THIN FILM FORMATION TECHNIQUES

1. Introduction

The deposited thin film is a few micrometers thick layer formed on a surface. Usually, the chemical signature of the substrate cannot be detected on the film, but the substrate can greatly change film properties like microstructure, adhesion, and crystallinity. The deposited surface layer greatly differs from surface conversion where a surface is converted to another material, eg, anodization of aluminum or carburizing of steel. In many cases, the thin film is formed by adding atoms or molecules to the substrate surface one at a time. Thicker layers are referred to as coatings. Although coatings can be formed by the same processes that are used for thin films, there are some coating processes that are not applicable for thin-film formation. An example of this would be thermal spray processes that melt small particles, accelerate to high velocity, and splat cool them on surfaces to form a coating.

2. Physical Vapor Deposition

Physical vapor deposition (PVD) is a process of film deposition in which atoms or molecules of a material are vaporized from a solid or liquid source and transported to the substrate though a low pressure environment. These vapors then condense onto the substrate to form the film. The PVD processes are by far the largest volume techniques for forming thin films. The use of vacuum and the control of the gaseous environment make it a very clean technique. It also provides a long mean-free path for collision for the vaporized material as it passes from the source to the substrate. The PVD processes can be used to deposit films of elemental, alloy, or compound materials. The films of these materials can be amorphous, fine or coarse grained, crystalline or even single crystal, depending on the deposition conditions. Typically, the growth rate of the film in a PVD process is $\sim$1–10 nm/s. It could be much higher for low vapor pressure materials, eg, Zn or Cd. Oxides and other simple compound thin films can be made by introducing O_2 or other gases in the system. In that case, the vaporized flux reacts with ambient gaseous environment to form an oxide or a compound film. Deposition with reaction is often referred as reactive deposition. Reactive deposition is successfully used in making thin films of a wide variety of materials, eg, TiN, TiO_2, and WC (1,2).

Figure 1 shows the components of a typical PVD system. The system consists of a main processing chamber, vacuum pumping system, an exhaust system, and gas handling system, if gases are to be used. The processing chamber contains the fixture to hold the substrates. In many cases, the substrate holder comes with the option of heating, cooling, or biasing (with either a positive or negative potential) the substrates. The entire process and the cycle time must be designed to provide a reproducible processing environment for the intended application. Among the several types of deposition chambers (Fig. 2) the batch system is the most common, however, the requirement that the system be

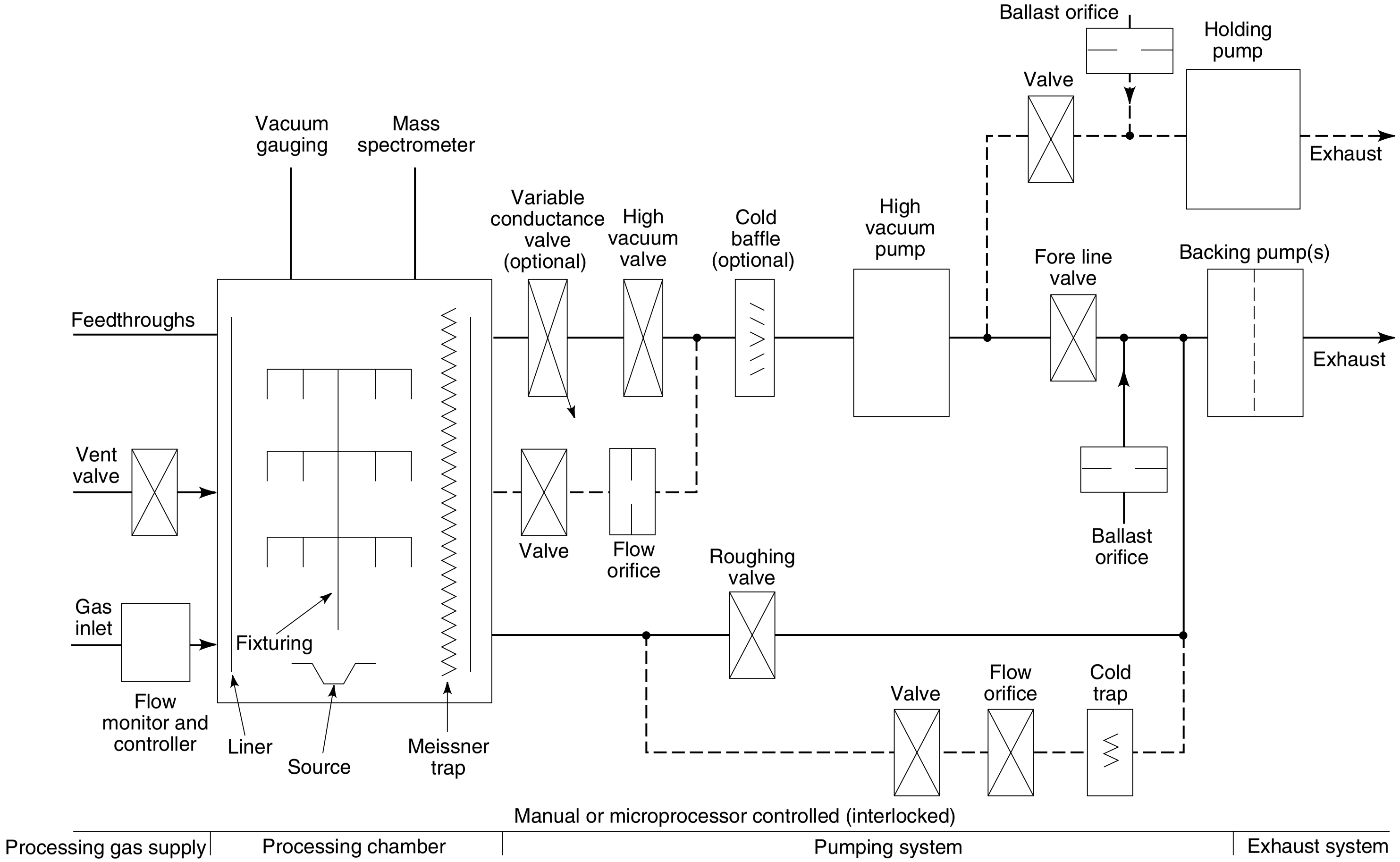

Fig. 1. Vacuum deposition system having a plasma processing capability, where the dashed lines represent optional additions to a system.

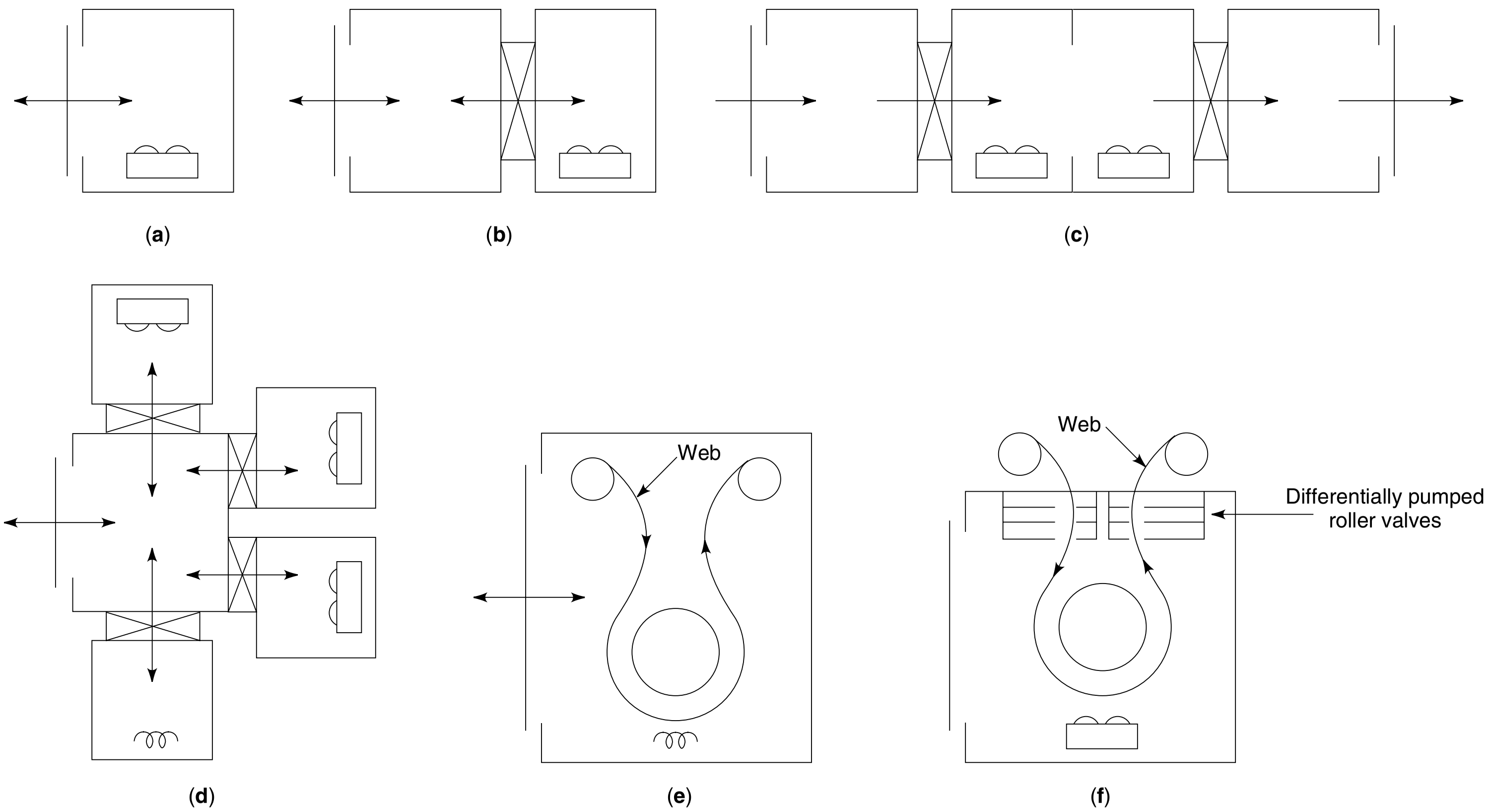

Fig. 2. Vacuum processing chamber configuration: (**a**) batch coater; (**b**) load-lock coater; (**c**) in-line coater; (**d**) cluster tool; (**e**) roll coater (batch); and (**f**) roll coater (air-to-air). [ccsq] represents the isolation valve with transfer tooling; [art1], the motion of fixturing; and [art2], the access door.

returned to same ambient conditions on each cycle can be an issue in such a system. To avoid this issue, a load-lock system can be used. The load lock, together with an in-line system, allows the main processing chamber to be kept under vacuum at all times and the substrates are introduced and removed through the load lock. A cluster-tool chamber allows random access to the processing chambers from the load-lock chamber. This is most widely used in semiconductor industries. A roll or web coating system is a specialized system for metallization of flexible polymer films for packaging and thermal control application. Although the load-lock system offers the best reproducible conditions, its main drawback is that it requires a long-lived vaporization source or a source, which can itself be renewed through the load lock since the main process chamber cannot be opened often.

2.1. Vacuum Evaporation.

Vacuum evaporation is a PVD process in which the material is thermally evaporated from the source and reaches the substrate either without collision or by reacting with the ambient gas environment (3). The trajectory of the vaporized flux is therefore line of sight. The usual pressure of operation is between 10^{-3} and 10^{-9} torr, depending on the level of contamination that can be tolerated in the resulting film. Figure 3 shows a typical vapor deposition chamber using a resistively heated filament vaporization source. The substrate fixture is an important component of any PVD system. The fixture allows the substrates to be held in a desirable orientation, provides a means for heating or cooling the substrates, and allows movement during deposition for obtaining a uniform film over the substrates. There is also a mechanical shutter near the source. This shutter blocks the volatile contaminants that might otherwise evaporate initially and contaminate the substrates. It also acts as a shield minimizing the radiant heat loss from the vaporization source. The shutter gives control over deposition time, and hence the thickness of the film. The glow bar allows the formation of plasma in the system for *in situ* cleaning of the substrates surface in the deposition chamber. The deposition rate can also be monitored *in situ* and also in real time by collecting the vapors over a quartz crystal oscillator. The deposition changes the frequency of oscillation. By calibrating, it is possible to relate this change in frequency to the thickness of the material deposited. In many cases, the amount of material deposited is controlled by evaporation-to-completion of a specific amount of material. In some cases, a physical property of films, eg, optical transmittance, is monitored during deposition and it used to control the film thickness. The residual gas can also be monitored in the system by using a Quadra-pole mass spectrometer.

The vapor pressure of the material is an important property to be considered. In a closed container at equilibrium, the number of atoms returning to surface is the same as those leaving the surface so the pressure above the surface is the equilibrium vapor pressure. Figure 4 shows the equilibrium vapor pressure of materials at different temperatures. Usually, resistive evaporation only works for materials with low vapor pressure. For materials with very high vapor pressure, eg, refractory materials, a focused high energy electron beam provides the heating that is necessary for vaporization (Fig. 5).

The vaporization rate from a hot surface into vacuum (free surface vaporization) depends on the temperature and the equilibrium vapor pressure

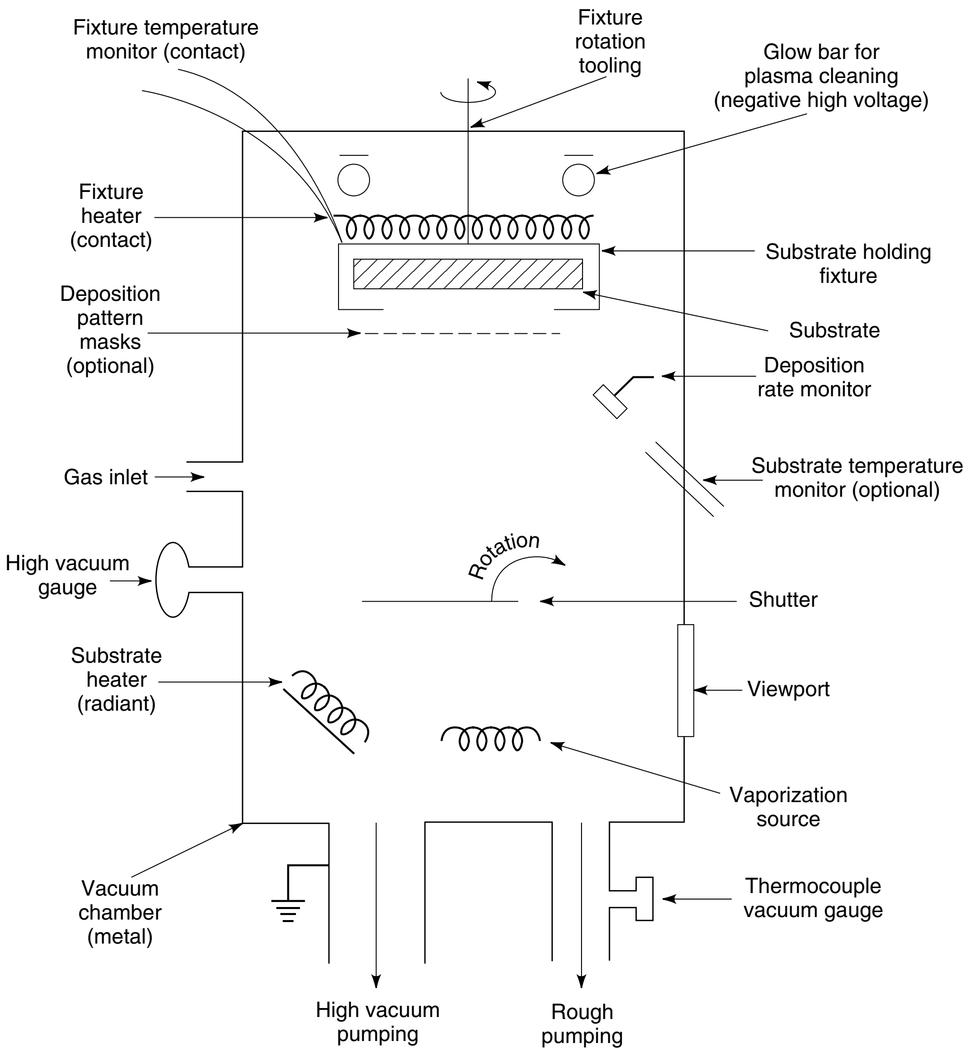

Fig. 3. Principal components of a vacuum deposition chamber.

of the material at that temperature (Fig. 4). For thermal evaporation, a reasonable evaporation can be obtained only if the free surface evaporation is fairly high. Materials having vapor pressures above the solid are described as subliming materials (examples are Cr and C), materials having vapor pressures above the liquid are described as evaporating materials. Many materials, eg, Ti, can be deposited by either sublimation or evaporation, depending on the temperature of the source. For some materials, eg, Al or Sn, the temperatures of the molten material must be significantly higher in order to have a high vaporization rate. For alloys, the thermal vaporization rate of each constituent is proportional to the relative vapor pressures (Raoult's law). Therefore, during vaporization the higher vapor pressure

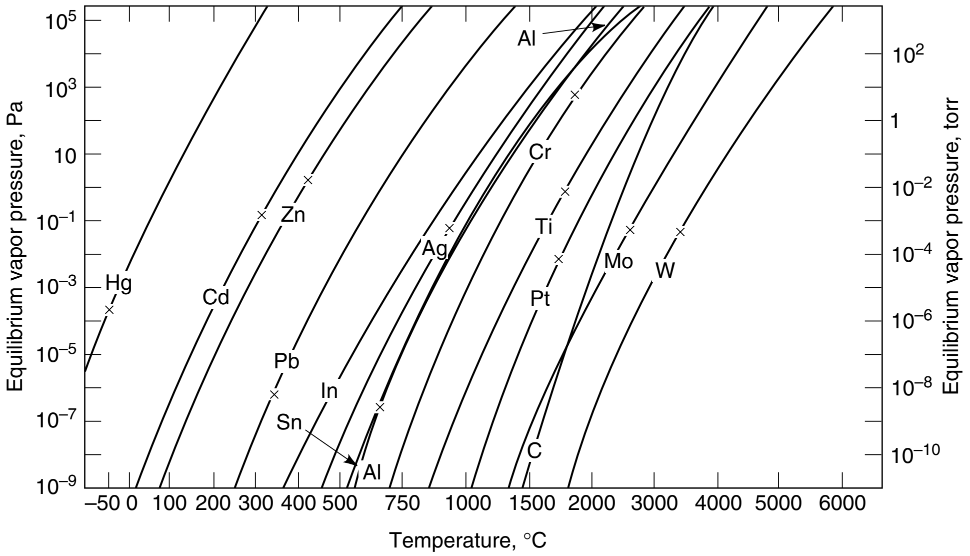

Fig. 4. Equilibrium vapor pressure of materials, where × indicates the melting point of the metal. The melting points for In and Sn are off the graph at 156 and 232°C, respectively. There is no melting point for C.

material vaporizes more rapidly and the vaporization source becomes progressively enriched in the lower vapor pressure material as time progresses. Although most materials thermally evaporate as atoms, some materials, eg, Sb, C and Se, have a portion of their vapor as clusters of atoms. For these materials, a special vaporization source called a baffle source can be used to ensure that the vapor is in the form of atoms. In a baffle source, the material is vaporized from multiple hot surfaces before it leaves the source.

Some compounds sublime as molecules, however, the molecules of many compounds partially dissociate on vaporization. Examples of materials that vaporize without dissociation are silicon monoxide (SiO) and magnesium fluoride (MgF_2). These materials are specifically used for optical coating as high (SiO has $n_d = 2$) or low (MgF_2 has $n_d = 1.38$) index of refraction materials. Most compounds, however, show some amount of dissociation. For example, in the evaporation of SiO_2, the resulting film is oxygen deficient leading to the formation of SiO_{2-x}. Using a reactive gas environment can compensate the loss of gaseous constituents. However, extra care has to be taken when using a reactive environment as in most cases the gas might react with the heating element itself.

Materials vaporized from a small area leave the surface with a cosine distribution with thermal energies of a few tenths of an electron volt (eV). The vaporized material arrives at the substrate having a mass per unit area given by:

$$\frac{dm}{dA} = M\left(\frac{1}{r^2}\right)\cos\phi\cos\theta \qquad (1)$$

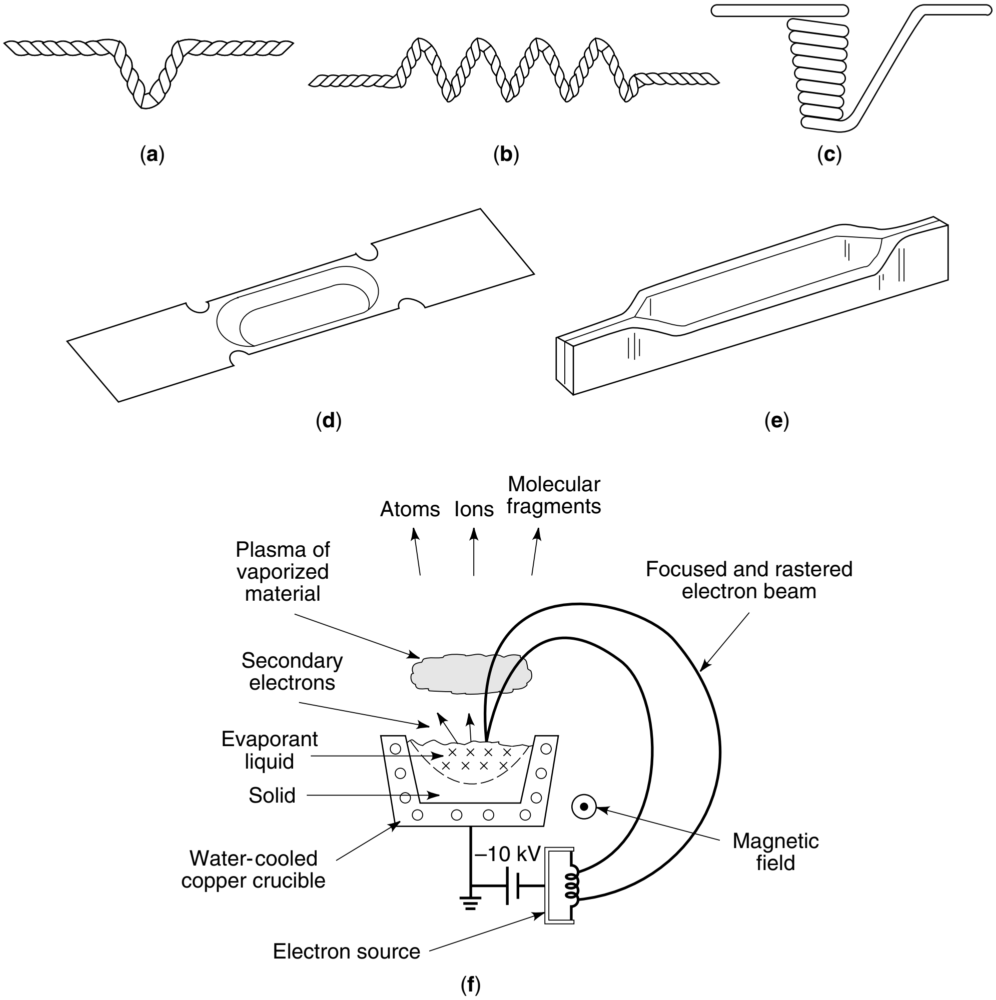

Fig. 5. Thermal vaporization sources: (**a**) hairpin; (**b**) spiral; (**c**) basket; (**d**) boat; and (**e**) canoe, which are all resistively heated sources; and (**f**) focused electron-beam evaporation from a high energy electron-emitting source.

where M is the mass vaporized, r is the source to substrate distance, and the angles ϕ and θ are shown in Figure **6a**. This flux distribution can be changed and may not be cosine dependant. Many factors, eg, source geometry and collisions in the vapor can change the distributions. The strong spatial dependence of deposition rate makes it important for the fixture, which holds the substrate, to randomize the substrate position. This ensures a greater uniformity in both thickness and in certain case the composition of the films. Changing the angle of incidence between the evaporated vapor and the substrate is also used in certain specific applications.

There are several advantages to using vacuum evaporation, the most notable are (*1*) high purity films can be formed from high purity source materials,

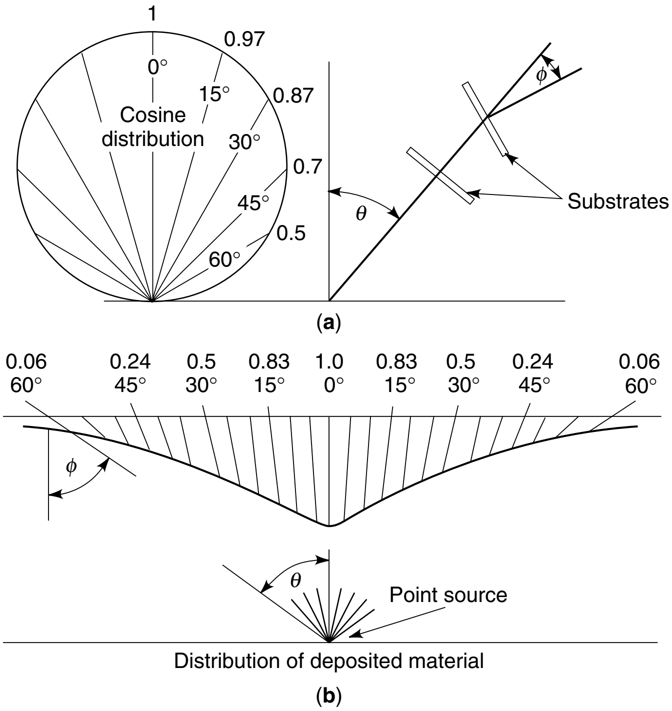

Fig. 6. Cosine distribution of vaporized material from a point source: (**a**) distribution of deposited material from a point source, and (**b**) distribution of film thickness on a planar surface above a point source. All thickness values normalized to 1.

(*2*) vacuum premelting with the shutter closed can remove volatile contaminants, (*3*) the source material can be a solid of any shape, (*4*) very high deposition rates can be obtained. Moreover, it is also the least expensive of the PVD process. The main disadvantages would include (*1*) alloys and compounds cannot be easily deposited; (*2*) since the source geometry changes during deposition, the deposition rate also changes; (*3*) poor surface coverage without proper fixture and fixture movement; (*4*) for vaporizing large amount of material, material must be added during deposition run; and (*5*) few process variables are available for film property control. Also, the source material utilization is the poorest among all of the PVD processes.

Vacuum evaporation is mainly used for optical coatings, reflective coatings, permeation barrier films on flexible packaging materials and electrically conductive films. A much more sophisticated vacuum deposition technique called molecular beam epitaxy (MBE) is used in semiconductor industry to form epitaxial films.

2.2. Sputter Deposition.

Sputter deposition, often referred to as sputtering, is the deposition of atoms vaporized from a target by physical sputtering (4,5). Physical sputtering is a nonthermal vaporization process where atoms are physically ejected by momentum transfer. This momentum is transferred from atomic sized energetic particles that are usually in the form of a gaseous ion

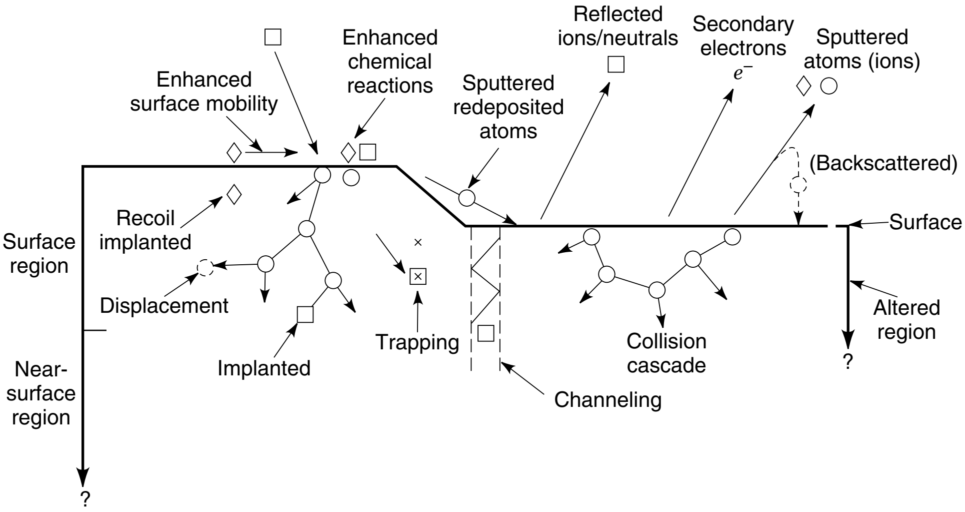

Fig. 7. Bombardment processes at the surface and in the near-surface region of a sputtering target, where □ represents the energetic particle used for bombarding the surface; ◇, an adsorbed surface species; ○, atoms; and ×, lattice defects.

accelerated from plasma or an ion gun. The most common gas used for sputtering is Ar. During the collision the energy is transferred from the incident particle (with energy E_i) to the target particle (with energy E_t) and is given by:

$$\frac{E_t}{E_i} = \left[\frac{4M_iM_t}{(M_i + M_t)^2}\right]\cos^2\theta \tag{2}$$

where M_i is the mass of incident energetic particle; M_t is the mass of the target atom, and θ is the angle of impact. The target atom that is struck can strike other atoms in the near surface region thus resulting in a collision cascade. If sufficient energy is transferred, the target atom can be ejected from the surface or sputtered. Figure 7 shows the cascade process occurring near the surface of the target. Most of the energy from bombarding the target ends up heating the target, not sputtering it. Some of the energetic particles also get reflected off the target surface. The flux of atoms that get sputtered off the target leave the surface and can reach the substrate to form a film. The sputtered atoms have kinetic energies higher than thermally vaporized atoms. Sputtering yield, which is the number of surface atoms that are sputtered for each incident energetic bombarding particle depends on the particle energy, the relative mass of both bombarding the particles and the target species, the incident angle of the bombarding species and the chemical bonding of the surface atoms. Figure 8 shows the sputtering yields of several materials sputtered with Ar ions at various energies. Since each surface atomic layer is removed consecutively in a sputtering process, the vapor flux leaving the target has the same composition as that of the bulk of the material being sputtered. This allows sputtering of alloys that could not be successfully thermally evaporated because of the differing vapor pressure of the alloy constituents.

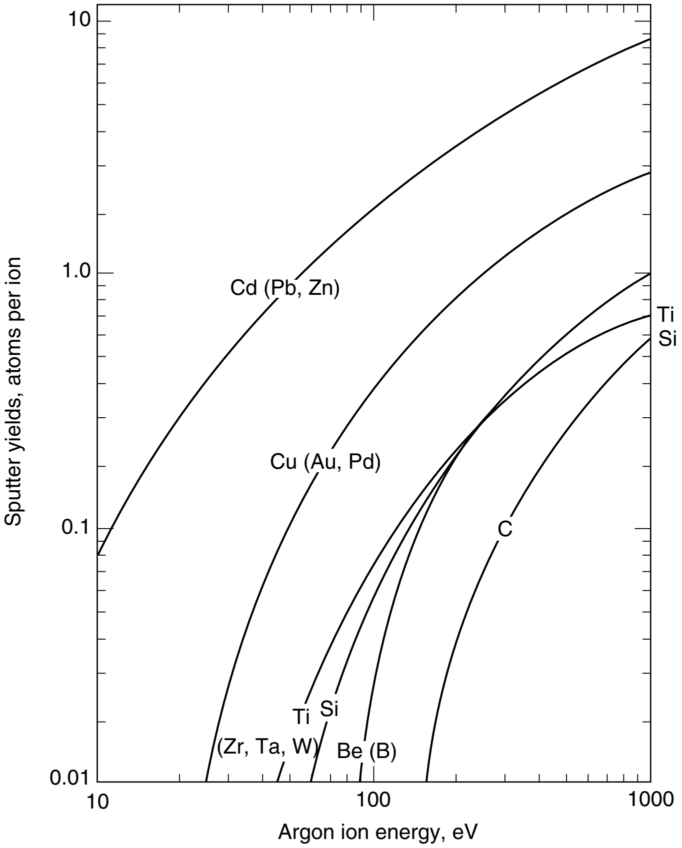

Fig. 8. Calculated sputtering yield of several materials bombarded with argon ions at various energy levels. The materials listed parenthetically also have similar sputtering yield curves.

The simplest configuration for plasma sputtering is direct current (dc) diode sputtering. In this process, a high negative dc voltage is applied to the surface of an electrically conductive target material (to be deposited) in a low pressure (usually in the order of 5–30 mtorr) inert gas environment. The discharge formed fills the container and positive ions are accelerated to the target. In the dc diode glow discharge, the electric field strength is high near the cathode and most of the applied voltage is dropped across a region called the cathode dark space. The accelerated ions impinge on the target surface with very high kinetic energies. The ion bombardment causes the ejection of electrons from the target surface. These electrons get accelerated away from the cathode surface and may cause further ionization of the gas atoms by electron–atom collisions. At equilibrium, enough electrons are created to sustain the plasma discharge. The rest of the space between the cathode and the anode is filled with the plasma where there is very little potential gradient as a dc diode plasma is a weakly ionized system consisting typically of 1 ion in 10^4 neutrals with an average temperature of a few electron volts. Since the number of electrons and ions are roughly the same (1 in 10,000) the plasma is quasineutral and behaves like an isopotenial surface. This potential is often referred to as the plasma potential and is usually very close to the system ground. The equipotenial field lines around the cathode surface are more or less uniform over the flat surfaces and gently curved along the edges. The accelerated ions impinge uniformly on the target surface giving rise to a uniform erosion of the target surface.

In the dc diode configuration, the ions that impinge on the target surface do not have the full cathode fall potential, because the gas pressure is high enough to give rise to charge exchange collisions and momentum transfer collisions between accelerating ions and residual gas neutrals. This creates a flux of ions and high energy neutrals that have a wide spectrum of energies impinging on the cathode surface. As the gas pressure gets higher the mean energy of the particles gets reduced. Since the mean energy of the particles are much less than the applied voltage, a very high voltage (in the range of 2000−5000 V) is typically required for dc sputtering in this configuration. However, the electrons that are accelerated away from the cathode may attain high energy, which in turn might lead to undesirable heating. This requires that the target is cooled appropriately. The simple dc diode sputtering process has the following advantages: (*1*) large areas can be sputtered with uniform utilization of the target surface, (*2*) the target can be made conformal with the substrate, and (*3*) the target-to-substrate distance can be made small. Some of the main drawbacks associated with dc sputtering are (*1*) very low sputtering rate, (*2*) very poor confinement of plasma, and (*3*) choice of sputtering targets limited to only electrically conductive materials. This type of sputtering is mainly used for nonreactive metals, eg, Ag and Cu. Since these may also be thermally evaporated, applications for this type of sputtering are very limited.

The idea of using a combination of both magnetic and electric fields to trap electrons was first proposed by Penning in 1936 (6–8). By using this idea, the technique of magnetron sputtering was introduced. In this system, a permanent magnet is placed behind the target surface, which traps the electrons in a plane above the target. When a charged particle moves in a magnetic field it experiences a Lorentz force given by:

$$\vec{F} = e\vec{v} \times \vec{B} \tag{3}$$

here e is the charge of the electron, $\vec{v}$ is the velocity of the charged particle, and $\vec{B}$ is the applied magnetic field. The magnitude of the vector cross-product is maximum when the two vectors are perpendicular to each other and zero when they are in the same direction. Thus the electron can continue moving in the direction of the field and the force it experiences is in the direction perpendicular to the target surface. By aligning the magnetic field in a plane parallel to the target surface, the secondary electrons can be trapped close to the target surface. In a conventional magnetron source, a ring of magnets around a central magnet provides the magnetic field. This whole assembly is located behind the target surface. The magnets are connected to each other by a plate made of highly permeable material, which prevents the magnetic flux from spreading to other regions. The magnetic force allows the charged particles to move in circular orbits whose radius of curvature is given by:

$$r = \frac{mv}{eB} \tag{4}$$

Thus, it can be seen that the presence of the magnetic field causes the original linear trajectories of the charged particles to deviate. In a real system, there is also an electric field (E) present (since the target acts as a cathode). This electric field will give rise to a force that will act along (or opposite) to the direction of electric field. Hence, the net force acting on the charged particles can be written as:

$$\vec{F} = e\vec{V} \times \vec{B} + e\vec{E} \tag{5}$$

The electric field exerts a force normal to the circular trajectory of the charged particle. Thus the net motion will be helical, which in turn increase the mean free path of the electron, and therefore the probability that it will ionize a gas atom. In a magnetron source, the paths followed by the electrons close on themselves. The electrons trapped near the surface increase the ionization and therefore the plasma density. This gives rise to a higher deposition rate when compared to dc diode sputtering. However, the main drawback remains that since the electrons move in an annular ring along the target surface, the target is sputtered off more strongly in this region. This results in the formation of a deep sputtered groove along the target surface, which is usually referred to as race track formation (Fig. 9). This leads to very low target utilization, often as low as 10–20% (9,10). The utilization may be improved by shaping the magnetic field, moving the magnets during sputtering, or moving the target material over the magnets. Since the electrons are confined near the surface and have a high electron density, the dc gas discharge can be sustained at much lower pressures than dc diode sputtering. This also reduces the collisions probabilities and allows the use of a lower cathode potential.

Confining the plasma to near the target surface also means that the plasma does not fill the space between the source and the substrates. Plasma can be formed near the substrate by utilizing radio frequency (rf) potential on the sputtering target along with the dc potential, by establishing an auxiliary discharge near the substrates or by using an unbalanced magnetron configuration. In this

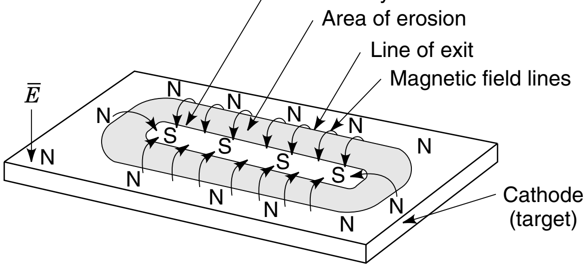

Fig. 9. Direct current diode planar magnetron sputtering configuration.

method, some of the electrons ejected from the target are allowed to escape by having a portion of the magnetic field normal to the target surface. This is usually achieved by unmatching the strength of the north and south poles of the magnet or by employing an auxiliary magnetic field. This method is called unbalanced magnetron sputtering.

It is assumed that the target provides a low resistance path for the neutralization of the ions reaching the target. This can only be true for metallic or conductive targets. If the target is insulating, the fraction of the ions that can be neutralized is limited by the current that passes through the target. If the target is highly resistive the current is small and this leads to charge build up in the target surface. Overall, the ion flux reaching the targets goes down and in turn the sputter yield drops significantly. One way to get around this problem is to use rf power instead of dc power. This was first accomplished by Davidse and co-workers (11,12) in 1966 where they sputtered dielectric targets using rf power. In an rf powered source, the target rapidly switches polarity thereby allowing the electrons in the plasma to neutralize the target surface. Conventionally, used rf power has a frequency of 13.56 MHz. Thus by using rf power, sputtering of insulators is also possible. However, it increases the process complexity and the main problem one has to address is effective transfer of power to the target surface. A typical rf power supply has an input impedance of ~50 Ω. The impedance of the target is much lower, which leads to reflection of power back to the source. Thus an external matching network is needed to compensate for the resistance mismatch.

An alternative to rf sputtering is to sputter a metallic target in a mixture of reactive gas. This process is called reactive sputtering. Although it cannot be used to sputter complex materials, it works for most oxide, nitrides, carbides, and other simple materials. Figure 10 shows a schematic of a reactive sputtering

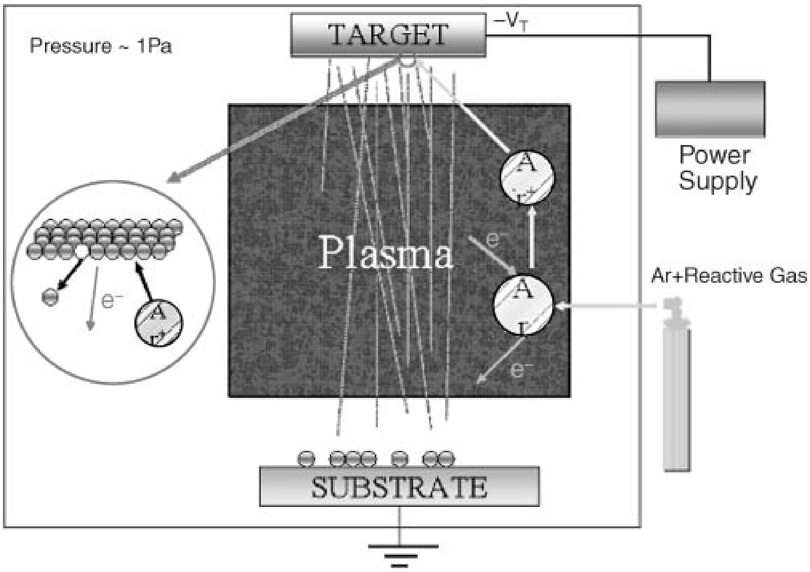

Fig. 10. Schematic of reactive sputtering process.

system. The inert Ar ions sputter the metal target to provide the metal flux, which in turn reacts with the reactive gas to form the appropriate compound material. Reactive sputtering is preferred over rf sputtering because (*1*) metal targets can be easily machined, (*2*) since they are metallic they can dissipate heat very efficiently without cracking, and (*3*) different compounds can be sputtered off the same target by changing the reactive gas. In reactive sputtering, the target can exist in either of the two states: metal mode or poison mode, depending on the gas mixture. The metal mode exists when the concentration of sputtered atoms is greater that the flux of reactive gas atoms (low concentration of reactive gas mixture). Pure compound films cannot be formed in this state since the reactive species concentration is not sufficient to react with the entire sputtered atom flux. Thus a higher concentration of reactive gas is needed to get the desired stochiometry. However, if there is an excess amount of reactive gas, the reactive species in the gas will start reacting with the target surface leading to poisoning of targets. This is poison mode, and if the compound is an insulator there will be target charging and arcing, which can greatly decrease the sputter yield. This entire process can be studied better by measuring the target current as a function of reactive gas concentration (Fig. 11). The metal-to-poison mode transition is usually accompanied by a sharp drop in target current. There is also a pronounced hysterisis behavior on the reverse path because of target poisoning. The optimal operating condition for reactive sputtering is the point of transition from metal-to-poison mode. However, because of the runaway situation experienced at the transition point, the system is highly unstable making it extremely difficult to control. A lot of work has been done in controlling the metal–poison mode transition. These include (*1*) pulsed reactive gas operation, (*2*) using very high pumping speeds, (*3*) using a fast feedback

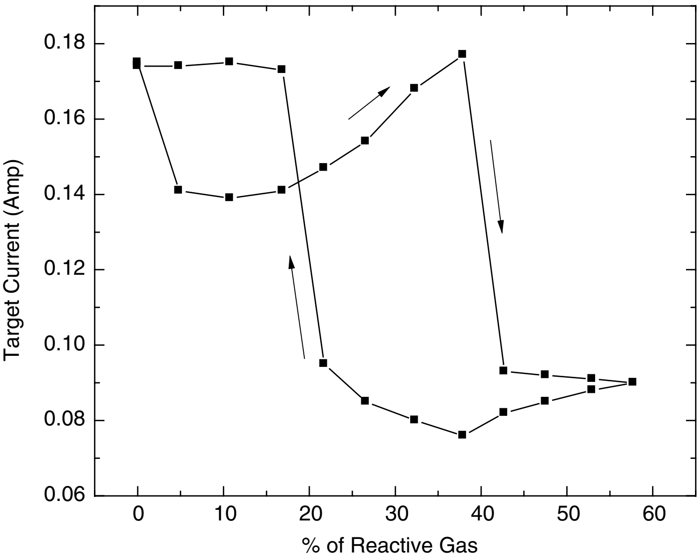

Fig. 11. Target current as a function of reactive gas partial pressure for the reactive sputtering of W in CH_4 atmosphere.

control to maintain the system at desired operating point, (*4*) superimposing an rf signal on the dc target power, (*5*) having a nonplaner geometry for the magnetron, and (*6*) using pulsed dc power.

Conventional magnetron sputtering (both dc and rf) is done using a planar geometry. Nonplanar sources, eg, cylindrical sources and inverted cylindrical or hollow cathode sources (HCS), have been recently used for specific applications. The hollow cathode source was first devised by Penning in 1936 (7). The method was greatly improved by Thorton and co-workers (13,14) and more recently by Glocker (15) and Shah and co-workers (16). For hollow cathode sputtering, sources are basically sputtering sources in which the material to be sputtered forms the inner surface of a hollow cylinder. Figure 12 shows a typical hollow cathode source. Here, the substrate is positioned along the long axis of the cylinder and the sputtered flux gets deposited conformally throughout the substrate surface. The target utilization is also much better than planar sputtering. The plasma is confined physically with annular end wings, which are maintained at the target potential. The inert gas is introduced through one end. Since the

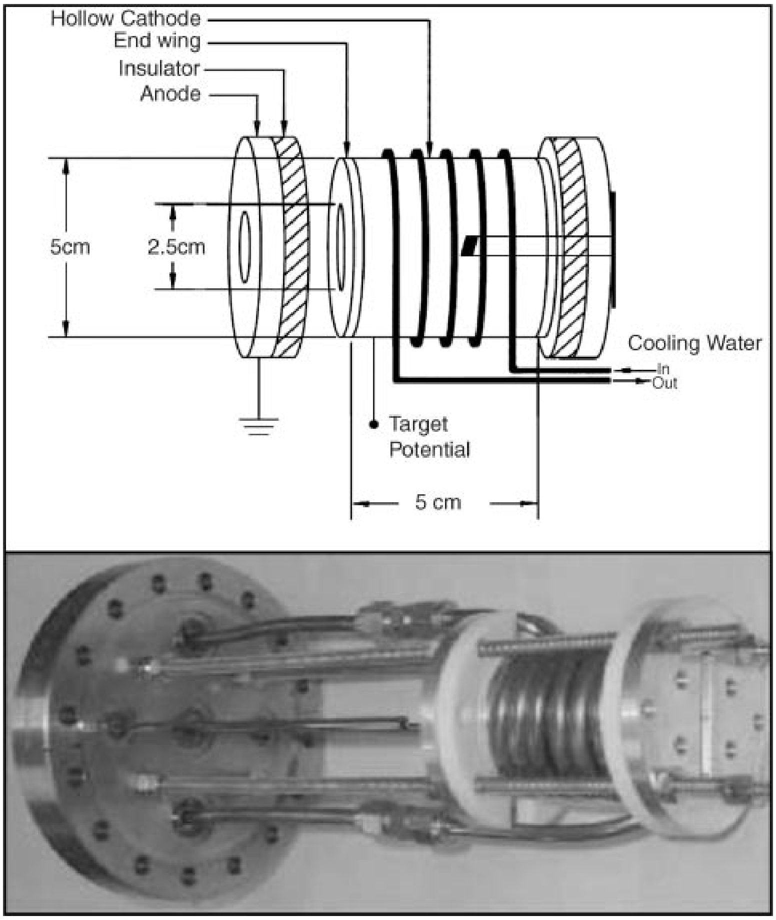

Fig. 12. A simple hollow cathode.

outside is a solenoid, the magnetic field is along the axis of the cylinder and the electrons move along the axis of the cylinder and do not experience any Lorentzian force. Other than the substrate, which serves as an anode, there is no other surface at ground potential within the hollow cathode. By restricting the electrons with the end caps, very high plasma density can be achieved. It also provides a more uniform deposition on the substrate. The biggest advantage of hollow cathode stems from the fact that it does not undergo a metal–poison mode transition during reactive sputtering.

Advantages of sputter deposition are as follows: (*1*) elements, alloys, and compounds can be deposited, (*2*) the sputtering target provides a long-lived vaporizing source having a stable geometry, (*3*) the substrates can be positioned close to the sputtering target, (*4*) this process gives a greater flexibility in deposition condition, and hence film growth and properties can be controlled. Disadvantages of sputter deposition include (*1*) the yield is smaller when compared to thermal evaporation, (*2*) in many configurations the deposition flux is nonuniform, (*3*) it requires the substrate position to be changed for uniform deposition, (*4*) target material utilization is poor, (*5*) sputtering targets are expensive, (*6*) there is a large amount of heat generated because of the energy transferred to the target that has to be removed to avoid cracking of the target, and (*7*) in some configurations, radiation and bombardment from plasma or sputtering target can degrade the substrate material. Sputter deposition is most widely used in depositing semiconductor materials, energy conserving coatings on glass, transparent conductive coating on glass, wear resistant coating, and decorative coating.

2.3. Ion Plating. Controlled concurrent bombardment of energetic particles of atomic or molecular size during thin-film deposition has been shown to greatly modify the properties of thin films. This form of PVD is called ion plating (17). In ion plating, the source material to be deposited can be evaporated, sputtered, arc eroded, or laser ablated. The energetic particles used for bombardment are usually ions of inert or reactive gas. However, when using arc erosion a high percentage of vaporized material is ionized and ions of the vaporized material can be accelerated and used to bombard the growing film. Ion plating can be produced in a plasma environment where the ions required for bombardment are from the plasma itself, or they may be produced in a vacuum environment where ions for bombardment are formed in a separate ion gun. The latter ion plating configuration is often called ion-beam-assisted deposition (IBAD). Figure 13 shows examples of plasma- and vacuum-based ion plating configuration. The most common form of ion plating is the plasma-based process, in which the substrate and/or its fixture is an electrode used to generate a dc or an rf plasma in contact with the surface being coated. This is achieved by applying a continuous dc potential to an electrically conductive surface or an rf potential to an insulating surface. If an element or an alloy is being deposited, the plasma can be of an inert gas. In reactive ion plating, the plasma is a mixture of an inert and a reactive gas. The substrate fixture is the cathode and the ions are accelerated from the plasma to the surface of the growing film. This bombardment of films with ions affects the nucleation and the surface mobility of the depositing atoms and also greatly changes the thermal energy of the film material. It might also increase the density of the film by introducing peening

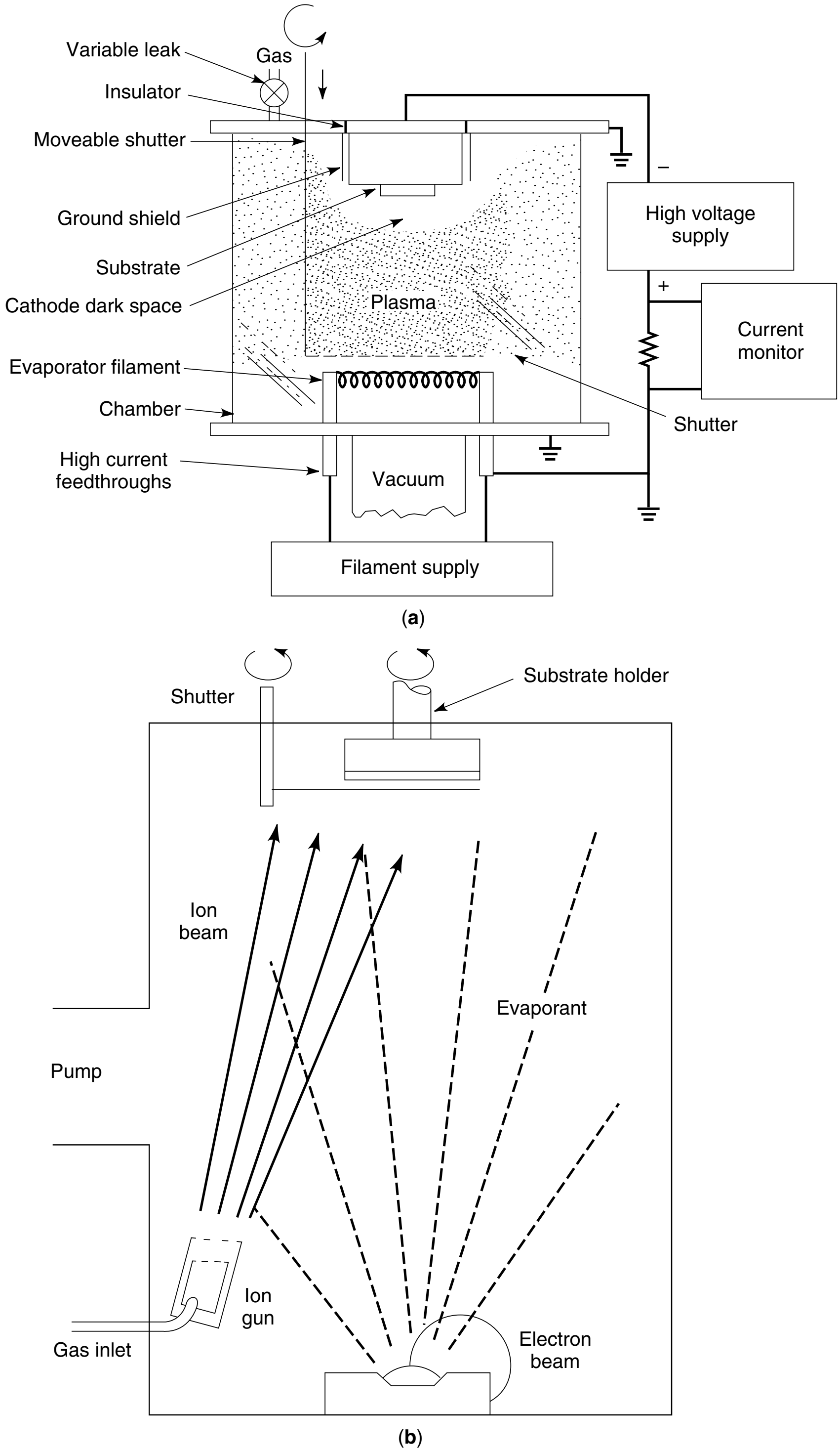

Fig. 13. Ion plating configurations: (**a**) plasma based, where the substrate fixture is the cathode of the dc circuit, and (**b**) vacuum based (IBAD).

sites and may introduce compressive strength by recoil implantation of the near surface atoms into the lattice structure.

For low energy (<50 eV) ion bombardment, the momentum transfer is not sufficient to displace the film atoms and produce atomic peening. However, it does increase the surface mobility of the depositing atoms and affect the nucleation and film growth on the substrate. If the energy of the bombarding ions is between 50 and 300 eV, atomic peening occurs in the near surface regions. For much higher energies, the bombarding species gets incorporated in the film unless the substrate temperature is high. This gas incorporation can result in void formation and microporosity in films.

A special case of ion plating uses arc vaporization of materials as the source of depositing materials. In an arc, very closely spaced electrode material is vaporized by the passage of high current. In the space between the electrodes, a positive space charge is developed as a result of low mobility of positive ions when compared with electrons. The positive ions of the electrode material are accelerated away from this space charge region and subsequently attain very high kinetic energy. In this process, both the vaporized electrode material and the gas species are ionized. In the gas, the ions of the electrode material are thermalized to the ambient gas temperature and both the gas ions and electrode material are accelerated to the substrate by applying a negative potential on the substrate. The main disadvantage of the arc vaporization is the formation of liquid droplets, called macros, during arcing process. These droplets give undesirable bumps on the film surface. The advantages of ion plating are as follows: controlled bombardment can modify film properties and also provides a good way to introduce dopants in the film. Surface coverage can be improved over vacuum evaporation and sputter deposition owing to gas scattering and sputtering–redoposition effects. Film properties are less dependent on the angle of incidence of the flux of the depositing material. In reactive ion plating, the bombardment can be used to improve the chemical composition of the film by bombardment-enhanced chemical reactions, which lead to increased reaction probability, and preferential sputtering of unreacted species from the growing surface. Ion plating is mainly used to deposit hard coating of compound materials, adherent metal coating, optical coating having high densities, conformal coating over complex surface, and also to introduce dopants to thin films.

2.4. Pulsed Laser Deposition. Pulsed laser deposition (PLD) is now established as a viable alternative technique for depositing good quality thin films (18). The basic idea of PLD is to utilize high power laser pulses to evaporate a small amount of matter from a solid target. The focused laser pulses are absorbed in the target surface in a small volume. The absorbed energy density is sufficient to break any chemical bonds of the molecules within the volume. The evaporated particle flux consisting of neutral atoms, positive and negative ions, electrons, molecules and molecular ions, and free radicals of the target material in their ground and excited states absorb a large amount of energy from the laser beam producing an expansion of hot plasma (plume). The ablated species condense on the substrate, placed opposite to the target, forming a thin film. A typical set up for laser ablation and thin-film deposition is shown in Figure 14. The ablation process takes place in a vacuum chamber, either in vacuum or in the presence of some background gas. A laser beam is focused on

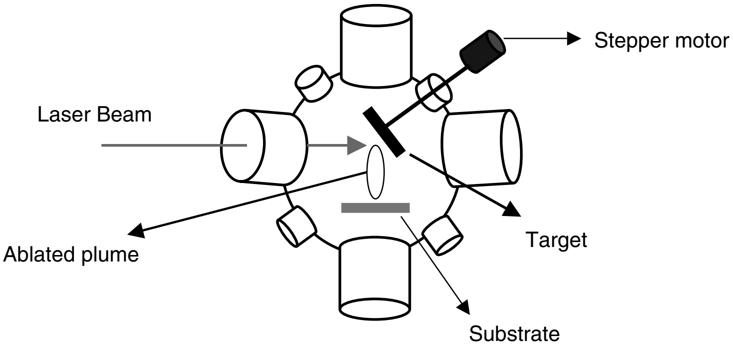

Fig. 14. Typical PLD chamber.

the target surface through a port in the chamber that evaporates material from the surface such that the stoichiometry of the material is preserved in the interaction. As a result, a supersonic jet of particles (plume) is ejected normal to the target surface. The plume expands away from the target with a strong forward-directed velocity distribution of the different particles (18). The ablated species condense on the substrate, placed a short distance from the target. The accumulation of target material on the substrate from a large number of laser pulses leads to the gradual formation of a film.

This technique was first used by Smith and Turner (19) in 1965 for the preparation of semiconductors and dielectric thin films and was further established through the work of Dijkkamp and co-workers (20) on high temperature superconductors in 1987. Since the work of Dijkkamp and co-workers, PLD has been intensively used for a variety of materials including oxides, nitrides, carbides, metallic systems, and even polymers and fullerenes. The PLD or laser ablation deposition (LAD) is now used on a worldwide basis to produce films of various kinds of materials such as semiconductors, high T_c superconductors, ceramics, ferroelectrics, metal and metallic compounds, polymer, biological material, and refractive materials (20–26). In particular, PLD is useful for ablating materials and combinations of materials that cannot be easily produced by other methods (18,25,26). Recently, PLD has also been used to synthesize nanotubes (27), nanopowders (28), and quantum dots (29).

The primary reason for the advancement of PLD is the preservation of the stoichiometry during the film production process. The fast and intense heating of the target surface by the laser beam ensures that all target components; irrespective of their binding energies evaporate at the same time. Evaporated flux gets further heated by absorbing the incoming laser radiation, forming a high temperature plasma, which then expands in a direction perpendicular to the target surface. Therefore, during PLD, the material transfer between target and substrate occurs in a material package where the separation of the species is small. Stoichiometric transfer between target and substrate is difficult to obtain with coevaporation or cosputtering of dissimilar material because, in general, the partial vapor pressures and sputtering yields of the components are different, which give rise to a different concentration of the thin film growing on the substrate.

PLD can be used to deposit films of any material irrespective of their optical properties and stoichiometry and has many more advantages other then stoichiometric preservation. It is fairly simple, versatile (can be performed in vacuum or background gas and with variety of materials), inexpensive, free of contamination (energy source is external), and fast (high deposition rates ~100 Å/min) as compared to other conventional techniques. The disadvantages, eg, particulate deposition and small deposition area have been overcome to a large extent by modifications in the experimental setup. For example, by using filters or off axis deposition particulate deposition can be suppressed (30). Film uniformity in thickness and composition can be achieved by rastering the laser spot across the target surface and/or moving the substrate during deposition (31).

During PLD, many experimental parameters can be changed, which then have a strong influence on film properties. The laser parameters, eg, fluence, wavelength, pulse duration, repetition, and preparation conditions, as well as system configurations including target-to-substrate distance, substrate temperature, background gas species, and pressure, all influence the film growth. Laser ablation for thin-film deposition can be performed in vacuum or in a gaseous background. The expansion of the plume is different in vacuum than in the presence of a background gas. In vacuum, the plume does not expand unidirectionally and backward velocity components appear as well, because of the high density of the plasma the ejected species diffuse in the plume and collide with each other, which leads to a rapid thermalization of the particle cloud. Moreover, the plume in vacuum is visible only in the immediate vicinity of the target. Film thickness profiles, depending on the angle of the plume from the target normal, can be obtained by solving hydrodynamic equations describing the expansion of the plasma plume (32).

Propagation of the plasma in a gaseous ambient is a complicated phenomenon. Collisions between gas atoms and ablated particles take place and the gas scatters, attenuates, and slows down the plume particles changing its spatial distribution, deposition rate, and kinetic energy distribution of the different species. This leads to a more spatially confined plume relative to the one obtained in a vacuum condition (33) with a broader angular distribution (34). In cases of reactive ambient gases, like oxygen, collisions can lead to formation of molecules or clusters that are essential for proper stoichiometry and oxygen content of the film. High kinetic energy deposition fluxes in a background gas induce gas-phase reactions, which aid in the deposition. For example, ablation of graphite in a nitrogen atmosphere under standard conditions gives rise to CN species (35) that are easily observed from their violet emission in the ablation plasma, and lead to the production of CN films with a nitrogen content that is related to the background pressure of nitrogen. As the plume expands, it can compress the ambient gas into a thin shell forming a shock wave between plume and ambient gas. This region has high pressure and temperature (36) and is thus suitable for many chemical reactions that form oxides, nitrides, etc, as some of the ablated material diffuses into the shocked region. It is shown that for the deposition of thin films of oxides and nitrides, etc, the position of the substrate should fall in the shocked region. Process parameters should be adjusted such that the tip of the plume should at least touch the substrate. Too short a plume does not provide enough material to the substrate and in the case of too long a plume, the oxidization of different elements is insufficient and adhesion to the substrate is weak. Ambient gas pressure has an influence on the length of the plume as increasing the pressure decreases the plume length. It is often the easiest parameter that can be slightly modified during the deposition.

The effects of high kinetic energy ablated particles bombarding the substrate include ballistic collisions, ion mixing, and thermally stimulated exchange mixing. These effects lead to raising the substrate temperature and govern film properties, eg, film stress and crystal structure. An important manifestation of the similarity of the effects of temperature and incident kinetic energy is that high quality films can sometimes be deposited at lower substrate temperatures by using a high kinetic energy deposition flux. Energy of the particles can be varied (50 to ~150 eV) by changing the fluence (from 2 to ~10 J/cm^2). This only slightly changes the film properties (37). The particle energy can be lowered by ambient inert gas, which has a much stronger influence on film properties. Gas interaction can reduce the energy to <1 eV. In an Ar atmosphere, well below ~0.1 mbar, the reduction of the average energy of the ablated particles can be described by the scattering of a dense cloud of ablated material moving through a dilute gas (37). On the way toward the substrate, mainly the energetic ions are scattered out of the deposition path, while the slower atoms reach the substrate surface without any hindrance. At higher gas pressures, the plasma expansion leads to a shock front between the plasma plume and surrounding gas, which hinders the plasma expansion and induces a further velocity reduction (38). A decrease of particle energy is accompanied by systematic changes in texture and microstructure.

Laser ablation in an inert gas background can be used to produce films of monodispersed nanoparticles (39). Changing the pressure of the ambient gas changes the average diameter of the deposited nanoparticles. Collisions between ablated atoms and/or ions near the target determine the nucleation and growth of the primary nanoparticles. At low ambient pressure, the ablated species expand into larger volume, resulting in a decrease of the density of atoms–ions and subsequent formation of thin film or smaller nanocrystals embedded in a thin film. An increase of the ambient gas pressure decreases the expansion volume causing the collision probability to increase. In such a situation, the kinetic energy of the ablated species is still high enough to allow the growth of nanoparticles and the growth process of primary nanoparticles dominates the process. At this medium-pressure range, the mean diameter of primary nanoparticles increases with increasing ambient gas pressure. Under higher ambient gas pressure, the ejected species frequently collide with inert-gas atoms and dissipate their kinetic energy, resulting in the quick quenching of the nanoparticles that disturbs further growth of the primary nanoparticles and promotes the formation of aggregates. As a consequence, larger aggregates with small primary nanoparticles are produced.

Different laser parameters also affect the properties of the thin-film shape. If the laser spot size on the target is reduced keeping the fluence constant, less material is removed from the target and the plume becomes wider and shorter (39). On the other hand, if the fluence is increased a longer plume is produced because the initial velocity of the particles is higher. This affects the deposition process. Also, the fluence of a laser pulse has to be larger than a certain threshold value so that all the species can be stoichiometrically removed from the target. In the case of YBCO, the threshold fluence is 1 J/cm (40). Typically, values of ~2–3 J/cm are used in order to reduce the number of particulates on the deposited film. On the other hand, too large a fluence may result in the ejection of large target fragments, which increases the number of droplets on the film surface.

Material properties, eg, reflectivity and absorption coefficient of the solid target depend on the wavelength of the laser used. Hence, the wavelength of the laser has a significant effect on the yield of the ablated particles. Reflectivity of most materials is much lower for lasers with short wavelength [ultraviolet (UV) region] than long infrared (ir) wavelengths (41). When the reflectivity decreases, a larger part of a laser pulse is absorbed increasing the number of sputtered particles. Also, the absorption coefficient is larger in the uv region such that the beam energy is absorbed in a thin surface layer and the ablation occurs more efficiently.

Pulse repetition rate and the material deposition rate depend on the material ablated and have to be determined individually, but there are some basic rules that have to be followed. Too high a deposition rate causes film deterioration because of the reduced opportunity for film relaxation. On the other hand, too small a deposition rate results in unacceptably long deposition runs. High deposition rates tend to put fewer demands on the vacuum quality. The lower the deposition rate, the higher the probability of the incorporation of gaseous impurities, like H_2O, CO_2, H_2 and N_2.

The temperature of the substrate is also a very important parameter influencing the film morphology. Deposited flux might reevaporate from the surface, nucleate into a cluster, be consumed by existing clusters, or be trapped on a surface defect site. All these processes depend on the mobility of the deposited atoms on the surface and they each have their characteristic activation energies. Surface rearrangements are possible at higher temperatures, while at low temperature they are inhibited. To obtain epitaxial thin films, the substrate has to be heated to a temperature of ~700–900°C. Some materials (eg, YBCO) are quite sensitive to a change in the deposition temperature. A decrease of only a few degrees from the optimal value may significantly degrade the crystal quality and the superconducting properties of the film. Moreover, a lower temperature increases the formation of particulates and lattice defects. The smoothness and crystallinity of the film can be further increased by rotating the target during the deposition so that laser pulses would not strike at the same spot on the target surface all the time. The microstructural morphology of the film is highly dependent on the growth temperature. As such, the temperature can be used as a process parameter to induce different structures. Metastable structures are grown preferentially at lower substrate temperatures, while the growth of crystalline materials requires higher substrate temperatures to induce reconstruction and surface relaxation (42–44).

The pulsed nature of the PLD process allows changing of the laser conditions for each target. Therefore, it becomes possible to produce complex composite materials like polymer–metal systems, where completely different laser fluences are necessary for the deposition of polymer and metal, respectively.

Dijkkamp and co-workers (20) established PLD as an alternative deposition technique with advantages like stoichiometric transfer and the possibility of different ambient conditions, eg, vacuum, inert gas, and reactive gas. Several different types of materials have been prepared by using PLD. Since the kinetic energy of the ions lie in the range of 100–150 eV, it is possible to operate systems far away from equilibrium (metastable alloys, nanocrystallites). Being able to control the energy of the ablated particles by using inert ambient gases make this method even more versatile as the energy can be adjusted according to the need of changing texture, stress, etc, of the deposited film. Dependence of film properties on other features like laser energy, wavelength, etc, demonstrates the versatility of PLD.

Modification of the conventional PLD technique has made the deposition of materials that would undergo photochemical changes like polymers, biomaterials, etc, possible (45). A combination of PLD, molecular beam epitaxy (MBE), and chemical vapor deposition (CVD) techniques has been developed to deposit thin, particulate-free, conformal layers of several materials (46). There are other modifications of conventional PLD like the combinatorial approach to explore novel materials phases, which can be used to systematically explore new functional and electronic materials. Such an experiment is best implemented in the form of a thin-film combinatorial library, where on a substrate as small as 1 cm^2, thousands of different compositions can be integrated, synthesized, and screened for the desired physical properties (47).

There was a 20-year gap between the discovery of PLD and its full exploitation. One cannot visualize now where it will lead to in the future when there will be a better understanding of laser–matter interaction. Also, new materials, new lasers, and new equipments can still modify the technique for applications that require synthesis of advanced materials.

3. Thin Films from Vapor

3.1. Chemical Vapor Deposition. Chemical vapor deposition or thermal CVD is a general term applied to the deposition of atoms or molecules from a chemical vapor precursor. The precursor may include chlorides, eg, titanium tetrachloride ($TiCl_4$); fluorides, eg, tungsten hexafluoride (WF_6); hydrides, eg, silane (SiH_4), or carbonyls, eg, nickel carbonyl [$Ni(CO)_4$]. The decomposition of the precursor is either by chemical reduction or by thermal decomposition. The process may employ various gaseous, liquid, or solid chemicals as sources of the elements of which the film is to be made of. The reaction results in the production of a nonvolatile solid that deposits on an appropriately placed substrate forming either particles or a thin film. In some cases, the deposited material might react with gaseous species to form compounds, eg, oxides, nitrides, carbides, and borides. These reactions are called synthesis reactions. The CVD processes have been used in various industrial applications and technologies, eg, the fabrication of electronic devices, the manufacture of cutting tools, and the formation of nanoparticles. Chemical vapor deposition has numerous other names and adjectives, examples include vapor-phase epitaxy (VPE), which is usually referred to CVD processes used to deposit single-crystal films; metalorganic CVD (MOCVD), when the precursor gas is a metalorganic species, plasma enhanced CVD (PECVD), or photo CVD (PCVD), when a plasma or light is used to induce or enhance the reaction.

Although each of the processes mentioned above use different systems, most CVD systems have many components in common. A CVD system must have the ability to deliver and control the reactant gases into the reactor, usually accomplished by using mass flow controllers. A reaction chamber equipped with a substrate holder where the reactant gases combine to form particles, which are collected on the substrate. The reaction chamber is typically tubular in shape and constructed of stainless steel, glass–Pyrex or quartz, etc, depending on the reaction conditions (temperature, pressure, reactivity, etc). The system must also contain a heating system with temperature control to supply heat to the reactor and substrate. The heat is necessary to ensure that the reaction can occur efficiently and provides the energy to dissociate the gases in CVD and MOCVD processes. For PECVD or PCVD, there is in addition to the heat source a plasma generator or light source present to assist in the dissociation. Finally, vacuum pumps are used for maintaining the system pressure and for the removal of reaction by-products and depleted gases (48,49).

3.2. Thermally Activated Chemical Vapor Deposition. Thermal CVD processes are initiated only with thermal energy (resistive heating, rf-heating or by ir radiation). They are usually performed at low down to ultralow pressure. High temperature CVD is the only way to achieve the growth of high quality epitaxial thin films; it is used extensively for metallurgical coatings and for *in situ* calcinations to obtain the desired crystalline phase. The CVD process is accomplished by using either a hot- or a cold-wall reactor. In the former, the whole chamber is heated, and therefore a large volume of processing gas is heated as well as the substrates. Hot-wall reactors are usually tubular in shape and are heated externally by use of resistance heating elements. Multiple temperature zones are essential for the efficient transport of matrix as well as dopant atoms. By carefully controlling gas flow rates and temperatures, the composition, doping levels, and particle size of the nanoparticles can be manipulated. In a cold-wall reactor, the substrate or the substrate fixture is heated, often by inductive heating. This heats the gas locally. In this configuration, the boundary layer defines the temperature gradient in the vapor in the vicinity of the substrate. This boundary layer can vary in thickness and turbulence, depending on the direction of gas flow. Direct impingement of the gas on the surface reduces the boundary layer thickness and increases the temperature gradient, whereas stagnant flow regions give much thicker boundary layers. Cold-wall reactors are utilized almost exclusively for the deposition of epitaxial Si films (48–50).

A unique CVD technique is used to deposit polycrystalline diamond films by passing a precursor gas mixture (H_2 and 5% CH_4) over a hot ($\sim$2200°C) tungsten filament. The hot filament is carburized, and then dissociates the CH_4 to carbon plus other species and the H_2 to hydrogen radicals. The activated hydrogen preferentially reacts with and etches the deposited carbon that has the sp^2 bonding (graphite-type bonding), as opposed to sp^3 bonded carbon (diamond-type bonding), leaving predominately sp^3 bonded carbon in the film. At substrate temperatures $>$600°C, the atoms arrange into the tetrahedral diamond structure, giving a polycrystalline diamond film. At lower temperatures, where the atomic mobility is less, the films may be composed of sp^3 bonded carbon without the diamond crystal structure. This is called diamond-like carbon (DLC). In DLC, the films have desirable properties of diamond, but the presence of some sp^2 bonded carbon and a high hydrogen concentration significantly affects its properties.

The morphology, composition, crystalline structure, defect concentration, and properties of CVD deposited materials depend on a number of factors. An important variable of a CVD reaction is the effect of vapor supersaturation over the substrate surface and the substrate temperature. Low supersaturations give rise to low deposition rates, nuclei initiate on isolated sites and grow over the surface, giving a high density film. If this is coupled with high temperatures, epitaxial growth can be obtained on appropriate substrates. This vapor-phase epitaxial (VPE) growth is used to grow doped layers of semiconductors, eg, boron doped silicon. At intermediate concentrations, a nodular growth structure may form. At high supersaturations, the decomposition gives whiskers and dendritic structures leading to low film density. In extreme cases, the decomposition can occur in gas phase and gas-phase nucleation produces ultrafine particles. These particles can be swept through, may deposit on a mesh, and can be collected later.

3.3. Metalorganic Chemical Vapor Deposition (MOCVD). Metalorganic chemical vapor deposition is also a thermal CVD processes, but the sources differ in that they are metalorganic gases or liquids. Metalorganic compounds are organic compounds that contain a metal atom, particularly compounds in which the metal atom has a direct bond with a carbon atom [eg, titanium tetraisopropoxide, $Ti(OCH\ Me_2)_4$]. With the availability of pure metalorganic precursors, their use offers significant advantages in the practical aspects of delivering the reactants to the substrate surface. The greatest advantage of using metalorganics is that they are volatile at relatively low temperatures making it easier to transfer the precursor to the substrate. Since all of the reactants are in the gas phase it is possible to achieve precise control of the flow rates and partial pressures of the gases allowing for efficient reproducible depositions. However, due to the organic nature of the precursors, carbon contamination becomes a problem making it difficult to produce high purity samples (51–55). Figure 15 shows the schematic of a typical MOCVD system.

3.4. Plasma-Enhanced (PECVD) and Photo (PCVD) Chemical Vapor Deposition. PECVD uses plasma to activate and partially decompose the

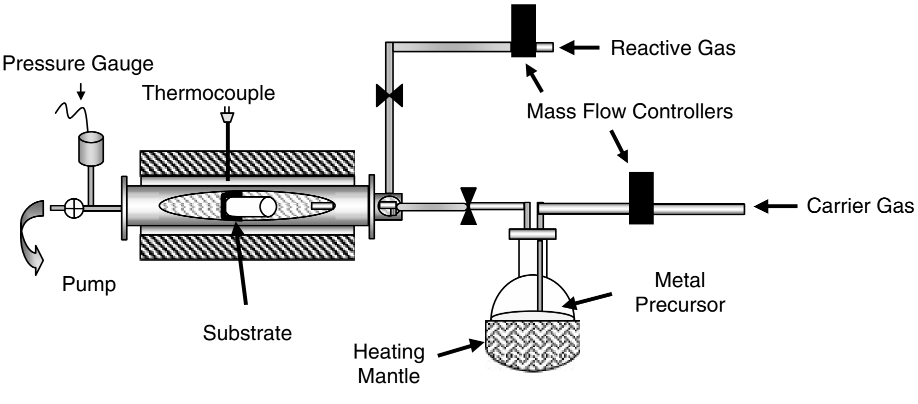

Fig. 15. Schematic of an MOCVD system.

precursor species, and perhaps in certain cases form new chemical species. This allows deposition to occur at much lower temperatures than thermal CVD. The plasmas are generated by dc, rf, or electrocyclotron resonance (ECR) techniques. The reactor can be coupled either inductively with a coil or capacitively with electrode plates forming plasma. This type of PECVD reactor is commonly used in semiconductor industry to deposit silicon nitride (Si_3N_4). The CVD mechanism under plasma is more complex, being a combination of plasma and surface processes. The radicals, unique species, and the excited species formed in the plasma can play an important role in adsorption and deposition of gaseous precursors (56). For example, in the deposition of silicon from silane, it has been proposed that disilane and trisialne are formed in the plasma, and their adsorption on the surface, along with low energy particle bombardment, is important for the low temperature deposition and high deposition rate of amorphous silicon. The PCVD uses light (lasers) to enhance the reaction rate. The effect of the radiation is either a local heating of the substrate to decompose the gases above it or a photochemical reaction where the energetic photons directly decompose the gases. The generated species are highly reactive, and their use enhances the particle growth rate allowing for deposition at much lower temperatures than in thermal CVD. Therefore, previously impossible reactions, eg, high temperature reactions on temperature sensitive substrates, may now be carried out (57,58).

Processing variables that affect the properties of films deposited with CVD techniques include substrate temperature, precursor vapor temperature, gas flow rate, gas composition and pressure, vapor saturation above the substrate, diffusion rate through the boundary layer and substrate material. For PECVD, plasma uniformity, ion and electron temperatures and densities, and energetic particle bombardment during deposition are also important. Safety is a primary concern in all CVD processes. The hazardous natures of some of the gases and vapors that are used have to be addressed properly. Advantages of the CVD technique consist of producing uniform, pure, reproducible particles, and films at low or high flow rates. Application of CVD thin films exists in semiconductor industries for semiconductor materials, eg, Si, Ge, group III–V compounds (GaAs), doped (As, P, B), epitaxial Si and amorphous Si for solar cells. However, when compared to other deposition techniques the CVD processes are perhaps the most complex to use. Unlike growth by physical deposition techniques, eg, evaporation, this method requires multiple test runs to establish the growth parameters to be used, especially for single-crystal growth. The complexity of this method results from several factors. First, CVD generally uses multiple reactant species in the chemical reactions compared to single sources for PVD or PLD. Second, CVD reactions generally produce intermediate products with the growth occurring in more consecutive steps rather than directly forming the product as in physical methods (ie, evaporation). Finally, the growth has numerous independent variables (flow rate, partial pressures, system pressure, etc) and all these variables must be monitored and controlled. Other disadvantages of the CVD process are the chemical hazards associated with the toxic, explosive, inflammable, or corrosive gases used and that not all materials have a precursor that can be economically and commercially available.

3.5. Plasma Polymerization. Many organic and inorganic monomers can be cross-linked in a plasma environment. Plasma can be used to polymerize organic monomers to form thin films (59). For example, plasma is used to polymerize organosilicone thin films for protective coating on aluminum reflector films for automotive headlights. The plasma deposited organosilicone films can further be oxidized by using an oxygen containing plasma. The films made by this technique have excellent surface coverage, are hydrophobic, hard, and relatively pinhole free when compared to the same films made by different techniques. Plasma-polymerized and oxidized films have been formed using tetramethyldisiloxane (TMDSO) to form quartz-like transparent films that show good gas and moisture permeation properties. Inorganic monomers can be used to plasma deposit polymer type film (60). At high plasma energies, monomers are largely decomposed and can be used to form materials, eg, amorphous hydrogen, containing silicon films from SiH_4 for thin-film solar cell materials.

4. Thin Films from Chemical Solution

When a metal is dipped into a solution containing its own ions, some of the surface atoms dissolve and some of the ions in the solution deposit. The difference in the rates establishes a potential specific to the material. To measure this potential, a second electrode is needed. All electrode potentials, reported with respect to hydrogen on platinum, give the relative tendency of the material to gain or lose electrons. The displacement or immersion plating results from the differences arising in the electromotive potential between the surface and the ions in the solution. In displacement plating, the ions from the surface go into the solution to be replaced by an ion from the solution. For example, if a copper rod is placed in an acidic gold solution, the gold plates out as a porous coating on the copper. The resulting deposit is porous and must be buffed to give a dense and a bright coating. Immersion plating can be used to plate Zn or Sn on oxide-free aluminum, uranium, or other active metals. This is called zincate or stannate process.

4.1. Electroplating. Electroplating is the process of deposition of metallic ions on a cathode in an electrolysis cell. This is a very easy method of depositing a limited number of materials on electrically conductive surfaces (61,62). Electroplating is often used to form coatings many micrometers thick. A thin film formed by electroplating is called a flash or a strike. Figure 16 shows an electrolytic-cell configuration for electroplating. When ionically bonded materials are dissolved in a solvent, some of the molecules dissociate into ions. The solvent might be water, an organic solvent, or a fused salt. A simple example is that of sulfuric acid or copper sulfate in water giving

$$H_2SO_4 \longrightarrow 2\,H^+ + SO_4^{2-}$$

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$

The electrolyte thus formed can conduct electric current by the movement of ions in the presence of an electric field. A cell using an electrolyte as a conductor and a positive and a negative electrode constitutes an electrolysis cell. If a dc voltage is applied to a cell having an inert electrode material, eg, platinum, the hydrogen

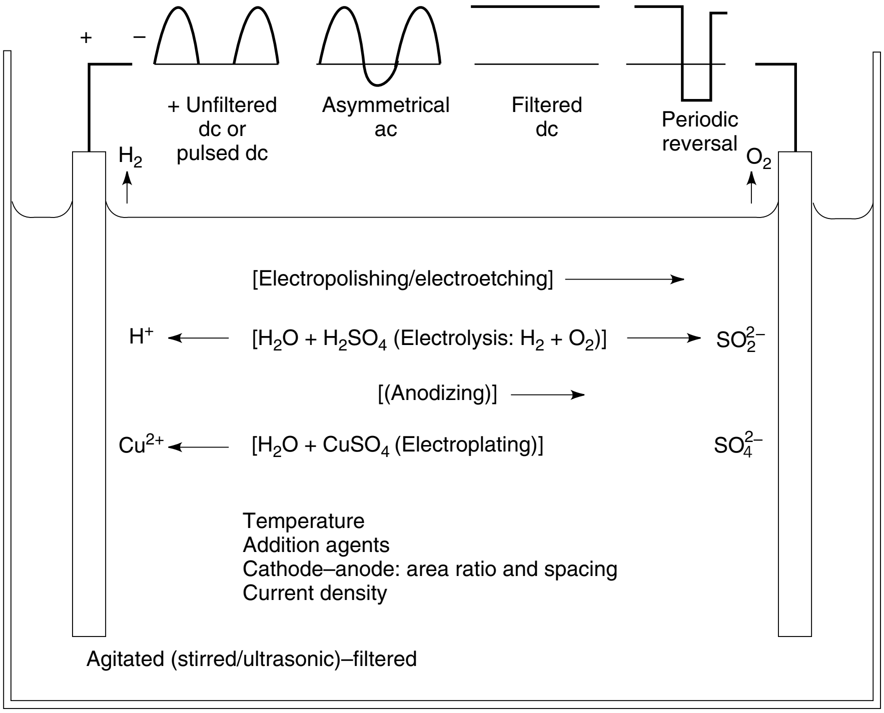

Fig. 16. Electroplating electrolytic cell.

ions (cations) migrate to the cathode where they accept an electron and form molecular hydrogen. The SO_4^- ions (anions) migrate to the anode, release the two electrons, and go back into the solution and release molecular oxygen. The result is electrolytic decomposition of water to give hydrogen and oxygen. If the cations in the solution are condensable as a solid, eg, copper, they can plate out on the cathode of the cell. Now the SO_4^{2-} ion can react with a copper anode by taking it into solution to replace the lost copper ions. Thus the anode is a consumable electrode in the process.

Apart from the potential due to the difference in rate of dissociation, there are other forms of potential associated with the electrodes of an electrolysis cell. One of them is generated by electrode polarization, also called an overpotenial electrical double layer or Nernst diffusion layer, owing to the changes in ion concentration near the surface. This polarization varies with ion concentration, ion mobility, temperature, agitation, etc. The polarization layer is an important factor in electrode effects and determines the current density though the electrolyte. In electroplating, an external voltage is applied to the electrolysis cell, which is greater than the sum of the electrode potentials of the two materials and also the polarization voltage. Faraday's law of electrolysis states that the amount of chemical change (amount dissolved or deposited) produced by an electric current is directly proportional to the quantity of electricity passed and that the amounts of different materials deposited or dissolved by the same quantity of electricity is directly proportional to their gram-equivalent weights defined as the atomic weight by the valence. Therefore, the weight, W, in grams of the material deposited is given by:

$$W = \frac{Itm}{\mathcal{F}} \tag{6}$$

where I is the current in amperes, t is the time in seconds, m the gram-equivalent weight and $\mathcal{F}$ is the Faraday constant.

The release of hydrogen in an electrolytic cell can compete with the deposition of the ions on the cathode. Ideally, minimum current should be used to release hydrogen or any other chemical reaction. Current efficiency is used to define the efficiency of the process. It is the ratio of the metal deposited to that, which would be deposited if no other reactions were to occur. In the deposition of some metals, eg, Cr, large amounts of hydrogen can be incorporated into the deposit and in the substrate. Hydrogen charging of high strength steel during cadmium electroplating leads to hydrogen embrittlement of the steel. Usually, a PVD process is employed in such cases to avoid this problem. Nonaqueous solvents can also be used for electroplating. They have the advantage that hydrogen is not given off during electrolysis. Moreover, the deposition takes place in a nonoxidizing environment, which allows the electrodeposition of oxygen active material like Al. The deposition of ions at the cathode creates a depletion layer across which the ions must migrate in order to deposit. This layer can vary in thickness depending on the surface morphology. The depletion layer is defined as the region where the ion concentrations differ from that of the bulk by $>1\%$. This depletion layer thickness can be decreased by agitation. Agitation plays an important role in electrodeposition by increasing ion transport in the solution and allowing higher current densities to be obtained. It also reduces electrode polarization effects and prevents stratification of chemicals. By using ultrasonic agitations, higher current densities, and therefore higher deposition rates, can be achieved. It also helps in suppression of hydrogen evolutions, reduces stress in the deposit, reduces porosity, and increases hardness. Increasing the bath temperature of the electrolyte also has similar effects.

Current can be passed through the electrolyte with various waveforms. These include dc, asymmetrical ac, and pulsed and periodic reversal of the polarity of the electrodes. A version of pulse plating uses an initial high voltage to increase the nucleation density followed by lower voltage pulses. This procedure is used to give a fine-grained deposit. Pulsed periodic reversal plating, where the voltage is periodically made anodic, is used to clean off plate, remove roughness, and decrease columnar morphology. Agents are added to the bath to modify deposition, growth, and properties of the depositing atoms. Often the purpose of adding agents is to poison the nucleation sites and make the depositing material continuously renucleate during deposition to give a fine-grained structure. Wetting agents are used to prevent hydrogen bubbles from adhering to the cathode surface and becoming incorporated into the electrodeposit.

Properties of electrodeposits can vary widely with plating solution and processing parameters. Plating variables are often interdependent. They include geometry, eg, spacing, shape, area ratio, and the field distribution; for substrate, cleaning, activation, and nucleation; for bath, addition agents, pH, temperature, agitation, impurities, compositions, concentration, valence of the species, and filtration; and for applied potential, voltage, waveform, current density, and waveform. Only a few elements, eg, Cr, Ni, Zn, Sn, In, Ag, Cd, Au, Pb, Rh, alloy deposition, eg, Cu–Zn (brass), Cu–Sn (bronze), Pb–Sn (solder), and Ni–Fe (permalloy) are commercially deposited from aqueous solution. Although most electrodeposited materials are crystalline, in some cases amorphous materials can also be deposited. Aqueous electroplating has the advantage of low capital cost, except for pollution control, which has become a significant portion of the capital cost, low unit production cost, excellent adhesion, and a chemical-etch surface preparation step that is easily incorporated into the processing. Disadvantages include hydrogen incorporation, limited number of materials that can be electrodeposited and the environmental aspect.

4.2. Spray Pyrolysis. In spray pyrolysis, the chemical solution is sprayed on a hot surface where it is pyrolyzed to give a thin film of either an element or a compound (63). For example, to deposit CdS, a solution of $CdCl_2$ plus NH_2CSNH_2 (thiourea), is sprayed on a hot surface. Materials that can be deposited by spray pyrolysis include electrically conductive tin oxide, indium/tin oxide (ITO), CdS, Cu–$InSe_2$, and CdSe. This is a very inexpensive technique and can be used on large-area surfaces.

4.3. Wetting. Films can be formed on surfaces by wetting the surface with a fluid containing the desired material usually dissolved in a solvent. When the solvent evaporates, the film material is left behind. This process is also called the sol–gel technique. The thickness of the film thus formed depends on the thickness of the fluid layer and the solid content of the fluid. The fluid films can be formed by either dip or spin coating. This is a very common way to form polymer and photoresist films. After the film is formed, it can be cured by heat, uv radiation (in case of photoresists), or by electron beam irradiation. For example, a hydrocarbon film, eg, furfarane, can be vacuum pyrolyzed to give a carbon film on the surface. Wetting techniques can also form inorganic coatings. The sol–gel coating technique can be used to form thin films of carbides, oxides or nitrides, which can also be doped with appropriate precursor solution (64,65). For example, a thin film of TiO_2 can be formed by the hydrolysis of a titanium tetrachloride precursor solution on appropriate substrates. The drying and sintering of the gel is sensitive to heating rates. Fully dense sintering requires high temperatures. Similarly, crystallinity and structure also depends on the sintering temperatures. Sol–gel techniques are used to apply antireflections coatings on glass. The coatings are left porous to reduce the index of refractions. Sol–gel coatings are also used in the coatings of optical fibers. Spin on glass (SOG) is a technique for applying a fluid coating that is converted into a glass film and is used to planarize surfaces in semiconductor device technology. A solution, eg, polysilicates or polysiloxanes, is applied by spin coating. The solution is then oxidized to form SiO_2 by baking at $\sim 450^\circ C$. Sol–gel is a relative inexpensive and simple technique, however, cracking, adhesion, coverage, and particulate formation still remains to be addressed in this technique.

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