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Review
Deposition processes for films and coatings

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Deposition of films and coatings on different substrates is carried out mainly by using physical and chemical vapour deposition (CVD). Various films and coatings of metals, oxides, carbides, nitrides, silicides, borides, etc., are successfully deposited by the CVD process. An update on the deposition process and its applications is discussed in this paper.

1. Introduction

Films and coatings are used mainly to fabricate electronic, metallurgical components and to protect the substrates from corrosion, reaction, and surface damage for various applications. Deposition processes include evaporation, sputtering, plating, dipping, spraying, and chemical vapour deposition (CVD).

Evaporated films are formed by heating a material under vacuum to a temperature where a large number of atoms or molecules leave the surface of the material and deposit on a substrate. In sputtering, a target is bombarded with high-energy particles that eject atoms from the surface and deposit them on to substrates. In electroplating, the electrodeposition of an adherent metallic coating takes place on a metallic electrode; and in electroless plating, the deposition of a metallic coating takes place by a controlled chemical reaction, which is catalysed by the metal or alloy being deposited.

In hot-melt dipping, the substrate is dipped in to the molten metal to produce a coating. In another dipping process, the substrate is dipped into a metallorganic resin at room temperature, dried, and the organics are evaporated to leave a finite-thickness coating. Films or coatings can be deposited by spraying a suspension on to a heated substrate, where the constituents react or thermally decompose. In the CVD process, the deposits are produced by vapour-phase chemical reaction at a controlled temperature.

Among these processes, evaporation, sputtering, plating, dipping, and spraying (termed here as non-CVD processes) are somewhat limited to relatively low temperature melting materials, and some of them are restricted only to metallic coatings. By contrast, the CVD process has the advantage of depositing metallic or dielectric coatings of low- and high-temperature melting materials. The reaction temperature in the CVD process can be obtained from various types of heat: resistance, infrared, induction, laser, and plasma.

This review provides a brief introduction of non-CVD processes, followed by a description and analyses of the development of CVD for the deposition of films or coatings on various substrates.

2. Non-CVD process

Films and coatings can be deposited by using the physical vapour deposition (PVD) processes, such as evaporation, ion plating, and sputtering.

2.1. Evaporation

The evaporation system consists of a vacuum chamber, vapour source, and a substrate with holder. Fig. 1 is a typical system ([1] Ch. 3). The evaporating material is placed in a basket which can be heated by resistance (wire filaments of helix, conical basket, boat, etc.), bombardment with high-energy electrons, high-frequency induction, radiation, or levitation. The gas liberated from the material condenses on the substrate. The condensation of evaporated materials takes place by adsorption of evaporated molecules on substrate surfaces. The nature of this primary deposit has a strong influence on subsequent growth. The main parameters that control the growth and structure of evaporated films are the type of substrate, substrate temperature, evaporation temperature, angle of incidence of the evaporant, and contamination. Adhesion of the evaporated, thin film depends on the strength of the bond between the evaporant and the first layer of material on the substrate. This process can deposit metals and metal alloys. Typical metals used in this process are aluminium, chromium, copper, gold, nickel, palladium, titanium, tungsten, tantalum, molybdenum, zinc, and cadmium. Most insulators and dielectrics dissociate by heating in a vacuum or by interaction with an electron beam.

2.2. Ion plating

This process vapourizes the material in a fashion similar to evaporation, but the vapour passes through a glow discharge on its way to the substrates. In the glow discharge, some of the vapourized atoms are ionized. The deposition rate is usually lower as some of the deposit is sputtered off and heats up the substrate by gas-ion bombardment. This process produces reasonably uniform deposition of all surfaces due to gas scattering in high gas pressure.

2.3. Sputtering

Sputtering ([1], Ch 4, [2]) has long been used to

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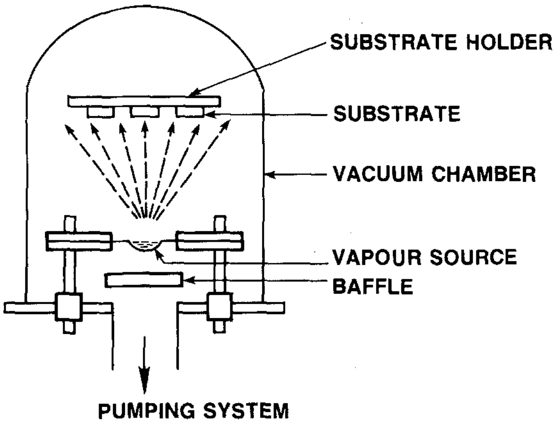

Figure 1 Schematic drawing of a typical evaporation system.

deposit thin films. In recent years, sputtering high-temperature metallic films for electronic applications has received considerable attention. There are several ways to generate the positive gas ions necessary for sputtering. Use of glow discharge produces ionized gas by setting a high potential between two flat, parallel electrodes in a low pressure gas. The positive ions of the ionized gas bombard the target (usually cathode), knocking out atoms deposited on substrates mounted on the anodes. The substrates should be as close as possible to the cathode for improved deposition. The velocities and energies of sputtered atoms are much higher than evaporated atoms. The gas pressure, applied current and voltage, and electrode geometry are the major factors in sputtering. High-temperature metallic films of tantallum, molybdenum, tungsten, etc., metallic alloys, and insulating and semiconducting compounds of various metals can be sputtered. Film bonding occurs through the formation of some metal–oxygen bond at the interface of the substrate. Oxide films are produced in oxygen discharge. Similarly, nitride and carbide films [3] are produced in nitrogen, carbon monoxide, and methane discharges.

2.4. Plating

2.4.1. *Electroplating*

In this process [4], a metal is coated with a similar or another metal in a plating bath that contains a cathode and anode. The cathode receives the deposits from the plating solution during the electrolysis process.

2.4.2. *Electroless plating*

This is an autocatalytic plating process [4] that is characterized by a selective reduction of metallic ions only at the catalytic substrate surface that is immersed in an aqueous solution. Uniform thickness on all areas of the immersed substrate is achievable.

Another type of plating is vapour-phase plating, which will be discussed in the CVD section.

2.5. Dipping

Low-melting metals or alloys are melted in a crucible, and the substrate is dipped into it. Metals like aluminium, tin, and antimony can be used for coating metallic or nonmetallic substrates.

With metallorganic dipping, the substrate is dipped into a metallorganic resin at room temperature, dried, and heated at a temperature sufficient to completely decompose the organics, thereby producing a coating on the substrates. Various metallorganic resins of gold, platinum, silver, antimony, barium, cadmium, chromium, iron, lead, magnesium, manganese, tin, titanium, tungsten, vanadium, zinc, zirconium, etc. are commercially available [5].

Also, by using metallorganics, the sol–gel process is now commonly used to deposit thin-glass films on various substrates, such as glass, metals, ceramics and plastics. The substrate is immersed in an alkoxide solution, pulled up and hydrolysed in air, and heated (200 to 500° C) to form a thin film on the substrate surface. The alkoxide solution must wet the substrate surface and solidify uniformly without precipitation.

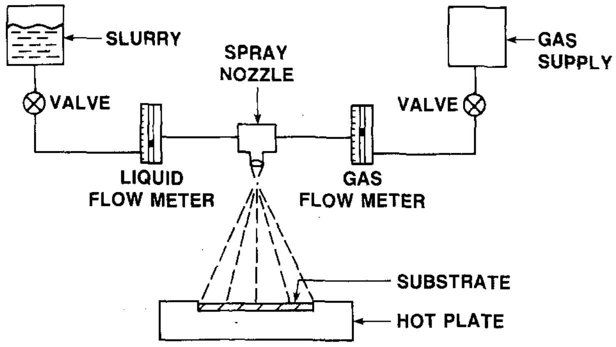

Figure 2 Spray deposition process for producing films and coatings.

2.6. Spraying

In this process, a thin coating is deposited by spraying [6–8] a slurry on a heated substrate, where the constituents react or thermally decompose into a coating material. Fig. 2 is a typical spray deposition process. Slurry constituents, atomization, nozzle-to-substrate distance, and substrate temperature are the important factors.

In this process (solar cells and mirrors), cadmium sulphide (CdS) [6], cadmium telluride (CdTe) [9], zinc oxide (ZnO) [10], zinc sulphide (ZnS) [11], indium sesquioxide (In_2O_3) and tin dioxide (SnO_2) [12] are fabricated by this relatively low-cost process.

3. CVD process

In CVD [13–17] or vapour plating, a volatile component of coating material is thermally decomposed, or it reacts with other vapours in the vapour phase or at the hot substrate surface so that the reaction product is deposited as a thin film or coating. If the reaction product is produced in the vapour phase, then it is a homogeneous nucleation process, and, if it is produced only at the hot substrate surface, then it is a heterogeneous nucleation process.

Pyrolysis is a particular type of CVD that takes place by thermal decomposition of volatile components on the substrate. Another CVD can take place by chemical reactions, such as oxidation, reduction, and reactions of chemicals with other gases: nitrogen, ammonia (NH_3), methane (CH_4), ethane (C_2H_4), water (H_2O), etc. In thermal decomposition, the substrate is normally heated above the gas decomposition temperature, and the rectant gases flow over

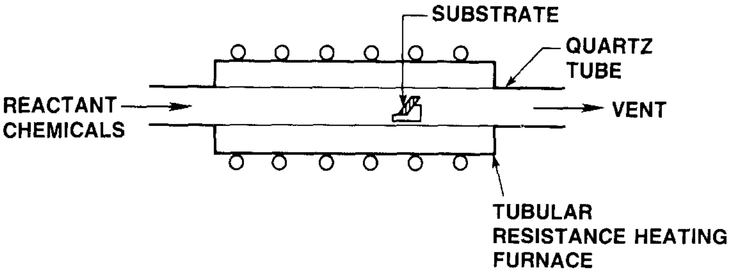

Figure 3 Resistance heating the substrate for the CVD process.

the hot substrate, decomposing into films or coatings. Examples are thermal decomposition of carbonyls, halides, and hydrides, and many organometallic compounds. In an oxidation reaction [18–21], metallic halides, such as tetrachlorides, can react with oxygen at an elevated temperature to produce corresponding oxides, such as silicon dioxide (SiO_2), titanium dioxide (TiO_2), germanium dioxide (GeO_2), etc.

Hydrogen is the reducing agent frequently used in CVD. Hydrogen reduction of metallic halides or hydrides can form metallic films or coatings, such as

$$WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g) \quad (1)$$

Besides hydrogen, other reducing agents, such as metallic vapours of cadmium, zinc, magnesium, sodium, and potassium, can be used with other vapours in CVD reactions. Zinc vapour is used to deposit silicon from silicon tetrachloride ($SiCl_4$) vapour.

Reactions with metallic halides or hydrides vapours with other gases, such as

(a) nitrogen and NH_3, produce metal nitride films or coatings:

$$3SiCl_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12HCl(g) \quad (2)$$

$$B_2H_6(g) + 2NH_3(g) \rightarrow 2BN(s) + 6H_2(g) \quad (3)$$

(b) CH_4 and C_2H_4 produce metal carbide films or coatings:

$$2SiH_4(g) + C_2H_4(g) \rightarrow 2SiC(s) + 6H_2(g) \quad (4)$$

$$WCl_6(g) + CH_4(g) + H_2(g) \rightarrow WC(s) + 6HCl(g) \quad (5)$$

(c) H_2O vapour to produce oxides by hydrolysis reaction:

$$SiCl_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4HCl(g) \quad (6)$$

Other types of chemical reactions involve direct reaction of vapours with the substrates, e.g. nitridation carburization, etc.

In the CVD process, the films or coatings are formed by nucleation and growth. The film's structure can be single crystal, polycrystal, or amorphous. The nature of the substrate surface has a definite effect on the structure of the film, for example, epitaxial films are produced on single-crystal substrates. Besides the substrate, the deposition temperature, concentration of reactants, gas flow and pressure, reactor geometry, and gas-flow dynamics can influence the film or coating characteristics. The deposition rate and uniformity depends mainly on the rate of mass transfer of reactants to the substrate surface and the rate of reaction of reactants at the substrate surface. At atmospheric-pressure CVD, these rates are usually the same order of magnitude. But in low-pressure CVD, a lower reactant gas pressure increases the mass transfer rate and produces uniform deposition.

The heat sources used in the CVD process play an important role in the coating process. Sections 3.1 to 3.5 discuss the various heat sources.

3.1. Resistance heating

A simple quartz tube is heated by a tubular-resistance furnace (Fig. 3). The substrate is placed at an angle inside the tube, over which the chemicals flow. The tube-wall temperature is monitored by a thermocouple and considered as the deposition temperature. For example: beta silicon nitride coatings [22] were recently produced by this technique using $SiCl_4$–NH_3 and nitrogen at 1300° C. It was found that if the temperature is lowered to 1150 and 1200° C, the formation of alfa and alfa plus beta phases predominate. The film formation inside the tube wall is the primary limitation of this process. This type of CVD reactor is called a hot-walled reactor. Film formation inside the tube wall can be avoided by using a cold-walled CVD reactor, in which the substrate-holder plate or the substrate itself is heated by resistance or other heating process, and the chemicals are passed over the hot substrate.

3.2. Infrared heating

Another way to avoid a hot-walled CVD reactor is to use an infrared (IR) heat source. Radiation can be passed through an IR-transmitting window and absorbed by the substrate or by the susceptor containing the substrates. Fig. 4 is a typical IR heating CVD

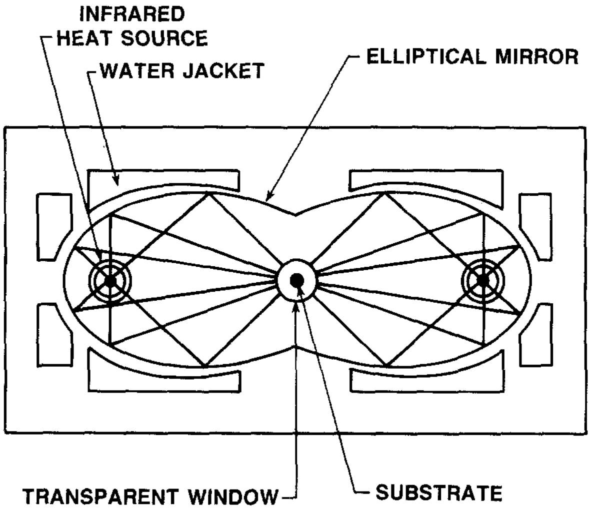

Figure 4 Dual elliptical infrared heating arrangements for the deposition of thin films.

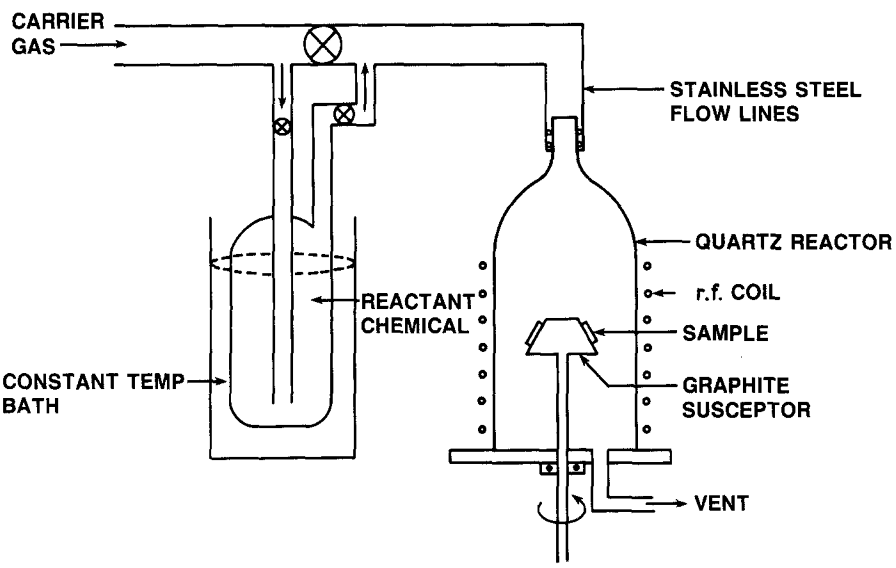

Figure 5 Cold walled CVD reactor and the induction heating assembly.

arrangement. The substrate is heated by infrared or quartz halogen lamps in elliptical mirrors. The mirrors may be single, dual, or quad elliptical, in which the lamps are located at a focal point of the ellipse. The wavelength of radiation should be such that the reactant gas molecules are not absorbed for premature reactions. Using an infrared-radiation-heated CVD reactor, a gallium-arsenide (GaAs) epitaxial layer [23] was recently grown.

3.3. Induction heating

Another cold-walled CVD reactor can be built by using radio frequency (r.f.) induction [24] in a CVD reactor. The samples are placed on the susceptor and the reactant gases are passed over the hot substrates (Fig. 5). Various films or coatings, such as aluminium, nickel, zinc oxide (ZnO), cadmium sulphide (CdS), GaAs, etc., on different substrates on a graphite susceptor, can be generated. For uniform thickness of the coating, the susceptor is usually rotated. Aluminium film can be deposited by thermal decomposition of trimethyl aluminium [24] or tri-isobutyl aluminium [25].

$$(C_4H_9)_3Al(g) \rightarrow (C_4H_9)_2AlH(g) \rightarrow Al(s) + 3/2H_2(g) + 3C_4H_8(g) \quad (7)$$

Nickel film can be deposited by the decomposition of nickel carbonyl [26]

$$Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g) \quad (8)$$

Zinc oxide, which is widely used thin-film material for electro-optic and photoconductive device applications, can be made by organometallic CVD reaction of diethyl zinc and water [27]:

$$(C_2H_5)_2Zn(g) + 2H_2O(g) \rightarrow Zn(OH)_2(g) + 2C_2H_6(g) \quad (9)$$

$$Zn(OH)_2(g) \rightarrow ZnO(s) + H_2O(g) \quad (10)$$

Epitaxial films for GaAs are grown by metallorganic CVD (MOCVD) reaction of trimethyl gallium and arsine [28, 29]:

$$(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4(g) \quad (11)$$

Cadmium sulphide films can be produced by reacting dimethyl cadmium ($(CH_3)_2Cd$) with hydrogen sulphide (H_2S):

$$(CH_3)_2Cd(g) + H_2S(g) \rightarrow CdS(s) + 2CH_4(g) \quad (12)$$

Many other organometallic or metallorganic chemicals can be used to produce films and coatings on various substrates. Dapkus [30] gives a recent review of MOCVD process.

3.4. Laser heating

The use of a laser as a CVD heat source has many advantages: (a) low-temperature CVD; (b) control of reaction zone; (c) homogeneous or heterogeneous chemical reactions; (d) precise process control; (e) high-quality of films or coatings; and (f) epitaxial growth, annealing, and diffusion of dopant films [31]. There are two ways to generate films or coatings by the laser CVD (LCVD) process:

1. Laser-induced homogeneous nucleation reaction by heating the reactant gases [32], which absorb a laser beam, reacts and deposits on a substrate.
2. Laser-induced heterogeneous nucleation reaction by heating the substrates, which absorb the laser beam, carrying out localized CVD reactions at the heated substrates [33–35].

3.4.1. Laser-induced homogeneous nucleation reaction

A continuous wave (CW) laser beam (10.6 μm wavelength) is passed through a transparent window and intersects the reactant gases in a perpendicular direction. The gases are heated by absorbing the laser beam and react to produce the film on the substrates, which is mounted on a stage positioned parallel to the laser beam axis (Fig. 6). The reaction zone can be controlled precisely by this process. As the reaction is taking place during the gas phase, it is regarded as homogeneous nucleation. High-quality silicon films [32] are produced by the pyrolysis of silane in a carbon dioxide (CO_2) laser beam., Deposition rates of 16 nm min^{-1} have been achieved. The deposition rate can be increased by increasing the chemical concentration, flow rate, substrate temperature, laser intensity, and gas pressure.

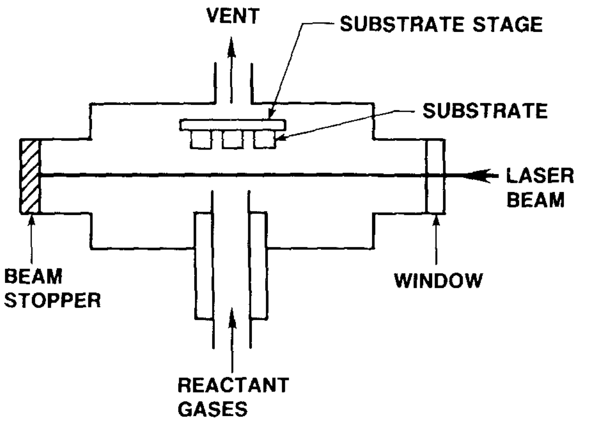

Figure 6 Laser-induced CVD reaction by homogeneous nucleation and reaction.

3.4.2. Laser-induced heterogeneous nucleation reaction

In this process, a CVD pyrolysis reaction takes place at the substrate surface, which is heated by absorbing the laser beam (Fig. 7). The absorptivities of the reactant gases and the substrates determine the type of lasers to be used in this process. Generally, the absorption peak at the CO_2 wavelength (10.6 μm) corresponds to insulating materials, such as ceramics, plastics etc., while an Nd : YAG laser (wavelength 1.06 μm) is more readily absorbed by conductive materials such as metals. Using a $CWCO_2$ laser and sodium-chloride (NaCl) window, nickel, TiO_2 and titanium carbide (TiC) were deposited [35] on a quartz substrate:

$$TiCl_4(g) + 2H_2(g) + 2CO_2(g) \rightarrow TiO_2(s) + 4HCl(g) + 2CO(g) \quad (13)$$

$$TiCl_4(g) + CH_4(g) \rightarrow TiC(s) + 4HCl(g) \quad (14)$$

Using a CW Nd:YAG laser, amorphous silicon films were deposited [36] on alumina substrates. The spot size and film thickness depend on irradiation time. Other films such as aluminium, carbon, boron, cadmium, chromium, germanium, iron, lead, silicon nitride (Si_3N_4), silicon carbide (SiC), tin oxide (SnO_2), titantium carbide (TiC), etc., were also produced.

3.5. Plasma heating

The use of electrical discharge (plasma) for depositing mainly amorphous films or coatings has been known for a long time. The nonequilibrium nature of plasma leads to dissociation of a gas and deposits films at a relatively low temperature compared to conventional CVD processes. At r.f., inductive or capacitive couplings are accomplished by passing the discharge tube through a waveguide. Fig. 8 illustrates simple inductive and capacitive coupling plasma reactors [37, 38]. Reactant gases are introduced where the discharge is active. The electrical power requirement for the discharge depends on the size of the reactors and mode of operation. By increasing the electrical power, a high degree of gas dissociation and eventually higher deposition rate of films can be achieved. The r.f. power supply (13.56 MHz [37, 39]) is commonly used. Reactor geometry, electrode configuration, power level, frequency, gas-flow rate, concentration, pressure and substrate temperature are the major variables for thin-film deposition by the plasma process.

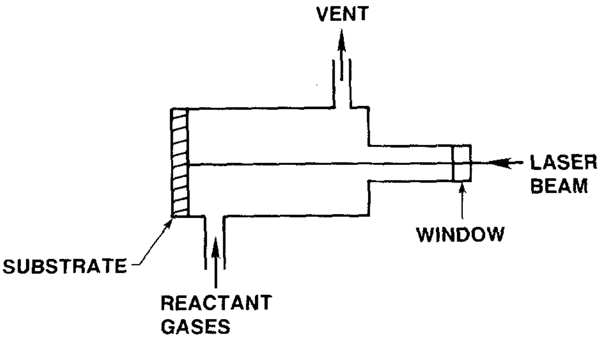

Figure 7 Laser-induced CVD reaction by heterogeneous nucleation and reaction.

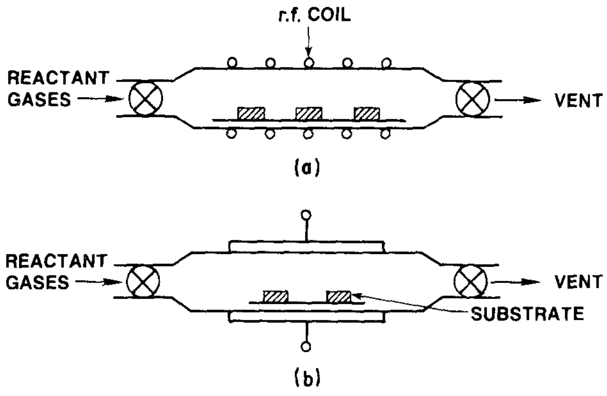

Figure 8 Simple inductive (a) and capacitive (b) plasma reactor configurations.

Diamond-like carbon films have been produced by ion-beam deposition [40] and r.f.-plasma deposition of butane [41–43] and alkanes [44]. Amorphous boron film can be produced by diborane (B_2H_6) [45] and boron trichloride (BCl_3) [46] in a discharge. Amorphous silicon and germanium films can be formed [47, 48] in r.f.-glow discharge by using silane (SiH_4), and germane. Amorphous arsenic films [49] were prepared from AsH_3 in argon glow discharge. Plasma deposition of silicon nitride films [47, 50–53] from silane, nitrogen and/or NH_3, has been extensively studied.

$$3SiH_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12H_2(g) \quad (15)$$

Plasma-deposited Si_3N_4 film can vary in stoichiometry [54]. The above reaction is followed by some intermediate reactions, e.g.

$$SiH_4(g) + NH_2(g) \rightarrow SiN(s) + 3H_2(g) \quad (16)$$

Initial Si_3N_4 deposition [47] was carried out in a quartz tube by decomposing silane and ammonia in a 1-MHz r.f. discharge with a deposition rate of 50 nm min^{-1}. The major effort now is concentrated in producing uniform Si_3N_4 films on silicon wafers [55] by using similar chemicals and controlling gas-flow uniformity.

Other nitride films, such as aluminium nitride (AlN), boron nitride (BN), phosphorous nitride (P_3N_5), can be produced by using the plasma CVD process. Aluminium nitride was prepared [38] by introducing a mixture of aluminium trichloride ($AlCl_3$) and nitrogen in a 3 MHz externally excited discharge. Boron nitride films were prepared [56] by reacting

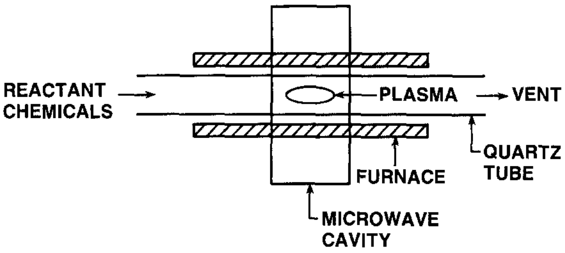

Figure 9 Plasma activated CVD process for producing optical waveguides.

diborane and ammonia in a plasma at 1000° C on various substrates on a graphite susceptor in a horizontal-tube reactor. The films were smooth, transparent, and exhibited improved properties compared to similar films made by high-temperature CVD process. Amorphous, transparent glass-like P_3N_5 films, were produced [57] by directly vapourizing elemental phosphorus in a nitrogen plasma, and decomposing phosphine and nitrogen in an r.f. plasma.

Amorphous SiC films were produced by flowing silane and methane [47] and ethane [58, 59] through an r.f. discharge. Titanium carbide films [60] were grown by a plasma CVD of titanium tetrachloride ($TiCl_4$), C_2H_6, and a hydrogen/argon mixture.

Silicon dioxide films were produced in a glow discharge by using SiH_4 and an oxidizing agent [61]. Similar films were also grown by using alkoxysilane [62] and oxygen. Recent, SiO_2 and GeO_2 films were grown by a plasma activated CVD process [63] inside a quartz tube, which was then collapsed into a transparent solid preform from which optical waveguide fibres were drawn. Fig. 9 illustrates the experimental apparatus. The quartz tube (8 mm o.d. with 1 mm wall), surrounded by a microwave cavity connected to a 2.45 GHz generator, maintains non-isothermal plasma within it. The tube temperature is controlled by an additional furnace. Silicon tetrachloride and oxygen are passed through the plasma, where the oxidation reaction takes place and films are deposited inside the wall of the quartz tube when the microwave cavity is moved along the tube axis:

$$SiCl_4/GeCl_4(g) + O_2(g) \rightarrow SiO_2/GeO_2(s) + 2Cl_2(g) \quad (17)$$

Another r.f. plasma process [64] to make optical waveguide preforms uses an oxygen plasma, which also is generated inside a quartz tube. The plasma is located at least 1 cm away from the tube wall, so that deposit vaporization and tube distortion due to high-plasma temperatures can be prevented. Similar chemicals are fed into the plasma, and the deposited films inside the tube are sintered by using a flame torch to form the transparent glass (Fig. 10).

Besides SiO_2 and GeO_2, amorphous alumina films [65] were grown by using a glow discharge inside a silica tube. The dissociation of $AlCl_3$ in oxygen plasma produced alumina film:

$$4AlCl_3(g) + 3O_2(g) \rightarrow 2Al_2O_3(s) + 6Cl_2(g) \quad (18)$$

Other oxide films of boron, titanium and tin are prepared [66] in microwave discharges by decomposing corresponding alkyls or alkoxides.

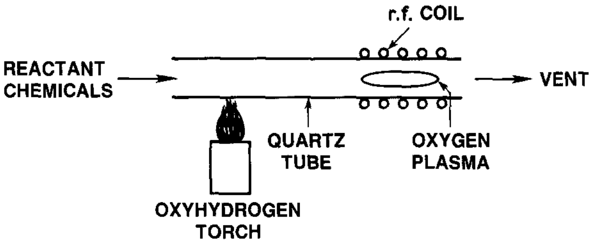

Figure 10 Simultaneous plasma CVD and sintering of glassy films to fabricate optical waveguide preforms.

4. Conclusions

Deposition of film and coating processes include evaporation, ion plating, sputtering, plating, dipping, and spraying. They are termed here the non-CVD processes. They are mostly limited to low-melting materials, and some of them are used only for metallic films or coatings. However, the CVD process has the unique advantage of depositing low- and high-temperature melting metallic and dielectric materials. Chemical vapour deposition is divided into two types of reaction process: thermal decomposition and chemical reactions that include oxidation, reduction, and reactions among different gases. If the reaction product is formed in the gas phase, followed by deposition on a substrate, it is called homogeneous nucleation. If the reaction product is formed at the substrate surface that provides the nucleation site, it is called heterogeneous nucleation.

The heat sources used in CVD are most important to the process and product development. Resistant heating of vapours normally produces metallic or dielectric films. Most of the heterogeneous CVD reactions take place by using infrared and induction heat sources that preferentially heat the substrate surface by using IR lamps, r.f. and laser beam. The reactant chemicals are then flown over the hot substrates to produce thin films or coatings. Heterogeneous CVD reactions are important for uniform deposition on complex substrate geometries. The low-temperature CVD process, important for temperature-sensitive substrates or electronic devices, can be accomplished by using the laser beam and plasma heating processes. A variety of films and coatings of metals, oxides, carbides, nitrides, etc. can be produced by the CVD process for many different applications, such as electronic devices, device passivation, solar cells, etc. The latest research and development is directed toward achieving defect-free uniform films and coatings on different substrates with high deposition rate for low-cost, mass-scale production.

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