

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Chemical Vapor Deposition (CVD)

Chemical vapor deposition of thin-film can be divided into three different types as follows (George, 1992):

##### 2.1.1 Thermal Chemical Vapor Deposition

In this technique, the surface reaction necessary for layer formation is thermally activated by heating the reactor and the sample (hot-wall reactor) or by heating the sample only (cold-wall process). These processes have the ideal temperature dependence necessary to meet the constant film thickness requirement.

##### 2.1.2 Plasma Chemical Vapor Deposition

This method has been developed to decrease the deposition temperature. A plasma is an electrically neutral gas in which neutral species, ions, and electrons are all present. Plasma are ignited by d.c. or a.c. In d.c. discharges, the sample is the cathode and the discharge is ignited between the cathod and the anode.

##### 2.1.3 Photochemical Vapor Deposition

Photochemical vapor deposition is an attractive vapor deposition technique for the preparation of high quality thin-film using low temperature with low energy requirement. The photochemical deposition takes place

through high energy photons which selectively excite the molecules absorbed on the surface or the gas phase molecules, leading to bond rupture and the production of free radicals. These radicals help to initiate reactions to form films on the substrate surface. This process is highly dependent on the wavelength of the incident radiation. Photochemical deposition can be achieved with either a laser or an ultraviolet lamp.

Recently Kim et al. (1988) prepared for the first time an undoped a-Si:H film by atmospheric pressure mercury-sensitized photo CVD as shown in Figure 2.1. Ar was used as the carrier gas for introducing  $\text{SiH}_4$  into the deposition chamber and a low pressure mercury lamp with radiations of  $2537 \text{ \AA}$  and  $1849 \text{ \AA}$  was used. It was found that the concentration of oxygen in the film was much lower than that of the film grown by low pressure photo CVD.

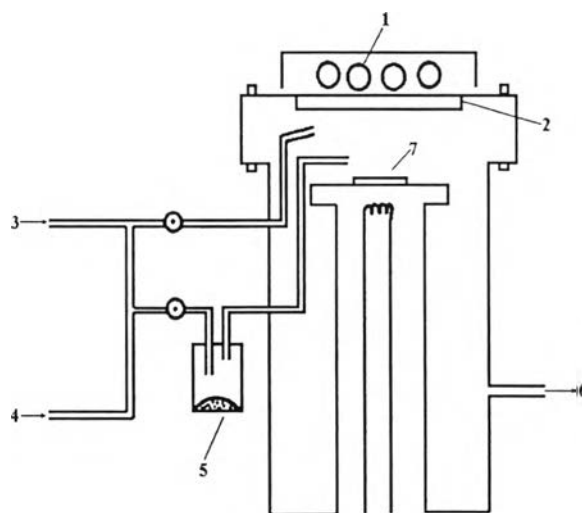


Figure 2.1 Schematic diagram of the set up for atmospheric pressure mercury sensitized photo CVD preparation of undoped a-Si:H films: (1) mercury lamp; (2) Quartz glass; (3) Ar inlet; (4)  $\text{SiH}_4$  inlet; (5) mercury; (6) exhaust; (7) substrate (Data from Kim et al. (1988)).

## 2.2 Polymer Film

Chemical vapor deposition is applied in industrial polymer processing by exposing organic materials to various forms of energy, such as electron bombardment, ultraviolet light, and glow discharge, to initiate polymerization of monomer resulting in the formation of a polymer film on substrate surface. Many applications make use of polymer thin-films. Examples are:

- printing ink drying in the printing industry,
- screen printing on glass,
- paint curing in the timber and furniture industries,
- adhesive curing and surface hardening,
- exposure of photopolymer layers in the reprography, microelectronic and silicon chip industries.

The advantages of this system are high quality film, room temperature treatment, non-polluting with solvent free formulations, and low costs. The polymerization of monomer to form a polymer film can be achieved by several techniques as described below.

### 2.2.1 Glow Discharge Polymerization

This technique involves the formation of polymeric film on surface in proximity to a low-pressure glow discharge in an organic or organometallic vapor. Films are produced with monomer pressure in the range 0.1 – 10 torr and an electrode gap of 5-40 mm (Goodman, 1960). The apparatus used is shown in Figure 2.2.

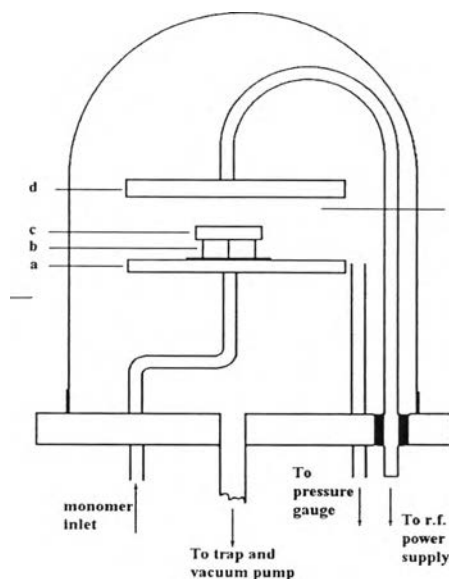


Figure 2.2 Parallel plate capacitively coupled plasma reactor, (a) Ground electrode; (b) Support pedestal; (c) Optical crystal; (d) Hot electrode; (e) Plasma.

### 2.2.2 Polymerization by Electron Bombardment

Since the first use of the electron microscope, production of polymer films has been observed at the anode. In 1953 Poole suggested that film formation arose from the interaction of electrons with residual oil vapors in the electron tube system. Buck and Shoulders (1958) demonstrated that polymer could be deposited in a controlled manner under an electron beam.

Figure 2.3 shows a typical form of apparatus. The electron gun and substrate, on which the film is to be deposited, are located inside a vacuum chamber where the pressure can be reduced to  $10^{-7}$  torr. Any material can be used as substrate which can be cooled to prevent excessive temperature rise on bombardment. The electron beam is obtained either from a flooding electron gun or a scanning electron gun as used in a cathode ray tube.

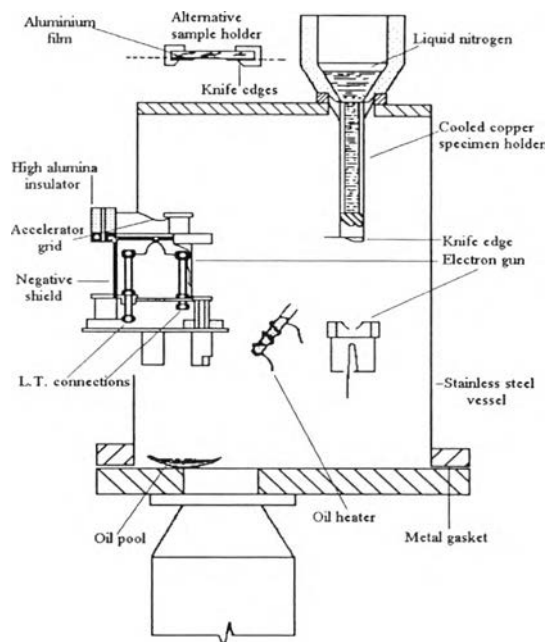


Figure 2.3 Schematic diagram of system for producing thin films by electron bombardment.

Haller and White (1963) examined the kinetics of the reaction to elucidate the mechanism of polymer formation on surface under electron bombardment using butadiene monomer. It is found that polybutadiene film was formed on a surface exposed to 250-eV electrons with butadiene vapor at a pressure between  $3 \times 10^{-4}$  and  $10^{-6}$  torr. The rate of growth for transparent film was found to be proportional to the square root of the current density and the rate increased with increasing pressure.

### 2.2.3 Polymerization by Heated Filament

This technique refers to the formation of polymeric film on surface with polymerization initiated by a linear tungsten filament.

Tamada et. al. (1991) studied polymerization of poly(octadecyl methacrylate) using the physical vapor deposition technique. The initiation

and polymerization reactions were investigated to determine the effects of filament temperature, deposition rate, and substrate temperature on polymer yield, thickness, and orientation. It was found that radical-initiated polymerization of octadecyl methacrylate (ODMA) occurred during its deposition. The polymer yield increased in conditions of high filament temperature, low density, and high substrate temperature. Low deposition rate and high temperature (up to 280 K) affected the orientation of the deposited film.

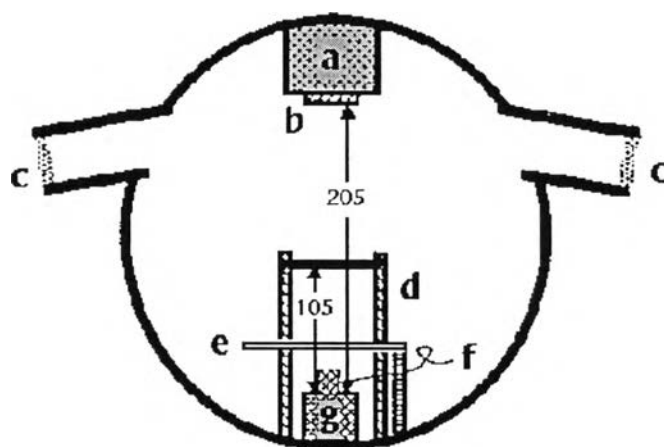


Figure 2.4 Inner layout of apparatus for VDP: (a) stage for substrate; (b) Ag coated glass slide; (c) thickness monitor; (d) electrodes; (e) tungsten filament; (f) Shutter; (g) crucible; (h) hot plate.

Tamada et. al. (1994) prepared a thin polymer film of N-methylacrylamide with vapor deposition polymerization based on a technique which combined physical vapor deposition with thermal vapor deposition as shown in Figure 2.4. The chemical structure of deposited film at various filament temperatures was investigated by Infrared spectrometer in the

reflection absorption mode. It was found that, at filament temperature of 2300 K, the polymerization stopped increasing. The deposition rate increased with increment of the filament temperature. At 2300 K, the deposition rate was independent of the electric field supplied for deposition. In the case of coevaporation with hydroquinone, the rise of filament temperature did not effect the deposition rate. The maximum polymer yield and molecular weight were 25% and  $2.1 \times 10^4$  respectively at the filament temperature of 2300 K.

#### 2.2.4 Photolytic polymerization

The essential features of an apparatus for thin film deposition by photolytic means is shown in Figure 2.5. A medium pressure mercury arc, which emits strongly in the ultraviolet region, is focussed through a quartz window onto a substrate contained inside a bell jar while the pressure is reduced to  $10^{-6}$  torr. It is also usual to incorporate a metal evaporation source for preparing suitable surface on which polymer is deposited.

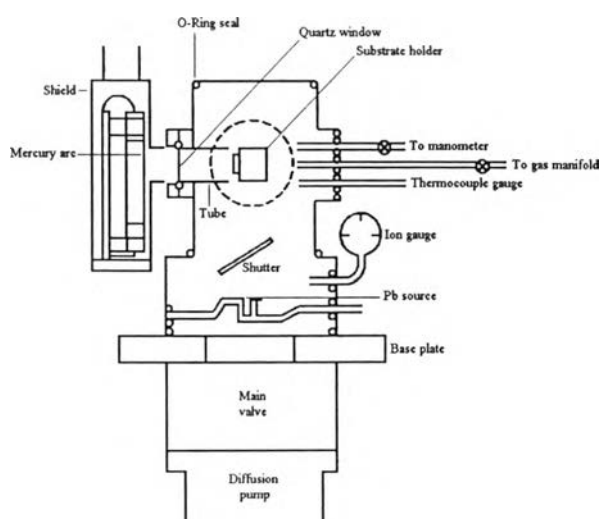


Figure 2.5 Schematic diagram of ultra-violet photolysis system. (Data from Mearns, (1969)).

Lind and Livingston (1930) observed that the polymerization of acetylene on a solid resembling cuprene can be induced either by activated mercury atom or by the direct absorption of ultraviolet light. The rate of polymerization was found to be proportional to the intensity of the absorbed light but independent of the acetylene pressure.

Wright (1967) has shown that gaseous 1,3-butadiene in contact with metallic substrate polymerized under the influence of ultraviolet light. This experiment used 700W medium pressure Hanovia mercury arc lamp with effective ultraviolet radiation over the range 2000-3500Å°. The system is pre-evacuated to a pressure of about  $10^{-6}$  torr to remove water vapor, and the gaseous monomer was then maintained at a pressure of about 4 torr during the irradiation. The growth rate for photopolymerization was found to exhibit a negative dependence on substrate temperature. It was found that when the film thickness was greater than about 5000 Å°, the film was unstable in the presence of air or moisture at high temperatures.

Recently Ranby (1985) developed a new method for surface modification of polymer by surface photografting. This work started with UV curing of surface coating by batch process in which the initiator and monomer were transferred through the vapor phase to the substrate surface. It was found that the reaction formed a very thin grafted coating of 2 to 10 nm thickness.

### **2.3 Poly(methyl methacrylate)**

Methyl methacrylate monomer can polymerize readily in the presence of UV radiation and heat. In commercial product, the monomer is supplied with up to 0.10% of an inhibitor such as hydroquinone (HQ) to prevent



polymerization. The inhibitor can be removed by distillation under reduced pressure or, in some case, by washing with an alkaline solution.

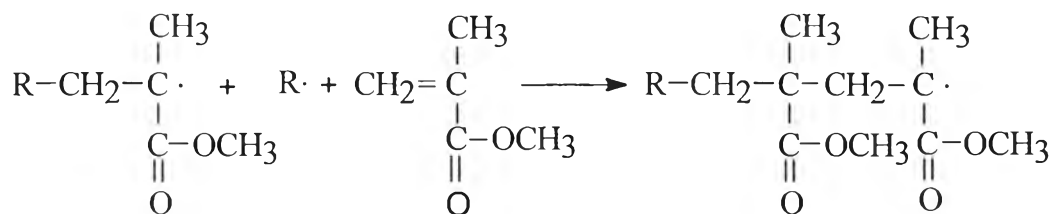
### Polymerization of methyl methacrylate

Free radical polymerization of MMA occurs in 3 steps as shown in the following reactions :

#### 1) Initiation



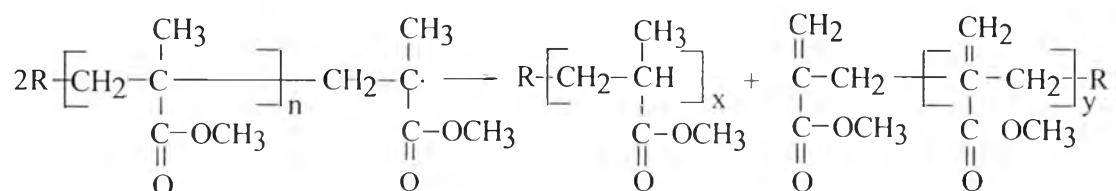
#### 2) Chain propagation



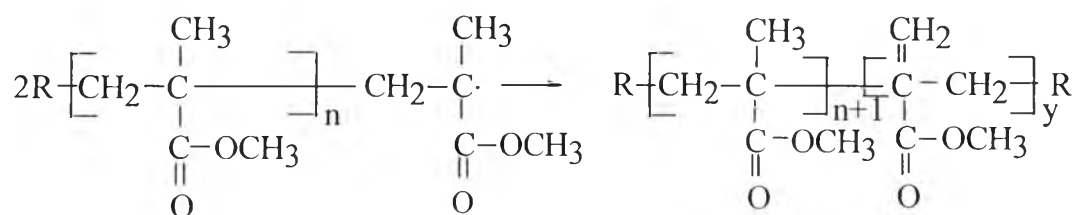
#### 3) Termination

Termination of MMA polymerization can occur in two ways: by combination or disproportionation.

Termination by disproportionation



Termination by combination



For MMA polymerization, chain termination is a bimolecular reaction. A chain termination by elimination reaction does not occur.

## 2.4 Photoinitiators

Normally, photo-induced polymerization reaction concerns the creation of a polymer (P) through a chain reaction that has been initiated by light. According to the type of reactive species (radical or cation) formed on the monomer (M), the reaction is called radical or cationic polymerization.

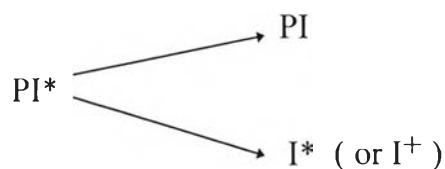




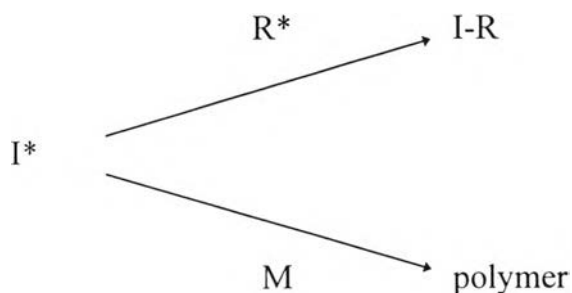
Since the direct formation of reactive species on the monomer by light absorption is not an efficient route, the initiation step of the polymerization reaction requires the presence of a photoinitiator (PI) :



The lifetime of  $PI^*$  is short, generally less than  $10^{-6}$  s. During this time,  $PI^*$  may participate in several processes: decaying back to PI (with emission of light and heat) or undergoing a chemical reaction yielding a reactive intermediate, such as  $I^*$  or  $I^+$ .



The intermediate  $I^*$  can either initiate polymerization by reacting with monomers, or react with another radical  $R^*$ .



In photolytic polymerization using a photoinitiator, it is important to fit the wavelength range of absorption of photoinitiator to the spectral range of the light source. Figure 2.6 shows the matching of absorption spectra of MMA and a photoinitiator with the radiation of a mercury lamp.

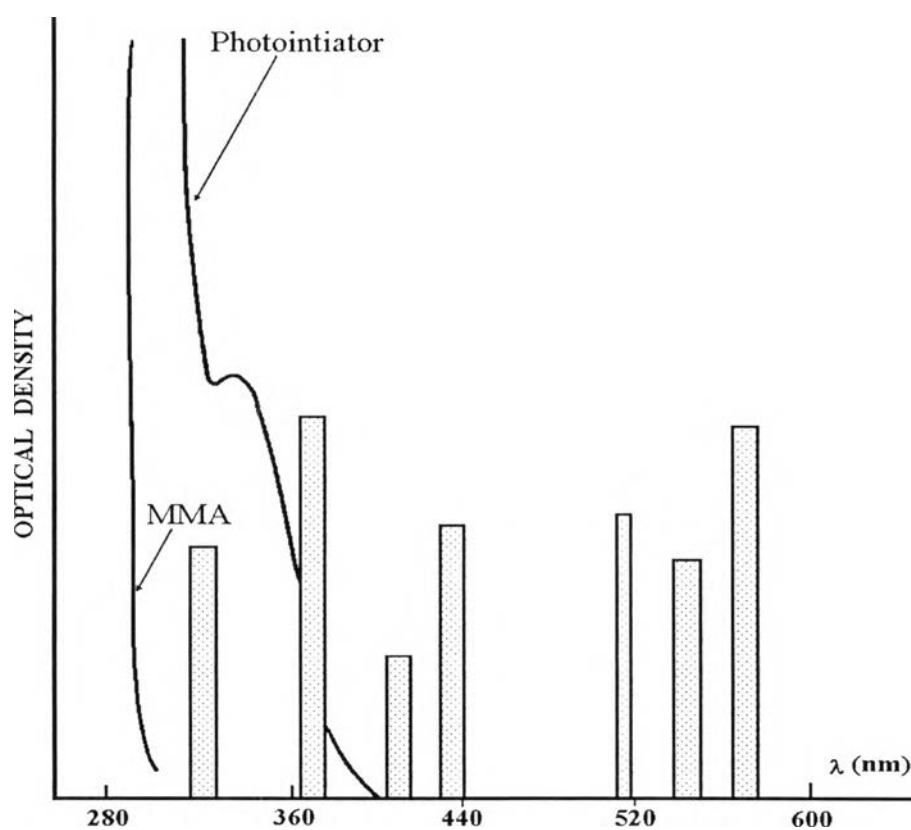


Figure 2.6 Absorption spectra of MMA and photoinitiator showing the matching effect with the emission spectra of a mercury lamp.

Chen et al. (1996) studied the rate of photochemical polymerization of styrene (St), *p*-chlorostyrene (Cl-St), methyl methacrylate (MMA) and butyl methacrylate (BMA) with polymethylephenylsilane (PMPS) as photoinitiator which shows maximum UV absorption at 334 nm. It was found that the polymerizations of St, Cl-St, MMA, and BMA with PMPS were different from those with AIBN as initiator. The initiator PMPS was found to give a greater

rate of initiation, a smaller rate constant of polymerization and termination, while a higher molecular weight polymer was obtained.