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Archives of Applied Science Research, 2016, 8 (5):1-8
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Physical Vapor Deposition (PVD) Methods for Synthesis of Thin Films: A Comparative Study

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ABSTRACT

In the present comparative study, the important physical vapor deposition methods of thin films viz., thermal evaporation, electron beam evaporation, molecular beam epitaxy evaporation, activated reactive evaporation, ion plating and pulsed laser deposition were studied. In this study we have discussed about deposition principle, working process of physical vapor deposition, their significance in the whole process of a making a substrate deposition or single wafer, advantages, disadvantages and various applications of these deposition methods. In order to optimize the desired film thickness and characteristics, good understanding of the deposition methods and process is necessary. These physical vapor depositions methods can be found in the fabrication and processing technology industries. They are mostly used for creating metalized substrates or wafers. They have their own unique way of depositing materials on the substrates or wafers and thus having their own advantages, disadvantages and limitations in their applications.

Key words: physical deposition, thin films, advantages, disadvantages, applications

INTRODUCTION

The thin solid films were probably first obtained by electrolysis in 1838. Bunsen and Grove obtained metal films in 1852 by means of chemical reaction. Faraday obtained metal films in 1857 by thermal evaporation of metallic elements. Thin films are two dimensional solids. In these solids the third dimension is negligibly smaller than the two dimensions. Thin films can be obtained from various deposition techniques. An improper selection of deposition technique causes varied and irreproducible results on the films. For this reasons the understanding of thin films has made tremendous advantages in past decade [1-3]. For the evaporation process the substance to be evaporated is heated in a dedicated container (ceramic crucible, Ta boat, W spiral wire) by the introduction of (electrical current, electron beam, laser, arc discharger) energy to a suitable temperature. The thermally released atoms or molecules leave the surface of the evaporated material and form a coating on the substrate. As the process is usually conducted under High Vacuum ($H, p < 10^{-5}$ mbar = 10^{-3} Pa) the coating particles basically move from the source to the substrates (without collisions with residual gas atoms) on straight trajectories [4, 5].

Evaporation sources can be categorized by the method of energy supply. One has also to consider that not each material can be evaporated from each source. Chemical reactions between crucible and evaporation material are possible which can lead to impurities in the film or to the destruction of the evaporation source. In addition the power density in different source types may vary strongly. Some electrically conductive elements which exhibit a vapor pressure $> 10^{-2}$ mbar below their melting point can be evaporated by sublimation. The evaporation material has the shape of wires or rods and is directly heated by a high electrical current. This method is not frequently employed since it is limited to only few (C, Cr, Fe, Mo, Ni, Pd, Rh, Ti, Al) materials. The principle of this frequently employed method is to put the evaporation material on or into a container, spiral wire, ribbon or crucible made from W or (Mo, Ta, C, Pt, BN, TiB₂) which is heated by a high electrical current and to evaporate it from there [6,7].

In inductive heating the evaporated material is heated by high or low frequency induction. The evaporated material has to be conductive. In electron evaporator, apart from a high power density which can be achieved there is also practically no reaction between the evaporation material and the crucible in these devices. The reason for this is that the evaporated material is kept in water cooled Cu crucible. Therefore highly reactive (Ta, Ti, Zr) materials and refractory (W, Mo, Pt, Rh) metals can be evaporated. Also dielectric substances can be deposited at high rates and high purity. Because of these properties electron beam evaporation has established itself as a universal method for the deposition of high quality coatings in large quantities [8].

Arc discharges (Hollow Cathode Arc, Low Voltage Arc, and Thermionic Arc) are extremely important for ion plating processes. In laser evaporator the continuous interaction of laser radiation with matter can lead to thermal evaporation. Pulsed laser beams, on the other hand, may release particles from the solid by alternative mechanisms because of their low pulse duration and high power density. Local plasmas and explosive evaporation play an important role. The use of pulsed lasers has gained considerable importance in the field of PVD methods starting in the 1990s. Solid coating materials can be used for evaporation in the form of elements, alloys, compounds and finely dispersed mixtures. They have to exhibit a defined grade of purity in respect to the demands on the process employed [9].

Amongst others, physical vapor deposition methods exhibit the following characteristics, the multitude of substrate materials which can be coated (metals, alloys, ceramics, glass, polymers) basically unlimited choice of coating (metals, alloys, semiconductors, metal oxides, carbides, nitrides, cermets, sulfides, selenides, tellurides) materials excellent coating adhesion, easy tuning of the microstructure by the choice of the coating parameters. There are the following disadvantages of physical vapor deposition methods: relatively low deposition rates and film thicknesses technologically demanding processes coating of geometrically complex parts is complicated. The main areas of application for physical vapor deposition processes are thin films used in optical, optoelectronic, magnetic and microelectronic devices. Other applications may be found in the areas of tribology, corrosion protection, thermal insulation, and decorative coatings amongst others [10, 11].

In the present comparative study, the important physical vapor deposition methods of thin films were studied. This study discusses about deposition principle, working principal, process of physical vapor deposition, their significant in the whole process of a making a substrate deposition or single wafer, advantages, disadvantages and limitations in their applications.

DISCUSSION

Classification of deposition methods of thin films

Broadly, the important methods of thin film deposition are classified as physical deposition and chemical deposition. Physical deposition method is again classified into thermal evaporation, electron beam evaporation, molecular beam epitaxy evaporation, activated reactive evaporation, ion plating and pulsed laser deposition. Chemical deposition method are further classified into chemical vapor deposition, solution growth, spray pyrolysis, electrodeposition, anodization and sputtering.

Classification of Physical deposition methods

1. Thermal evaporation method

This method is the one of the most well known physical deposition methods. This is simple method and one can evaporate a large variety of materials on various substrates. In this method, deposition material is created in a vapor form by heating bulk material in vacuum with resistive heater. The vapor atoms are transported through vacuum to get deposited on desired substrate. Almost all materials are vaporizing from a solid or liquid phase as neutral atoms or molecules. This vapour deposition is done only at pressure less than 5^{-10} torr. Due to this the mean free path between collisions becomes large enough so that the vapor beam arrives at substrate unscattered. A low vacuum has an effect that the gas molecules strike the substrate, which results in contamination of film that is being deposited. Fig. 1 shows the experimental set up of thermal evaporation [12].

The evaporation of the desired material is done in vacuum system, which consists of a diffusion pump backed by a rotary pump. The desired evaporant material is supplied by a continuous source which is then heated to a sufficiently high temperature to produce desired vapour pressure. As per the shape (wire, foil or ingot) of the evaporant material evaporation temperature varies from 1000 to 2000 °C. To obtain the uniform desired thickness, the substrate has to be rotated in such a way that each point on the substrate should receive almost the same amount of vapor material during the deposition [13]. In order to obtain the stoichiometric compound film by this method, the evaporation rates from the two sources should have carefully controlled.

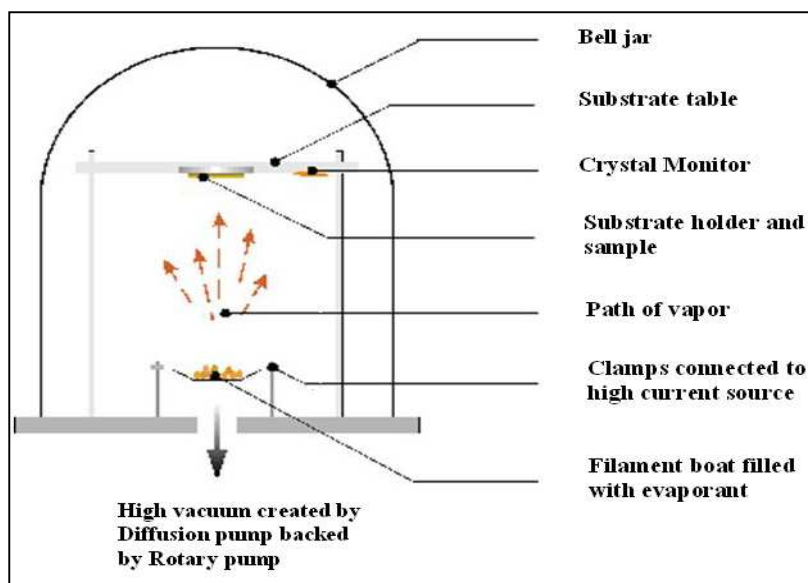


Fig. 1 shows the experimental set up of thermal evaporation

The advantages of this deposition method are it is simple and cheap with less substrate surface damage. Excellent purity and desired thickness of the films can be achieved. The disadvantages of this method are the deposited films have poor density and adhesion. It is limited to low melting point metals. Therefore, dielectric materials cannot be evaporated by this method.

2. Electron beam evaporation method

In this method, an electron gun is used for evaporation. It consists of a heated filament for electron emission. The filament is normally shielded to prevent any sputtering by vapor species and gaseous ions. An electron beam is accelerated through potential of 5 to 10 KV and focused on the material. The electrons lose their kinetic energy mostly as heat. The temperature of the evaporant material can be raised by electron bombardment instead of resistive heating. The temperature at the focused spot could be rise up to 3000 °C. At this high temperature, extremely high rates of evaporation achieved even for high melting point materials. Fig. 2 shows the experimental set up of electron beam evaporation method [14]. Electron guns are of two types. In both the types of electron guns, the path of the electron beam is straight line and electrostatic or electromagnetic focusing is used to focus the electron beam [15].

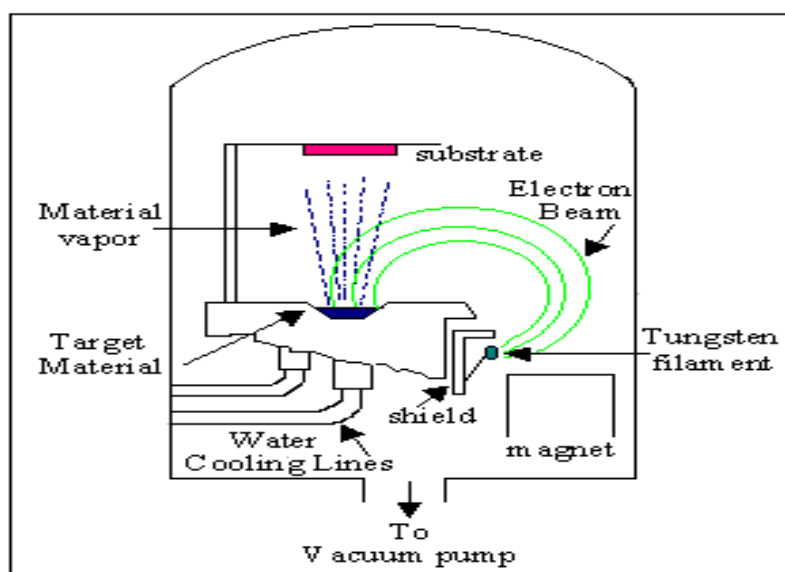


Fig. 2 shows the experimental set up of electron beam evaporation method

The advantages of this deposition method are the material utilization efficiency is high as compared to other deposition methods. This process offers structural and morphological control of films. Due to very high deposition

rate, electron beam evaporation method has potential applications in aerospace industries, hard coatings for cutting and tool industries, and semiconductor industries. The disadvantages of this method are the filament degradation in the electron gun results in non uniform evaporation rate and it cannot be used to coat the inner surface of complex geometries.

3. Molecular beam epitaxy (MBE) method

It is one of the several methods of depositing single crystals and invented in the late 1960s. The deposition of single crystal films by the condensation of one or more beams of atoms and molecules from Knudsen sources under ultra high voltage (UHV) condition is called molecular beam epitaxy. The term 'beam' means the evaporated atoms do not interact with each other or with other vacuum chamber gases until they reach the substrate or wafer. Epitaxial growth takes place due to the interaction of molecular or atomic beams on a surface of a heated crystalline substrate. Fig. 3 shows the experimental set up of molecular beam evaporation [16]. The Knudsen effusion source consists of a metallic chamber, containing the evaporant with a small orifice. The orifice dimension is smaller than the mean free path of the vapor in chamber. Flow of the molecules from source is by effusion. The effusion molecular beam has a large mean free path compared to source substrate distance. The flux of beam is precisely determined by the partial pressures of the vapor species within the chamber, their molecular weight, and source temperature and orifice dimension. The beam is directed on the substrate by orifice slits and shutters.

Molecular beam epitaxy takes place in high vacuum or ultra high vacuum (10^{-8} Pa). The most important aspect of MBE is the deposition rate less than 3000 nm per hour that allows the films to grow epitaxially. These deposition rates require proportionally better vacuum to achieve the same impurity levels as other deposition techniques. The absence of carrier gases as well as the ultra high vacuum environment results in the highest achievable purity of the grown films. During operation, reflection high energy electron diffraction (RHEED) is often used for monitoring the growth of the crystal layers. A computer controls shutters in front of each furnace, allowing precise control of the thickness of each layer, down to a single layer of atoms. Intricate structures of layers of different materials may be fabricated this way. Such control has allowed the development of structures where the electrons can be confined in space, giving quantum wells or even quantum dots. Such layers are now a critical part of many modern semiconductor devices, including semiconductor lasers and LEDs.

In systems where the substrate needs to be cooled, the ultra high vacuum environment within the growth chamber is maintained by a system of cryopumps, and cryopanel, chilled using liquid nitrogen or cold nitrogen gas to a temperature close to 77 Kelvin. Molecular beam epitaxy is also used for the deposition of some types of organic semiconductors. In this case, molecules, rather than atoms, are evaporated and deposited onto the substrate or wafer. Other variations include gas source MBE, which resembles CVD. MBE has many key characteristics which make it an industry and research standard thin film growth system [17]. There are three types of MBE such as Solid Source MBE (SS-MBE), Plasma Assisted MBE (PA-MBE) and Reactive MBE (R-MBE).

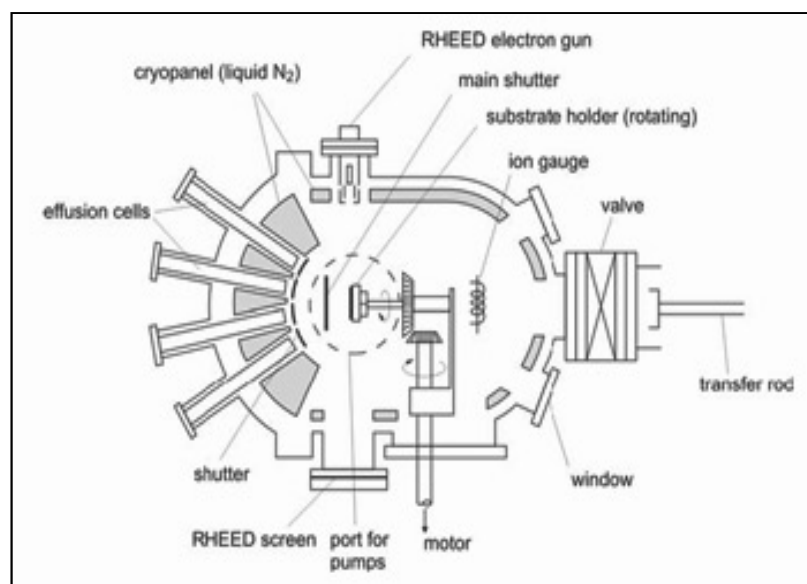


Fig. 3 shows the experimental set up of molecular beam evaporation

MBE is a very versatile technique, allowing a wide variety of semiconductor alloys to be grown, under non equilibrium conditions, through the combined evaporation of its constituent elemental sources. Abrupt doping

profiles (δ doping) can be synthesized. The slow growth rates provide for great control over the epitaxial layer thickness. Therefore, it is widely used in the manufacture of semiconductor devices, including transistors for cellular phones and Wi-Fi. MBE has excellent thickness uniformity, minimal foreign contamination as a result of the UHF conditions, yielding high purity crystals, real time in situ characterization during growth and high quality multiwafer growth for high volume production. MBE is less hazardous as it does not employ any dangerous chemical precursors. Disadvantages of Molecular beam epitaxy are substrate rotation is required for uniformity in thickness and conformity. MBE has individual effusion cells for each element. Large effusion cells and efficient heat dissipation make multiwafer scale up more difficult.

4. Activated reactive evaporation (ARE) method

The evaporation of a metal occurs in the presence of a reactive gas and plasma to deposit compounds with increased adhesion and increased deposition rates. The deposition technique has been mainly used to deposit highly adherent films of oxides and carbides. Fig. 4 shows the experimental set up of activated reactive evaporation [18]. In this evaporation process, metal is heated and melted by a high acceleration voltage e-beam. Metal has a thin plasma sheath on top of it. Low energy secondary electrons from the plasma sheath are pulled into the reactive zone by an interspaced electrode placed above the pool. The electrode is biased to allow positive dc or ac potential (20 to 100 V). Low energy electrons have a high ionization cross section, thus ionizing or activating the metals and gas atoms.

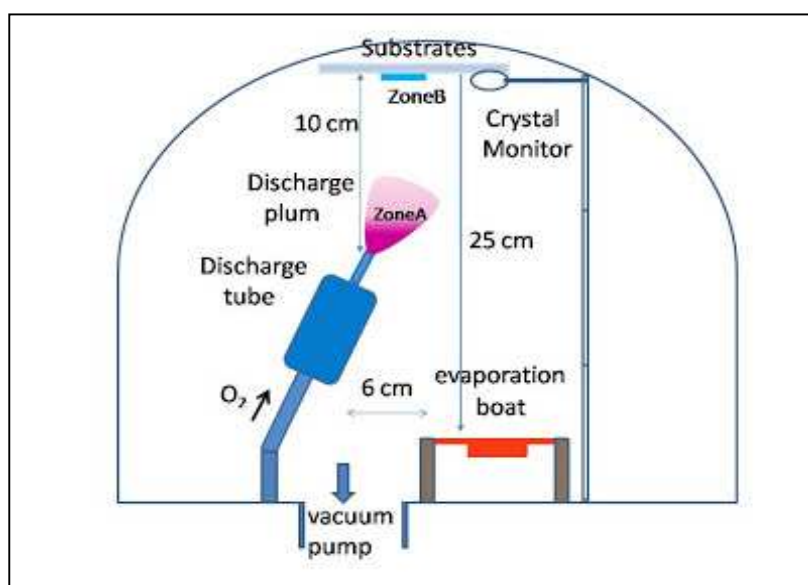


Fig. 4 shows the experimental set up of activated reactive evaporation

In addition, collisions between ions and neutral atoms result in charge exchange processes yielding energetic neutrals and positive ions. It is believed that these energetic neutral atoms activate the reaction, thus increasing the reaction between the reactants. Plasma enhances the reaction between the reactants, cause ionization of both the coating metal and gas atoms in the vapor phase. It is generated by when using e-beam as evaporation source, an interspaced positively biased electrode. When using resistance heated source, low energy electrons injected to the vapor phase from a thermionically heated filament [19]. Activated reactive evaporation technique is divided in two main types.

Biased ARE

The substrate is biased normally negative to attract the positive ions and positively biased electrode between source and substrate is used to create the plasma.

Enhanced ARE

The plasma in ARE is enhanced by accelerating electrons emitted from tungsten filament under electric field perpendicular to the vapor beam. The ionization can be further enhanced using a magnetic field. This has the advantages that deposition can be done at a lower pressure.

Advantages of ARE technique are extremely high deposition rates, variety of coating compositions, precise control of stoichiometry, better adhesion and denser microstructure than direct evaporation. Disadvantages of ARE are high substrate temperature, addition of an extra electrode, slightly complicated compared to evaporation, and substrate must generally be rotated for uniform coating [20].

5. Ion plating method

Ion plating is a PVD process that uses electron beam evaporation. The material used in this type of coating is ionized and vaporized through the aid of an electric arc and then forced toward the target at high speed. This process is commonly performed within a vacuum chamber or an inert gas setting. It is also known as physical vapor deposition. Fig. 5 shows the experimental set up of ion plating [21].

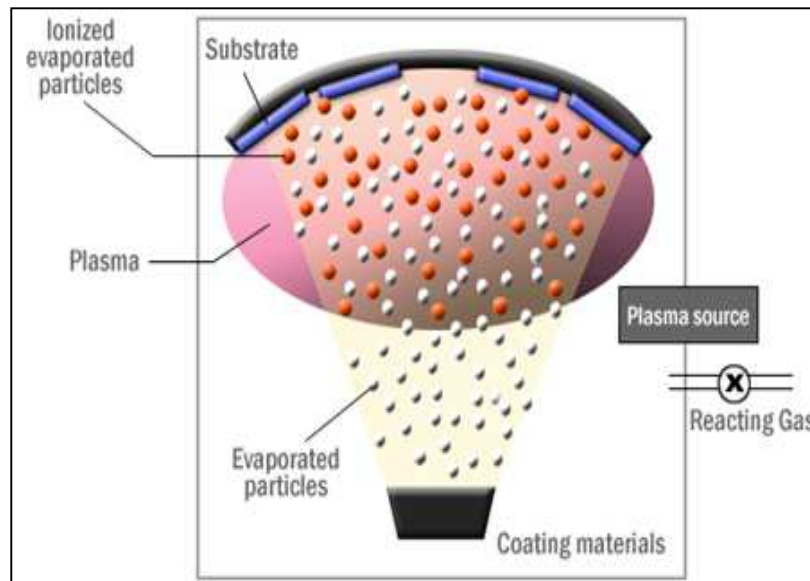


Fig. 5 shows the experimental set up of ion plating

Materials that are to be subjected to ion plating are usually treated prior to plating in order to thoroughly clean them and eliminate foreign materials. This is also performed in the environment where plating is to be accomplished, a process called sputtering. Plating and sputtering can be two identical processes, but with the former, the target is typically bombarded with other materials ions, like argon gas, that can strip off all foreign particles rather than promoting a bond. When the target is prepared and treated for coating application, the process of ion plating commences. The coating material undergoes vaporization with the help of electric arc current that makes use of the high flow of current and low voltage. This is done in order to ionize all atoms that repel each other because of similar electric charges, as well as to vaporize the material used for coating. The vapor produced is propelled onto the target and delivered in opposite weak electrical charge to be a magnet for the ionized coating. This process makes ion vaporization possible and in turn results in the adhesion of coating to the surface [22, 23].

Ion plating application techniques can be altered in several ways. One way is the introduction of other types of vaporized ions and various gases within the closed setting. It is also possible to mix vaporized ions of one material with another in order to form different compounds that adhere to the surface target. Combining different materials also allows a broad variety of coatings. Coatings applied through ion plating are usually even and ultra thin, making them ideal for materials with uneven or irregular shapes. Most importantly, coatings applied by ion plating possess impressive hardness, high durability and corrosion resistance capabilities.

6. Pulsed laser deposition (PLD) method

Pulsed laser deposition is a physical vapor deposition technique. In PLD, a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited. This material is vaporized from the target which deposits it as a thin film on a substrate. This process can occur in ultra high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films. Fig. 6 shows the experimental set up of pulsed laser deposition [24]. While the basic setup is simple relative to many other deposition techniques, the physical phenomena of laser target interaction and film growth are quite complex. When the laser pulse is absorbed by the target energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy resulting in evaporation, ablation, plasma formation and even exfoliation. The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, before depositing on the typically hot substrate [25, 26].

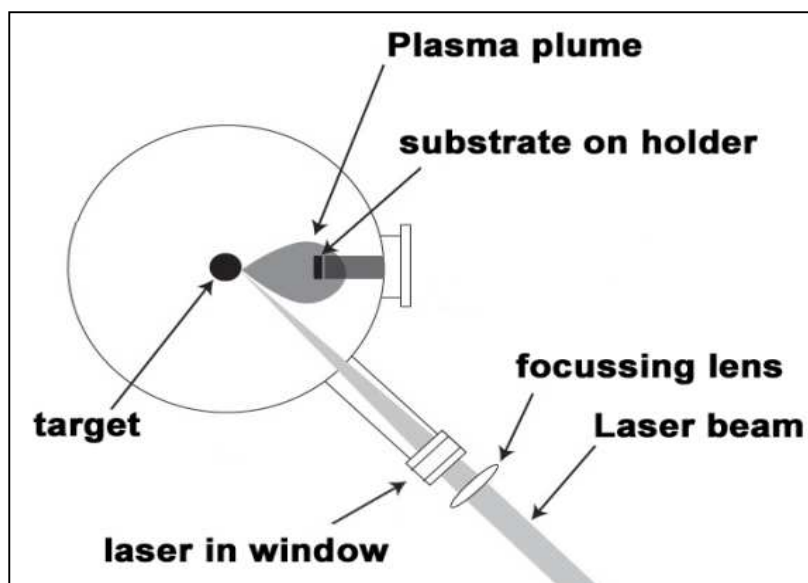


Fig. 6 shows the experimental set up of pulsed laser deposition

In pulsed laser deposition, the solid is irradiated by high power laser pulses in a background pressure of few Torr to 10^{-6} Torr. Due to absorption of the laser power, surface layers of the solid can vaporize and is collected on the substrate to form a thin film. Except laser wavelength transparent material this method is useful for deposition of various composite materials.

CONCLUSION

In order to optimize the desired film thickness and characteristics, good understanding of the various deposition methods and processes is necessary. The important physical vapor deposition methods of thin film deposition are thermal evaporation, electron beam evaporation, molecular beam epitaxy evaporation, activated reactive evaporation, ion plating and pulsed laser deposition. In this study, the process of physical vapor deposition methods and their significance in the whole process of making a substrate deposition or single wafer are understood. They are mostly used for creating metalized substrates or wafers. These physical vapor deposition methods can be found in the fabrication and processing technology industries. They have their own unique way of depositing materials on the substrates or wafers and thus having their own advantages, disadvantages and limitations in their applications.

REFERENCES

- [1] K.S.S Harsha, Principles of Physical Vapor Deposition of Thin Films, Elsevier, Great Britain, 2006, pp.400.
- [2] J. George, Preparation of thin films, Marcel Dekker, Inc., New York, 1992.
- [3] Kasturi Chopra, Thin Film Phenomena, McGraw Hill Book Company, New York, 1969.
- [4] Glocker, I. Shah, Handbook of Thin Film Process Technology, Institute of Physics, 2002, Vol.1&2.
- [5] Mattox, M. Donald, The Foundations of Vacuum Coating Technology, Noyes Publications, 2003.
- [6] Mahan, E. John, Physical Vapor Deposition of Thin Films, John Wiley & Sons, 2000.
- [7] K. L. Chopra & S. R. Destin, Film Solar Cells, Plenum Press, New York, 1983.
- [8] K.L. Chopra, L. K. Malhotra, Thin film Technology and Applications (Proceeding), THM, New Delhi, 1984.
- [9] A. B. Bhalerao, R. V. Zavare, B. G. Wagh, C. D. Lokhande, Everyman's Science, 2015, Vol. XLIX No. 6, Feb 15 – Mar 15 pp. 368-376.
- [10] W.L. Winterbottom and J.P. Hirth, J. Chem. Phys., 1962, vol. 37, no. 4, pp. 784-793.
- [11] G. Biasiol and L. Sorba1, Molecular Beam Epitaxy: Principles and Applications, Eds., Edizioni ETS, Pisa, 2001, pp. 66-83.
- [12]https://www.google.co.in/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAYQjB1qFQoTCJaWj4_d88gCFcqaAodqlkBoA&url=http%3A%2F%2Fwww.betelco.com%2Fsb%2Fphd%2Fch3%2Fc34.html&psig=AFQjCNFMmy18h4bugdqr2IZ4eNga3d_BUG&ust=1446622019799269
- [13] Roitan F. Bunshah, Handbook of Deposition Technologies for Films and Coatings: Science, Technology and Applications, second edition, Noyes, Park Ridge, NJ, 1994.
- [14]https://www.google.co.in/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAYQjB1qFQoTCOCg_6_d88gCFUGY1AodzCsOoQ&url=http%3A%2F%2Fwww.optics.rochester.edu%2Fworkgroups%2Fcm1%2Fopt307%2Fspr13%2Fgreg%2F&bvm=bv.106379543,d.dGo&psig=AFQjCNEt3M5Hi26aPR89IPpa4XPOtQjhQ&ust=1446622073794433

- [15] K. Robbie, and M. J. Brett, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, **1997**, 15.3, pp. 1460-1465.
- [16]https://www.google.co.in/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAYQjB1qFQoTCO52unc88gCFYKPIAodhwEJnw&url=http%3A%2F%2Fwww.eee.manchester.ac.uk%2Four-research%2Fresearchroups%2Fsisp%2Fresearchareas%2Femds%2Fmolecular-beam-epitaxy%2F&psig=AFQjCNFb_3XMWZOCA4jQfcfOk13w9O01-A&ust=1446621940979154
- [17] Aeger, C. Richard, *Film Deposition, Introduction to Microelectronic Fabrication* (2nd Ed.). *Upper Saddle River: Prentice Hall*, **2002**.
- [18]https://www.google.co.in/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAYQjB1qFQoTCOixvOLd88gCFUE9IAodx5YInw&url=http%3A%2F%2Fnanoflowers.blogspot.com%2F2009_09_01_archive.html&bvm=bv.106379543,d.dGo&psig=AFQjCNGP3rk1WSVeE9Rv5EQAIH6Jd2vgg&ust=1446622189891662
- [19]<http://engineering.dartmouth.edu/microeng/courses/es194/student/jiaying/sem/II.1.p3.html>
- [20] Smith Donald, *Thin Film Deposition: Principles and Practice*, *Mc Graw Hill, New York*, **1995**.
- [21]https://www.google.co.in/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&cad=rja&uact=8&ved=0CAYQjB1qFQoTCO52unc88gCFYKPIAodhwEJnw&url=http%3A%2F%2Fwww.eee.manchester.ac.uk%2Four-research%2Fresearchroups%2Fsisp%2Fresearch-areas%2Femds%2Fmolecular-beamepitaxy%2F&psig=AFQjCNFb_3XMWZOCA4jQfcfOk13w9O01-A&ust=1446621940979154
- [22] Anders, Andre, *Handbook of Plasma Immersion Ion Implantation and Deposition*, *Wiley-Inter science*, **2000**.
- [23] Willey, R. Ronald, *Practical Equipment, Materials, and Processes for Optical Thin Films*, *Willey Optical, Consultants*, **2007**.
- [24]http://www.google.co.in/imgres?imgurl=https://upload.wikimedia.org/wikipedia/commons/thumb/7/77/Configuration_PLD.png/220pxConfiguration_PLD.png&imgrefurl=https://en.wikipedia.org/wiki/Pulsed_laser_deposition&h=173&w=220&tbnid=G9ILPd3wEbudrM:&docid=f-YhKrm
- [25] S.M. Metev and V.P. Veiko, *Laser Assisted Microtechnology*, *Springer, Berlin, Heidelberg*, **1994**.
- [26] D.B. Chrisey and G.K. Hubler, *Pulsed Laser Deposition of Thin Film*, *John Wiley & Sons, Inc., New York*, **1994**.