chamber configured for fabricating a hydrogen loaded metallic structure, said deposition chamber comprising:
  - a substrate for on which the metallic structure is deposited;
  - a vacuum pump for evacuating the deposition chamber;

a gas valve for introducing one or more process gases into the deposition chamber, wherein the one or more process gasses comprise a hydrogen gas; and

a target configured to provide a metallic material to be deposited onto the substrate in a partial pressure of the one or more process gases.

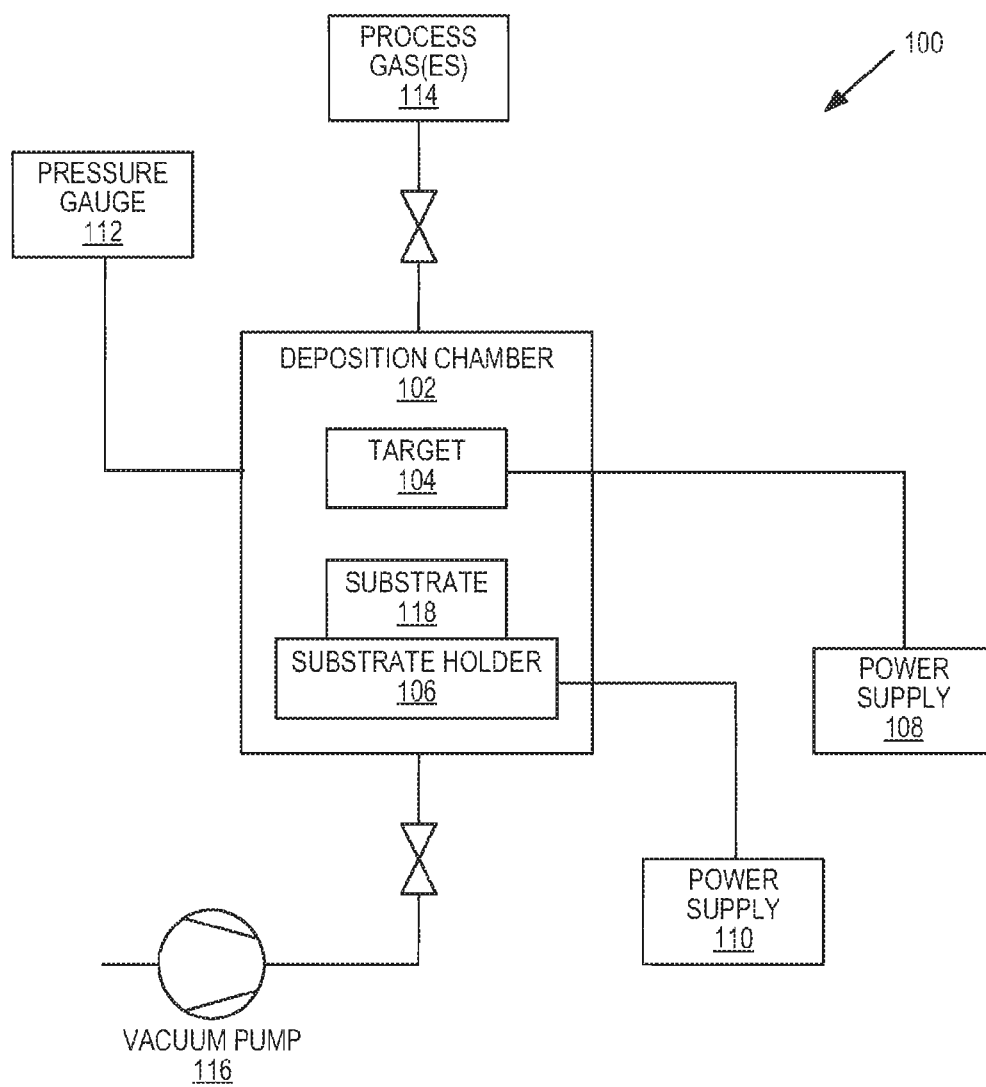
14. The deposition chamber of claim 13, wherein the one or more process gases comprises a second gas.
15. The deposition chamber of claim 14, wherein the second gas is fluorine.
16. The deposition chamber of claim 14, wherein the second gas is chlorine.
17. The deposition chamber of claim 13, wherein the metallic material is deposited onto the substrate via a physical vapor deposition (PVD) process.
18. The deposition chamber of claim 13, wherein the metallic material is deposited onto the substrate via a chemical vapor deposition (CVD) process, and wherein in the CVD process, the metallic material is introduced as molecules in a gas and deposited as a metal coating on the substrate.
19. The deposition chamber of claim 17, wherein the target device is a sputtering deposition device.

20. The deposition chamber of claim 13, further comprising one or more power supplies for providing a voltage bias between the substrate holder and the ground.
21. A method for fabricating a hydrogen loaded metallic structure in a deposition chamber, wherein the deposition chamber comprises a substrate holder and a target, the target comprising a metallic material, the method comprising:
- sputtering a metallic material onto the substrate;
  - suspending the sputtering process;
  - introducing one or more process gases into the deposition chamber, wherein one of the one or more process gases is hydrogen;
  - after a pre-determined time period, evacuating the deposition chamber and re-introducing an argon gas; and
  - resuming the sputtering process.
22. The method of claim 21, wherein the one or more process gases comprise a second gas.
23. The method of claim 22, wherein the second gas is fluorine.

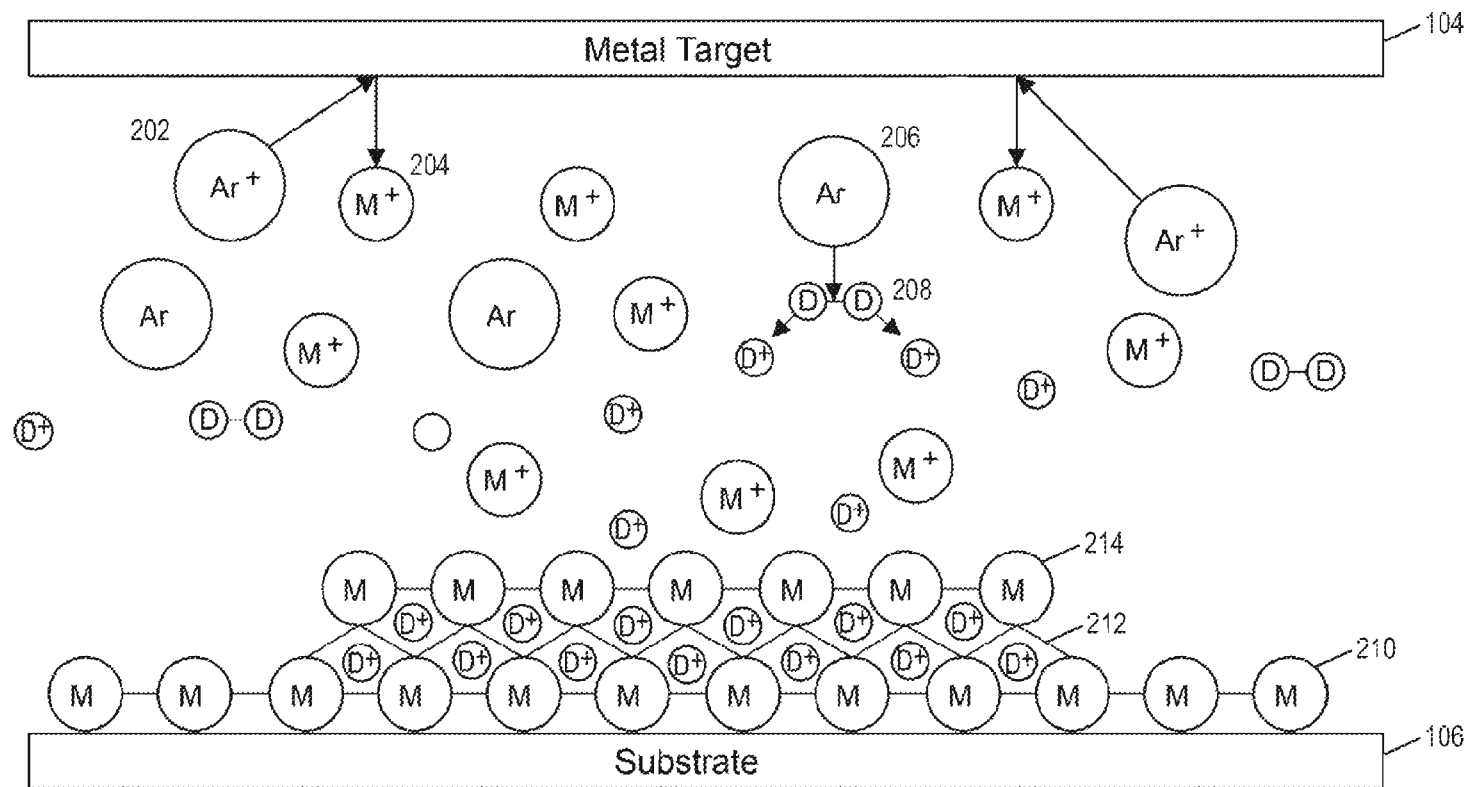
24. The method of claim 22, wherein the second gas is chlorine.
25. The method of claim 22, wherein during the pre-determined time period, a layer of hydrogen atoms is adsorbed on and absorbed into the metallic material sputtered onto the substrate and wherein the adsorbed and absorbed hydrogen atoms are of a desirable amount.
26. The method of claim 22, wherein the sputtering process is suspended after the metallic material sputtered onto the substrate is of a desirable thickness.
27. The method of claim 22, wherein the recited steps are performed cyclically.

**Abstract**

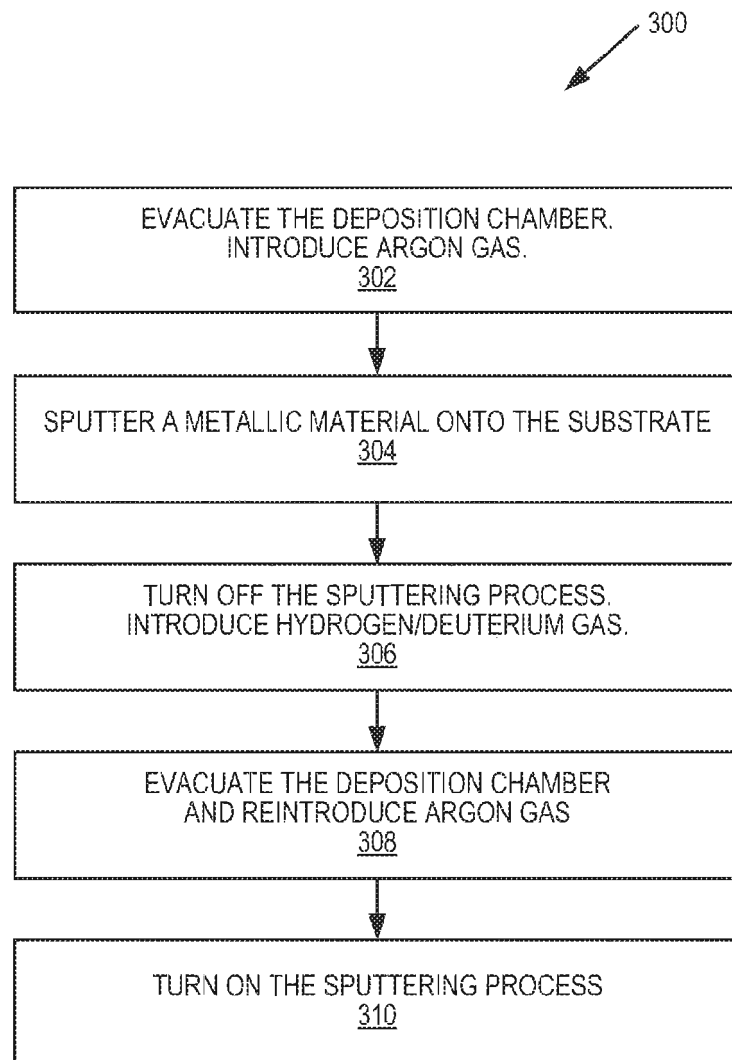
Methods and apparatus are disclosed for fabricating a hydrogen loaded metallic structure in the presence of a hydrogen/deuterium partial pressure. The present disclosure teaches that physical vapor deposition and chemical vapor deposition can be used for gas phase co-deposition to fabricate a hydrogen loaded metallic structure.

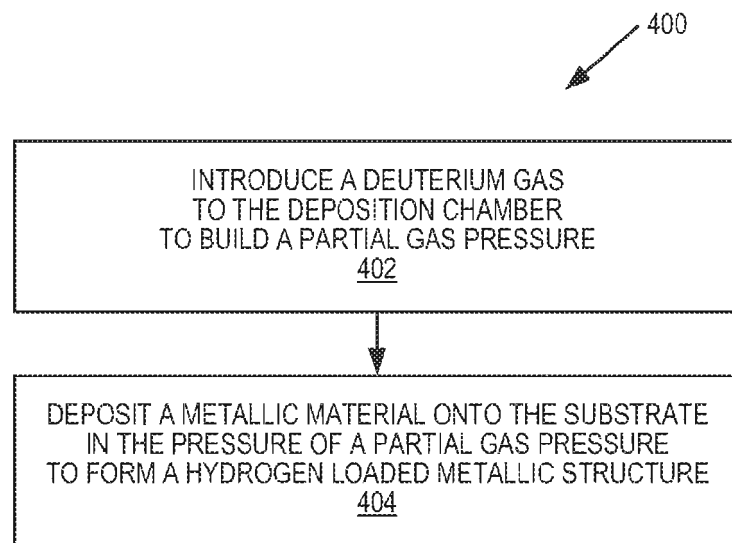
**FIG. 1**



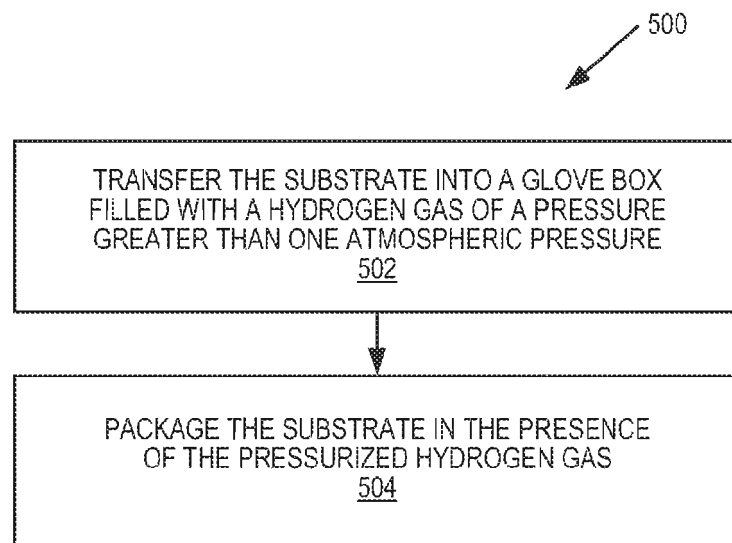


**FIG. 2**

**FIG. 3**



**FIG. 4**



**FIG. 5**