

CHAPTER I

INTRODUCTION

1.1 Types of Thin-Film Deposition

1.1.1 Physical Vapor Deposition (PVD)

The basic PVD process is classified into two general categories: sputtering and evaporation. The PVD process is used to produce the high temperature superconducting film. Generally, PVD can produce film thickness in the range 10^{-10} to 10^{-3} m. The advent of an electron beam-heated source makes it possible to generate the very high deposition rate in the range of $\mu\text{m}/\text{sec}$. A very large number of inorganic materials, metals, alloys, compounds, and mixtures as well as organic materials, can be deposited by PVD technology. The source of the depositing species are usually in the form of evaporating or sputtering gases or vapors.

1.1.1.1 Sputtering Deposition. Sputtering is the momentum transferring from an indirect energetic projectile, such as an ion, to a solid or liquid target, resulting in the ejection of surface atoms or molecules. Both the target and substrate are placed facing each other in the vacuum chamber (Figure 1.1) which is normally evacuated to a pressure of 10^{-2} to 10^{-5} Pa. A negative voltage is supplied to the target (cathode). A glow discharge is initiated after an inert gas (usually argon) is introduced into the evacuated chamber with the typical working pressure of 2.5 to 2.0 Pa. An example of equipment set up for sputtering deposition is shown in Figure 1.1.

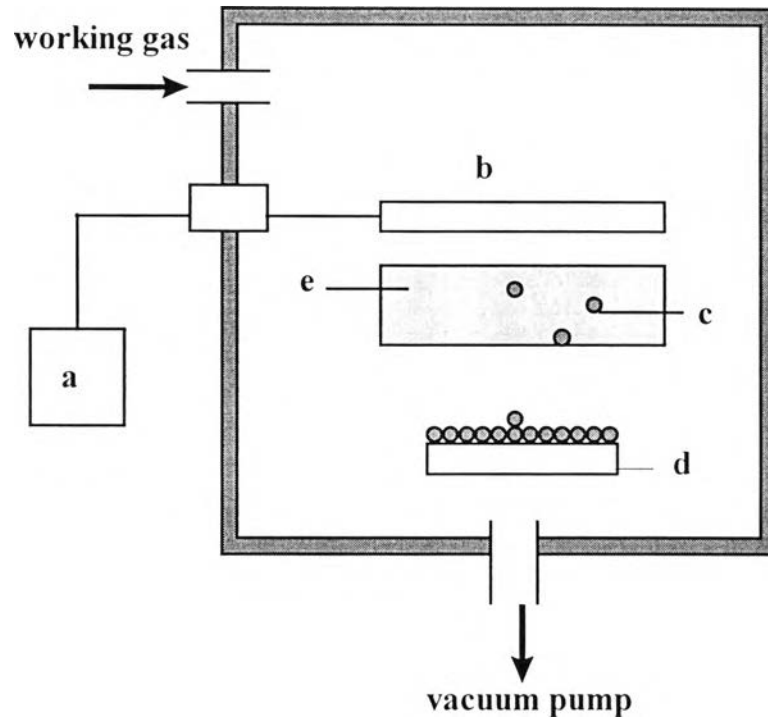


Figure 1.1 Sputter deposition process (a) Power supply;
(b) Cathode (target); (c) Ion; (d) Anode Substrate; (e) Plasma.

1.1.1.2 Evaporation Deposition. In the evaporation process, vapor is produced from a material located in a source which is heated by various methods (Figure 1.2). The deposition system consists of an electron beam-bombardment heated evaporation source to vaporize the desired material. The substrate is located at an appropriate distance facing the evaporation source. Resistance induction, cathodic and anodic arc, electron beam, or lasers, are the possible heat sources. The substrate can be heated and/or biased to the desired potential with a d.c./r.f. power supply. Evaporation is carried out in vacuum at 10^{-3} to 10^{-8} Pa. In this pressure range, the mean free path is very large (5×10^{-2} to 10^{-7} cm.) compared with the source-substrate distance. Hence the evaporated atoms essentially undergo

collisionless transportation prior to condensation on the substrate, thus leading to thickness buildup directly above the source and decreasing steeply away from it.

One of the disadvantages for this techniques is the problem of droplet ejection from the target causing major flaws in th deposited film. One way around the droplet problem is the use of a filtered arc. where the ion stream from the cathodic arc is extracted by an electromagnetic field and the ions are condensed to deposit a film.

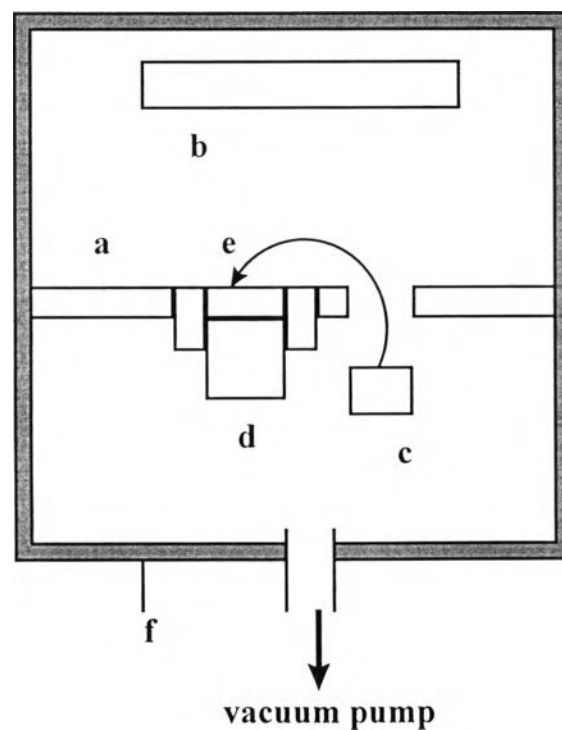


Figure 1.2 Evaporation deposition process with an electron beam source
(a) Separator plate; (b) Substrate; (c) Electron beam gun;
(d) Ingot rod; (e) Molten pool; (f) Vacuum chamber.

1.1.2 Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) produces thin films from the gas phase with thickness in the range ca. 0.1-10 μm by means of chemical. Typical pressure ranges are different from those used in PVD (<1 hPa); ca. 1-50 hPa for low-pressure CVD, 50 to <1000 hPa for medium-pressure CVD, and atmospheric pressure for atmospheric CVD. Accordingly, the *Knudsen number* (λ/d) [the ratio of the mean free path of molecules in the gas phase to a typical reactor dimension] is small, and diffusion and convection processes are the main transport mechanisms.

In contrast to chemical transport processes, CVD is an open system with a gas inlet and outlet. The equipment (Figure 1.3) has the following main parts: a gasification system (a, b, c, j), a chemical reactor which contains the samples to be coated (d, e, f), and an exhaust system for the reacted gas (g, h, i). Precursor compounds can be inorganic (e.g., halides, hydrides, carbonyls) or organic (alkyls, β -diketonates, alkoxides or organometalics) materials. Almost all compounds can be deposited by CVD, provided the material can be generated in the gas phase. Usually, the possibility of depositing material from a gas mixture and the expected phase composition can be calculated by thermodynamic equilibrium calculation to minimize the Gibbs energy. These estimates are especially suitable for CVD processes at high deposition temperature (e.g., SiC deposition at ca. 1000 C). At low temperature, kinetic effects are often important, and the deposition of metastable phases (e.g., amorphous SiO_2 phase) is possible.

The structure of the coating is the result of several steps: adsorption-desorption processes, surface reaction, surface diffusion, nucleation, growth of critical nuclei, layer formation, and aging processes in the layer during deposition. The result is often the formation of preferred orientations of the deposited layer on crystalline and amorphous substrates,

depending on the deposition conditions. On monocrystalline substrates, epitaxy is possible since the lattice misfit is not too large.

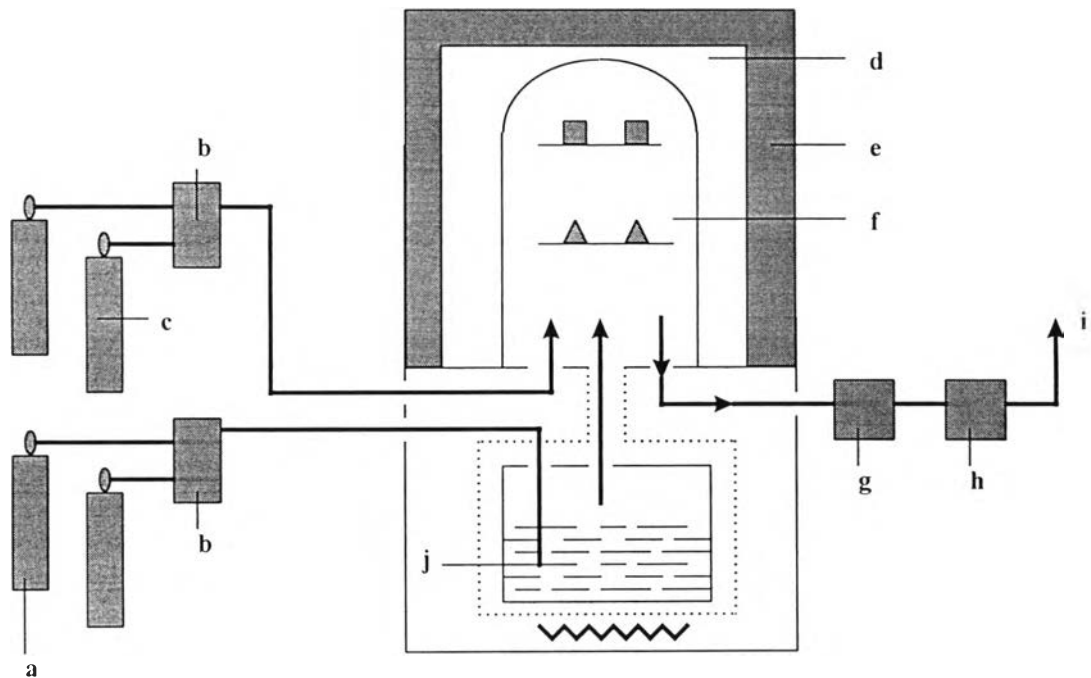


Figure 1.3 CVD system for deposition on tools (e.g., TiN, TiC); (a) Gases; (b) Gas control unit; (c) Gas for evaporation unit or precursor gases; (d) Interspace to remove reactor from the heating system for cooling; (e) Heating system; (f) Deposition reactor (hot-wall reactor); (g) Filter; (h) Pump; (i) Ventilation; (j) Evaporator (liquid or solid).

There are a number of methods used to activate the chemical reactions necessary for deposition. Some of them are described below.

- Thermal CVD.

To generate the homogeneous reaction or surface for layer formation, the thermal CVD is introduced by heating the reactor, including samples (hot-wall reactor; Figure 1.3) or heating the sample only (cold wall process) to the deposition temperature. These processes have the ideal temperature dependence which affects the constant film thickness requirement.

- Plasma CVD.

Due to the very high temperature of the conventional CVD; plasma-activated-enhanced CVD has been developed to decrease the deposition temperature. A plasma is defined as an electrically neutral gas in which neutral species, ions, and electrons are all present. They are ignited by d.c. and a.c. for positive ions and insulating coating respectively. Plasma CVD process are used for the production of hard coatings on steel and on the electronics industry.

1.1.3 Plasma Polymerization

Plasma polymerization refers to the formation of polymeric films on surfaces in proximity to a low-pressure glow discharge in an organic or organometallic vapor. The deposited film from this technique have these following unique properties: thickness up to ca. 2 μm , good adhesion to a variety of substrate, and variable physical properties such as hardness. There are several parameters are known to affect the polymerization process, such as pressure, flow rate, power and frequency of the discharge, and reactor geometry.

A typical bell jar reactor with horizontal, parallel plate electrode (Figure 1.4) is designed for deposition of fluorinated polymers from tetrafluoroethylene (TFE) and chlorotrifluoroethylene (CTFE) monomers. Normally, the reactor must have a good vacuum integrity.

Unlike conventional condensed-phase polymerization, which requires the monomer to contain one or more unsaturated functional groups, no such restriction applies to plasma polymerization and almost any organic molecule with a vapor pressure of a few hundred Pascals is amenable to this treatment. The widely used monomers are as follows; hydrocarbons, fluorocarbons, silane and silicon compounds (siloxanes and silazines), and organometallic species.

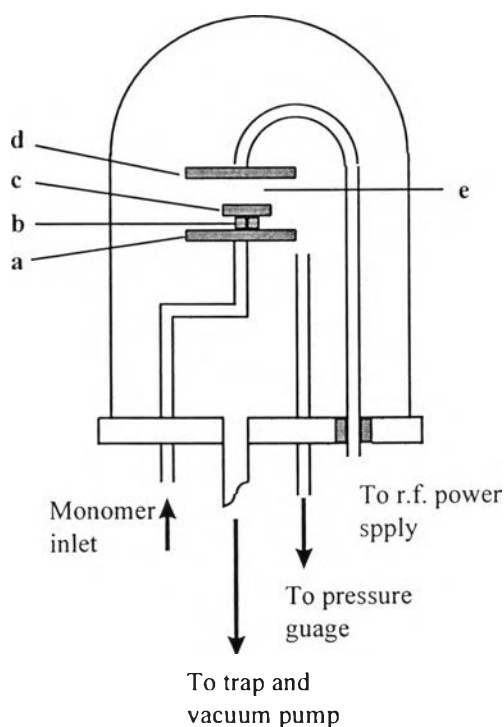


Figure 1.4 Parallel plate capacitively coupled plasma reactor.(a) Ground electrode; (b) Support pedestal; (c) Optical crystal; (d) Hot electrode; (e) Plasma.

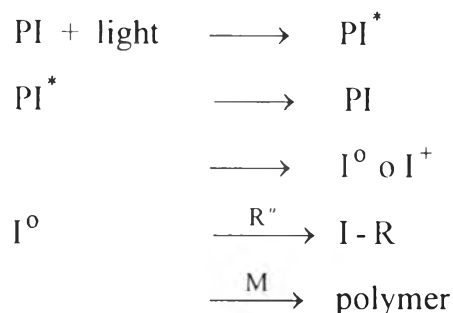
1.2 Photopolymerization

Photopolymerization is the kind of polymerization which utilizes the electromagnetic irradiation (or light) as the energy source for the polymerization of functional monomers and oligomers. It is the basis of many important commercial processes with very wide applications. An example is UV curing of coating. Typical process usually involves the absorption of light by a photoinitiator to initiate polymerization reaction.

1.2.1 Photoinitiator

A photoinitiator is a chemical substance which absorbs light in UV spectral range (250 to 450 nm) and then converts this energy into chemical energy in the form of reactive intermediates such as free radicals and reactive cations, which subsequently initiate polymerization of functional monomers and oligomers. Normally monofunctional monomers form a linear polymer, whereas multifunctional monomers form the three dimensional cross-linked networks.

1.2.1.1 General Mechanism. For the photoinitiator to be effective, the radiation from the light source must overlap with the absorption band characteristic of the photoinitiator. The mechanism consists of raising the photoinitiator (PI) to an electronically excited state of (PI*). The life time of the excited state (PI*) is short, generally less than 10^{-6} sec. The excited state can undergo two types of reaction: decaying back to PI (with emission of light and heat) or entering a chemical reaction yielding a reactive intermediate, such as I° or I^+ . The reactive intermediate, e.g. I° , can in turn react with another radical R° or initiate polymerization of a monomer M as shown in the following reaction schemes.

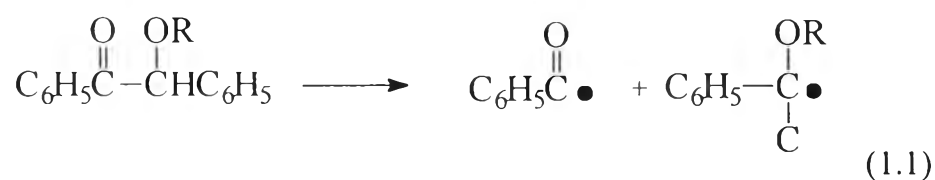


1.2.1.2 Air Inhibition. Photoinitiated polymerization conducted in air is complicated. Oxygen can deactivate the initiation mechanism on both photoinitiator species (PI^*) and even initiator radical species (I°). These undesirable reactions with O_2 occur primarily at the air interface, where the air concentration of O_2 is highest, and thereby retarding the surface curing. The common way to minimize this effect is to increase the incident intensity and/or the PI concentration which will increase the absorptivity. However, the increasing of PI concentration reduces the light availability at the lower layers which may retard curing resulting in poor mechanical properties as well as poor adhesion.

Another way to solve this side effect is by utilizing the photoinitiators with absorption bands in two regions corresponding to two different emission lines from the light source. The low molar absorptivity (ϵ) produces the uniform absorption curing, whereas the high molar absorptivity provides the high intensity at the surface to counteract the air inhibition.

The problems of air inhibition may be eliminated by conducting the photo-polymerization *in vacuo* or in an inert atmosphere, such as N_2 . Under these conditions, lower intensity light source and lower PI concentration may be used. Nevertheless, cost factor favors photo-polymerization in air when feasible.

1.2.1.3 *Important Types of Photoinitiator.* One kind of widely used photoinitiator is the intramolecular bond cleavage consisting of “notable α -cleavage of an aromatic ketone group”. Benzoin is a well-known photoinitiator and is more efficient than the diketone benzil. Benzoin ether, which is much used in photocuring processes, undergoes dissociation into two different radicals as shown in equation 1.1.



Recently, it has been reported that both types of radical can initiate polymerization at high concentrations of acrylates and methacrylates, and at high radical and low concentration of styrene monomer. The main initiator is the benzoyl radical with the ether radical entering into termination reactions. Other well-established photoinitiators of this type are shown in Figure 1.5.

Darocure has been used in laser flash photolysis to photocleave into benzoyl and dimethylhydroxymethyl radicals. Furthermore, Darocure and Irgacure are considered to have the advantage of minimizing yellowing in photocuring.

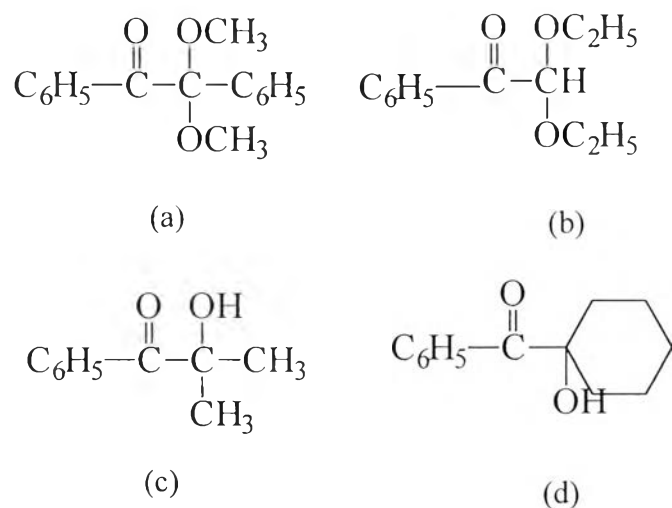


Figure 1.5 Structures of benzoin photoinitiator

(a) DMPS; (b) DEAP; (c) Darocure; (d) Irgacure.

Two new types of photoinitiator have recently been introduced viz. acylphosphine oxide and acylphosphonates as shown below. Some chemicals of this type absorb light relatively strongly between 350 and 400 nm, and can be used in pigment coating. They show negligible yellowing.

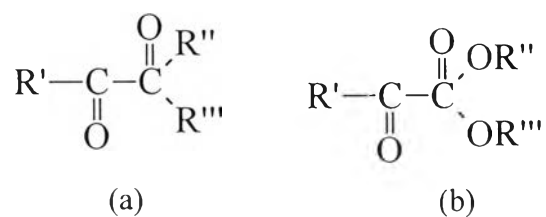


Figure 1.6 Structures of (a) acylphosphine oxide ; (b) acylphosphonates.

1.3 Atmospheric-Pressure Vapor-Phase Polymerization

An atmospheric-pressure vapor-phase polymerization technique has recently been reported in the deposition of thin-film coating onto polyester film and poly(vinyl) film. The conventional system is shown in Figure 1.7.

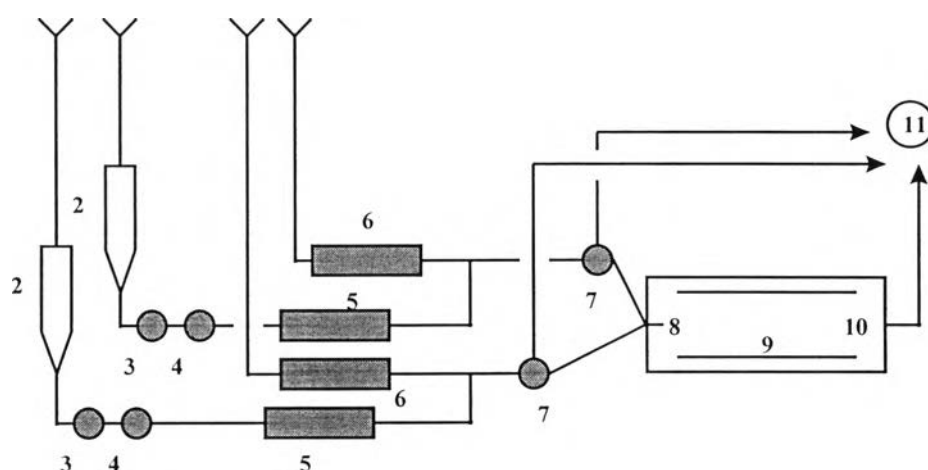


Figure 1.7 Schematic diagram of a vapor-phase deposition system: (1) dry N₂ source; (2) liquid monomer storage container; (3) metering valves; (4) calibration dump valve; (5) vaporizer; (6) N₂ heater; (7) bypass valve; (8) reactor “Y”; (9) film substrate; (10) reactor; (11) cyclone, bag collector, and water scubber.

In this system, the liquid monomer is metered into the vaporizer before mixed with a carrier gas which is usually an inert gas such as nitrogen. The two vapor streams are mixed at one end of the reactor at a “Y” stainless steel tubing before introducing into the chamber. The monomer is then deposited onto a substrate and the exhaust gas exits at the opposite end of the reactor. A similar apparatus set up was used in the present study.

1.4 Objective

The objective of this work is to develop a thin-film vapor deposition system under atmospheric pressure and to study the effects of deposition time, irradiation intensity, substrate temperature and vapor flow rate on the deposition process.