

CHAPTER II

LITERATURE SURVEY

2.1 Vapor Deposition Polymerization of Organic Monomer

Iijima and Takahashi (1997) fabricated the organic functional thin-film using the Vapor Deposition Polymerization (VDP) method. They determined the reaction rate and activation energy of the reaction by measuring the evaporation rate, vapor pressure and residence time of the monomers. An infrared reflection absorption spectroscopy (IR-RAS) was used to observe the deposition process.

Tamada et. al. (1994-1996) studied the VDP of various materials, such as N-methylolacrylamide and vinylcarbazole. Their VDP process was based on the technique which combined Physical Vapor Deposition (PVD) with Thermal Chemical Vapor Deposition (T-CVD). The deposition of these materials were real-time in-situ observed with infrared reflection absorption spectroscopy. The heated filament was used to activate the initiator for further polymerization. Polymer yield was obtained from Gel Permeation Chromatography (GPC) and via the indirect calculation from IR-RAS data. It was found that two ways of polymerization were possible, i.e. polymerization during the deposition and post polymerization. The results also show that polymerization can be initiated by the use of a heated filament.

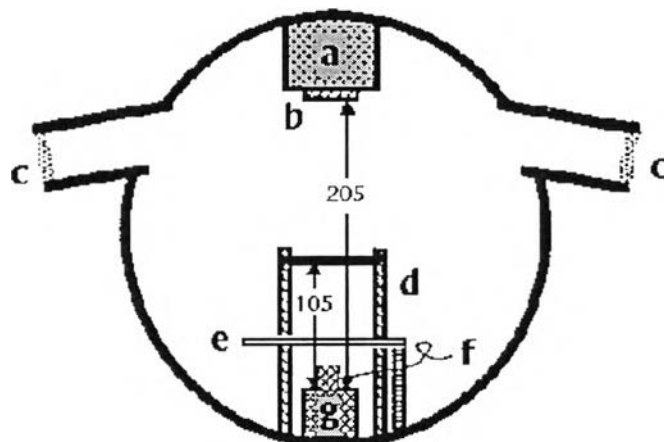


Figure 2.1 Chamber of vapor deposition polymerization designed by Tamada et. al. (a) substrate holder; (b) substrate; (c) ZnSe (IR window); (d) heated filament (wolfram); (e) shutter; (f) monomer container; (g) monomer heating source.

Takahashi et. al. (1993) determined the evaporation rate and vapor-pressure of organic monomers used for vapor deposition polymerization. The thermogravimetry and the Langmuir equation were employed for the determination of the temperature dependence of the evaporation rate and standard pressure of monomers used in vapor deposition polymerization. The ranges of the evaporation rate and saturated pressure of monomer determined by TG technique were found to vary from 10^{-2} to 10^{-5} mol/M².s and 1 to 10^{-3} Pa respectively. Comparison of the evaporation rate against temperature and the melting point of monomer determined whether the evaporation involved sublimation from a solid surface or evaporation from a liquid surface.

Tamada et. al. (1991) deposited octadecyl methacrylate (ODMA) monomer in the presence of a heated-wolfram filament. The polymer yield was found to increase in conditions of high filament temperature, low deposition rate and high substrate temperature. Moreover, the low deposition

rate and high temperature (up to 280 K) were found to affect the orientation of deposited thin-film. A low degree of supersaturation led to high polymer yields and improved orientation. Thus, the annealed deposited film had a structure like that of a Langmuir-Blodgett (LB) film.

Takahashi and Iijima (1991) prepared an ultrathin film of aromatic polyamides and aromatic poly(amide-imides) via the VDP technique. In their work an aromatic amine with terephthaloyl chloride was evaporated under reduced pressure to produce an ultrathin polyimide film on substrate. The evaporation of 4-(chloroformyl)-phthalic anhydride together with an aromatic diamine was also used to form a film of poly(amide-amic acids) which was later converted to ultra thin poly(amide-imides) film by heat treatment. The rate of deposition and the molecular weight of the polyamides were found to be highly dependent on the vapor pressure of the monomers and the temperature of the substrate.

Ito et. al. (1990) fabricated about 300 nm in thickness of polyimide thin-film via VDP from pyromellitic dianhydride and 4,4'-diaminodiphenylether. The structure of the films obtained was analyzed by means of IR spectra and X-ray diffraction. The main observation from IR showed that the film was transformed into polyimide by curing with the precursor, polyamic acid. Figure 2.2 shows the lay-out of the chamber used in his work.

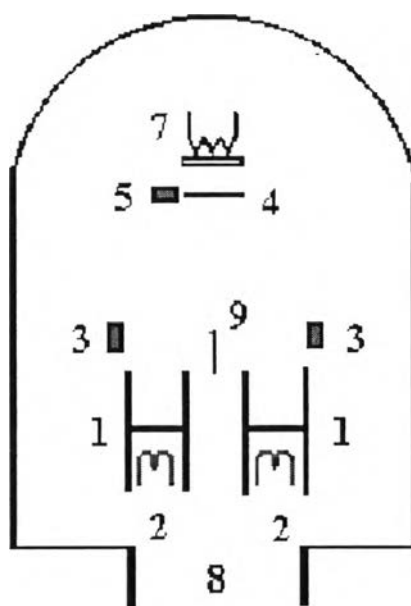


Figure 2.2 Chamber of vapor deposition polymerization (Ito 1990) (1) monomer container; (2) halogen lamp; (3) and (5) thickness monitor; (4) shutter; (6) substrate; (7) heater; (8) to vacuum; (9) partition.

Jou et. al. characterized polyimide thin-film deposited via VDP technique by using thermogravimetric analysis, scanning electron microscopy, atomic force microscopy, FTIR, and bending beam technique. The thin-film properties; thermal stability, wet-etching characteristics, surface topology, imidization characteristic, internal stress upon curing, and thermal cycling, were investigated.

The main observation revealed that polyimide obtained via VDP had better mechanical properties than that of the conventional ones, but was somewhat less thermal resistance.

2.2 Atmospheric Vapor Deposition

Recently Kim et. al. (1988) prepared undoped a-Si:H film by atmospheric pressure mercury-sensitized photo CVD. The schematic diagram was shown in Figure 2.3. The SiH_4 gas was led into the chamber using Ar as a carrier gas. A low pressure mercury lamp with 2537 and 1849 Å resonance lines is used. This less complicated system was developed to replace the use of mechanical pump. The system has the advantage of low contamination in vacuum system by purging the system with an inert gas.

Ikeda et. al. (1979) deposited an atmospheric-pressure vapor-phase polymerization of poly(*p*-phenyleneterephthalamide) coating onto polyester film and other sheet substrates. The minimum critical deposition temperature was found to be 170 °C. The lower temperature gave powder-like film with poor adhesion and low molecular weight, whereas higher temperature resulted in film which was well-adhered and had high molecular weight.

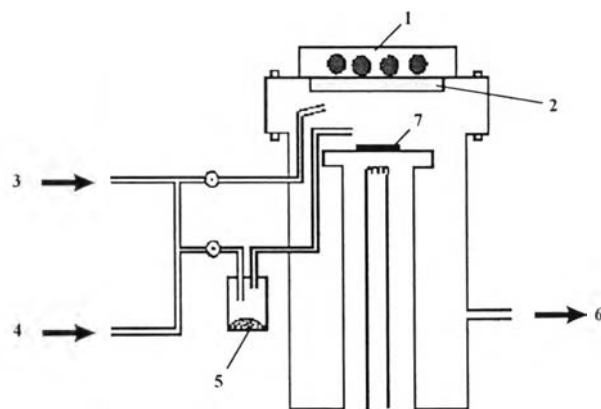


Figure 2.3 Schematic diagram of the set up for atmospheric pressure mercury sensitized photo CVD preparation of undoped a-Si:H films; (1) mercury lamp; (2) quartz glass; (3) Ar inlet; (4) SiH_2 inlet; (5) mercury; (6) exhaust; (7) substrate.

2.3 UV-Initiated Polymerization of Polystyrene

Pichayanont (1997) studied the UV-initiated polymerization of styrene in oil-in-water microemulsion using sodium salt as surfactant. It was found that 0.5-3.0% of styrene monomer solutions were initiated by 4 and 100 W UV lamps. The polymerization time was found to depend on the radiant power of UV lamp.

2.4 Thin Film Preparation of Polystyrene

Shuto et. al. (1993) investigated the preparation of 2-dimensional ultra-thin film polystyrene by a water casting method. Transmission electron microscopy (TEM) was used to observe the film. They found that the spreading state of the solution on the water surface and entanglements among PS chains were strongly related to the formation of homogeneous ultra thin film. The thickness of ultra thin film was found to be smaller than the dimension of an unperturbed PS chain.

Aubert and Mcnamara (1993) have studied the techniques for producing free-standing thin films on frames. The techniques of vapor-deposition polymerization, spin coating, and orientation-dependent etching have been employed to make free-standing thin film of parylene-N, parylene-D, polystyrene, polycarbonate and perfluoro-dimethyl-dioxole/tetrafluoroethylene copolymer. The polymeric materials were vapor-deposited or spin-coated onto substrates of polished single-crystal silicon wafers and removed on frames of various shapes and sizes after application of adhesive and an etching process

using potassium hydroxide. The film thickness obtained was in range of 2000

A to 12000 A .