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Vapor deposition and characterization of parylene films

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Abstract – Deposition of parylene (PA) films has been explored at substrate temperatures below 20°C and pressures below 4 torr. The film thickness was measured using AFM and the film properties were evaluated using DSC, TG, SEM, C-V, and I-V techniques. The film thickness measured was 3,500-12,000 Å and the growth rate was 20-70 Å/min. The dielectric constant of the deposited PA films was found to be 2.66 and the dielectric strength was in excess of 2×10^5 V/cm. The growth rate became a maximum at a precursor decomposition temperature of 600°C. It was found that the growth rate decreased with increasing substrate temperature, whereas it increased with increasing pressure. At a precursor decomposition temperature of 750°C or at a deposition pressure above 1 Torr the film surface became rough due to particle formation in the gas phase. The condensation of a p-xylylene monomer on the substrate surface turned out to be a rate-limiting step in the growth of the PA films.

I. Introduction

Presently, the trend in integrated circuits (IC) fabrication is pointing toward submicron dimension, high aspect ratio topography, and multilevel interconnection structure [1]. As the feature scale reduces to the submicron range, line width control over high aspect ratios becomes increasingly difficult. Current materials and technologies are unable to overcome the barrier for the production of the future IC where high speed and packing density are demanded. In addition, as the devices continue to scale down, RC delay, cross talk, and power dissipation become serious performance issues, especially at very high frequencies [2, 3]. Currently, silicon dioxide whose dielectric constant is about 3.9 is employed as an interlayer dielectric, but it should be replaced with a low dielectric material to increase the speed of the IC and to reduce the cross talk between wires.

Potential candidates for new interlayer dielectrics must not only have low dielectric constants but must also possess desirable properties such as low moisture uptake, good thermal stability, good adhesion, superior uniformity, and excellent conformality. Recently, some of organic polymers have attracted attention as new interlayer dielectrics because they meet the above requirements. Polyimides have low dielectric constant (2.7) and can be spun-on to form thick dielectrics reducing capacitance. However, difficulties arise in incomplete expelling of the solvent leading to outgassing during later metal deposition steps. Moisture take-up can cause shifts in polyimide dielectric constant. The formation of polyamic acid can leach metals like Cu. Since polyimides have high viscosity, it is difficult to fill submicron gaps with these materials in the multilayer metallization. Also their high curing temperature introduces stress. Amorphous teflon has a lower dielectric constant of 1.8. However, it has drawbacks of low thermal stability and poor adhesion [2].

Parylene (PA) is a vapor-depositable organic polymer [4-9]. The dielectric constant of this material ranges from 2.35 to 3.15 depending on its type. This polymer has an extremely low water permeability and its breakdown voltage is very high. Unlike polyimide, PA is capable of coating submicron crevice without developing pinholes. Since it is deposited at a low temperature, its thermal expansion coefficient is low and the stress is not high in the film. PA is also very inert chemically and exhibits good solvent resistance. This is due to the simple aromatic ring structure that forms the bulk of the monomer unit. The conformality of the deposited film is very good even with high aspect-ratio trench structures [7].

Although PA has such desirable properties possibly suitable for use as an interlayer dielectric in ultra large scale integrated (ULSI) circuits as mentioned above, the detailed mechanism is not still understood well. In earlier work, PA films have usually been deposited by sublimating the precursor at a constant temperature without using a diluent gas. However, it would be difficult to achieve a constant precursor concentration or pressure during deposition under these experimental conditions. To date most studies have focused on investigating the properties of the PA films to apply them to interlayer dielectrics. Growth rates and film properties as a function of operating conditions have not been reported in the literature. In this study, PA films were deposited using [2.2]paracyclophane as a precursor by the Gorham method [4]. To better understand the PA deposition mechanism, we investigated the effects of operating conditions including diluent gas flow rate, precursor vessel temperature, precursor decomposition temperature, pressure, and substrate temperature on growth rate and film property.

II. Experimental

2.1. Experimental Apparatus

A schematic diagram of the PA deposition apparatus employed in this work is illustrated in Fig. 1. The precursor, [2.2] paracyclophane (>99 %), in the form of white powder was obtained from Fluka. Argon (99.999%) was used as a diluent gas and its flow rate was controlled with a mass flow controller (MKS, Type 1259C). Mixed with argon the precursor was directed into a quartz tube reactor (φ300 mm × 1 m L) which was located in a tube furnace (Lindberg, Model 55342-4). The quartz tube reactor was supported with flanges at both ends. Its temperature was maintained by resistive heating with the tube furnace. The precursor was pyrolyzed into p-xylylene (PX) monomers in the quartz tube reactor at temperatures above 600°C. Monomers generated by pyrolysis of the precursor entered into a deposition chamber. They then condensed on the substrate surface and polymerized to produce PA films below room temperature. The unreacted reagents flew out of the chamber and were captured in a cold trap immersed in liquid nitrogen. Fig. 2 shows the process of making PA films from [2.2]paracyclophane.

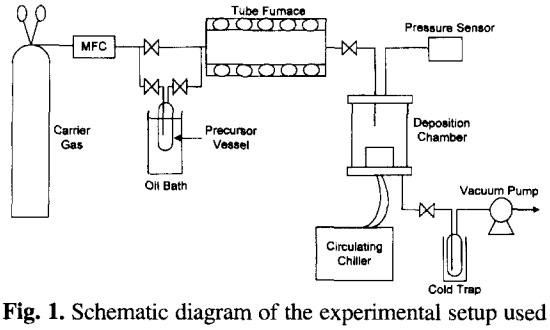

Fig. 1. Schematic diagram of the experimental setup used for PA deposition.

The precursor vessel made of pyrex glass was thermostatted by an oil bath with an accuracy of ±0.2°C. The whole upstream line of the tube furnace was heated above 140°C with a heating tape to prevent the precursor from condensing on the line. The deposition chamber was made of 316 stainless steel. It was wrapped with heating tapes to prevent deposition on the reactor wall. The susceptor on which the substrate was placed was maintained below room temperature by circulating a coolant with a circulating chiller (LAUDA, Type RC20B). The coolant was made with mixing water with glycerin by 3:1 volume ratio. The deposition pressure was measured with a capacitance manometer (MKS Baratron, Model 622A). It was maintained at a desired value by adjusting an exhaust valve (Vacuubrand, DIN-DVGW-G-PN 1). Low pressures were

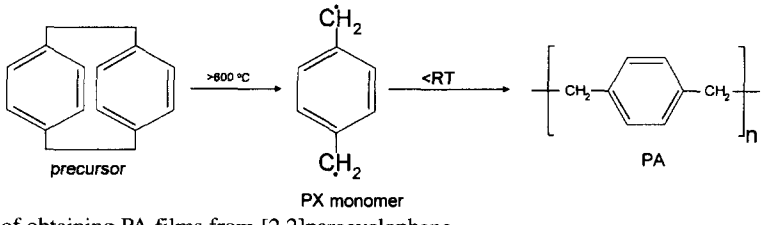

Fig. 2. The process of obtaining PA films from [2.2]paracyclophane.

obtained by a direct-drive rotary vacuum pump (ULVAC, Model G-100D).

2.2. Experimental procedure

The substrate (2 cm × 2 cm) was prepared by cutting 4-inch-diameter p-type (100) Si wafers with a resistivity of 1-30 Ω-cm with a diamond pencil. Prior to being loaded into the deposition chamber, the substrate was cleansed with H_2SO_4:H_2O_2 (vol% 3:1) solution, HF:H_2O (vol% 1:7) solution, and deionized water consecutively and was purged with nitrogen (>99.999%) to remove moisture. Deionized water with a resistivity of 16-17 MΩ-cm was obtained by distilling tap water and passing it through an ion exchanger (Vaponics, Model Aries 110V).

The precursor vessel that contained about 0.5 g of the source material was connected to a precursor feeding line. Then the line was evacuated and the feeding valve was closed. The deposition chamber was purged with nitrogen when loading the substrate to keep impurities such as dust, moisture, or oxygen from entering into the chamber. The system was evacuated to a base pressure of 10^{-3} Torr. The diluent gas, argon, was then allowed to flow through a bypass line and the pressure stabilized to a desired value. With argon flowing the susceptor was cooled to a deposition temperature by turning on the circulating chiller. The upstream line was heated above 140°C. The precursor vessel was immersed into the oil bath and it was typically maintained at 110°C. After desired conditions were achieved, the precursor feeding valve was opened to start deposition. At the end of the run, it was shut off to finish deposition.

2.3. Film Characterization

The deposited PA films were characterized by AFM, TG, DSC, SEM, C-V, and I-V techniques. The PA film thickness was measured by the line profile scanning of atomic force microscopy (AFM) using a Park Scientific Instrument Auto Probe M5. Since it is hard to etch PA films by a common etching solution, part of the substrate was masked with a tape before deposition to form a step required for thickness measurements. A thermal behavior of the deposited film was examined by thermogravimetry (TG) using a Du Pont 951 Thermo-gravimetric Analyzer and by differential scanning calorimetry (DSC) using a Du Pont 910 Differential Scanning Calorimeter. The film morphology was measured by scanning electron microscopy (SEM) using a Joel JSM-820 Scanning Electron Microscope. The dielectric properties of the deposited PA film were measured on a metal-insulator-semiconductor (MIS) capacitor structure with C-V and I-V techniques. MIS structures were fabricated by coating a thin aluminum electrode on the PA-deposited sample by thermal evaporation through a metal mask. The C-V measurements were performed at a high frequency of 1 MHz.

III. Results and Discussion

The base conditions for the PA deposition experiments performed in this study are: diluent gas flow rate = 50 sccm, precursor vessel temperature = 110°C, precursor decomposition temperature = 700°C, deposition pressure = 1 torr, and substrate temperature = 1°C. We have explored variations of growth rate and film property with the above operating conditions. It was observed that as the deposition proceeded, the color of the substrate surface was changed. In this work, the mole % of the precursor in the reactant gas entering into the tube reactor ranged from 0.13 to 0.48. Therefore, the precursor was highly diluted in the carrier gas in our experiments. The deposition was typically performed for 3 h. The thickness of the deposited film was 3,500-12,000 Å. The surface of the film obtained from the base conditions was smooth.

3.1. Precursor Feeding Rate

The mass flow rate of the precursor entering into the tube reactor to produce PX monomers depends on the diluent gas flow rate, pressure, and precursor vessel temperature. The precursor feeding rate is plotted as a function of diluent gas flow rate in Fig. 3a in which the pressure is 1 torr and the precursor vessel temperature is 110°C. One can see that the precursor feeding rate increases from 0.848 mg/min to 1.12 mg/min as the diluent gas flow rate is raised from 20 sccm to 80 sccm. The reason for this is that the mass transfer is enhanced with increasing diluent gas flow rate, thereby augmenting the amount of the precursor sublimated. However, the concentration of the precursor in the gas phase diminishes due

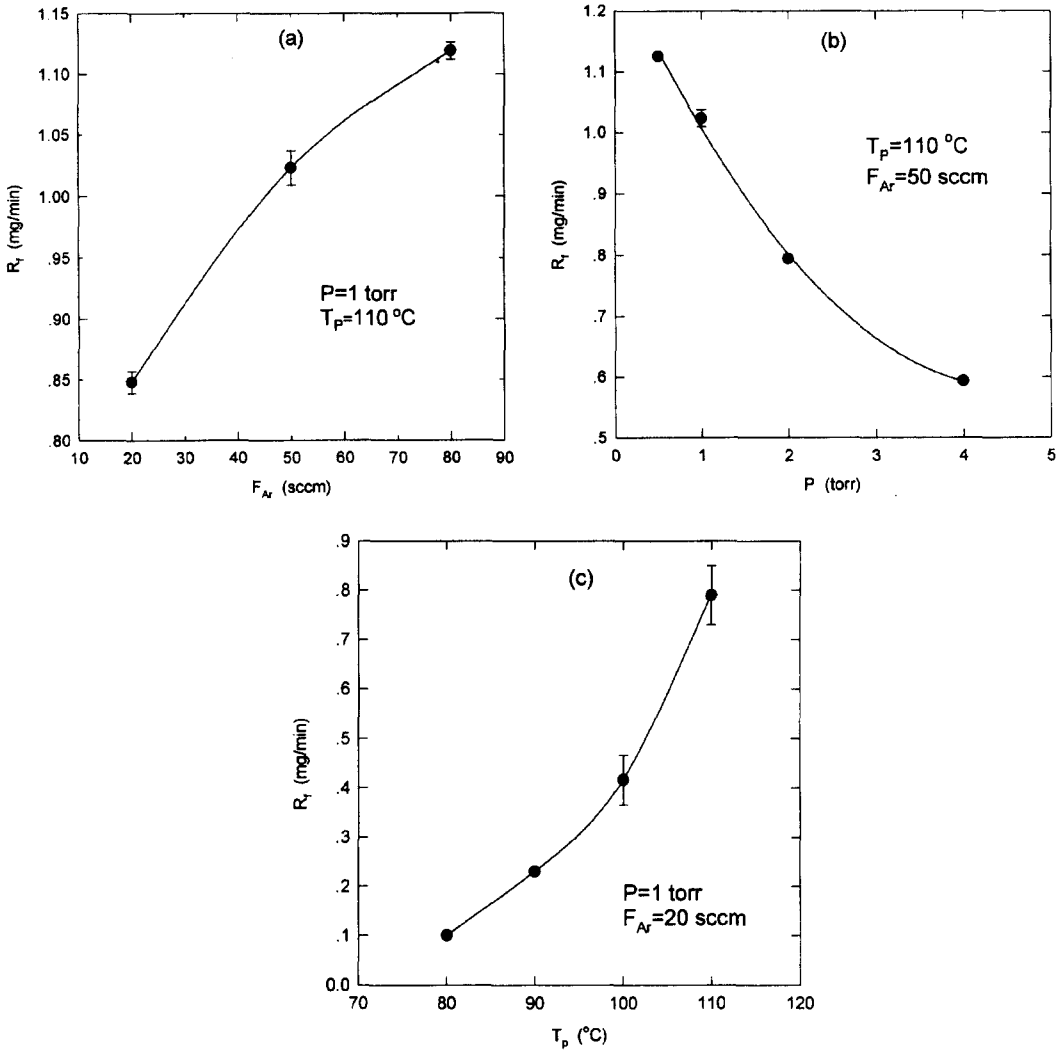

Fig. 3. Dependence of precursor feeding rate on (a) carrier gas flow rate, (b) pressure, and (c) Precursor vessel temperature.

to an increase in diluent gas flow rate larger than precursor feeding rate. Fig. 3b shows the effect of pressure on precursor feeding rate. Here the precursor vessel temperature is fixed at 110°C and the diluent gas flow rate is 50 sccm. It can be seen in Fig. 3b that the precursor feeding rate decreases to about a half value from 1.13 mg/min to 0.593 mg/min as the pressure is increased 8 times from 0.5 torr to 4 torr. As a result, the precursor concentration in the gas phase is increased in spite of a decrease in precursor feeding rate. Shown in Fig. 3c where the pressure is 1 torr and the diluent gas flow rate is 20 sccm is the effect of precursor vessel temperature on precursor feeding rate. In Fig. 3c, the precursor feeding rate hugely increases from 0.100 mg/min to 0.789 mg/min as the precursor vessel temperature is lifted from 80°C to 110°C. At a precursor vessel temperature above 110°C some precursors were found to condense on the upstream process line and the precursor feeding valve causing a serious problem with reproducing the experimental results. Therefore, in our experiments the precursor vessel temperature was maintained below 110°C. From the above results the precursor feeding rate depends most strongly on the precursor vessel temperature. Accordingly, it is crucial to

precisely control the precursor vessel temperature to obtain a constant precursor concentration during deposition. In this work, the precursor vessel was immersed into the oil bath to maintain a constant precursor vessel temperature with an accuracy of ±0.2°C.

3.2. Film Properties

The thermal behavior of the deposited PA film is illustrated in Fig. 4. In TG analysis in Fig. 4a, the sample was heated in nitrogen from 100°C to 700°C at 10°C/min. As can be seen in Fig. 4a, the weight is maintained stable up to 450°C or so and is sharply decreased to about 15% at around 500°C. Since the benzene ring of PA is stable at 500°C, this thermal degradation seems to be due to random chain scission. The results shown in Fig. 4a are reasonably consistent with those reported by Joesten [6]. DSC data of the deposited PA film are illustrated in Fig. 4b. In DSC measurement, the sample was heated in nitrogen from 350°C to 450°C at 10/min. As shown in Fig. 4b, endothermic transition appears which peaks near 420°C, suggesting that the melting point

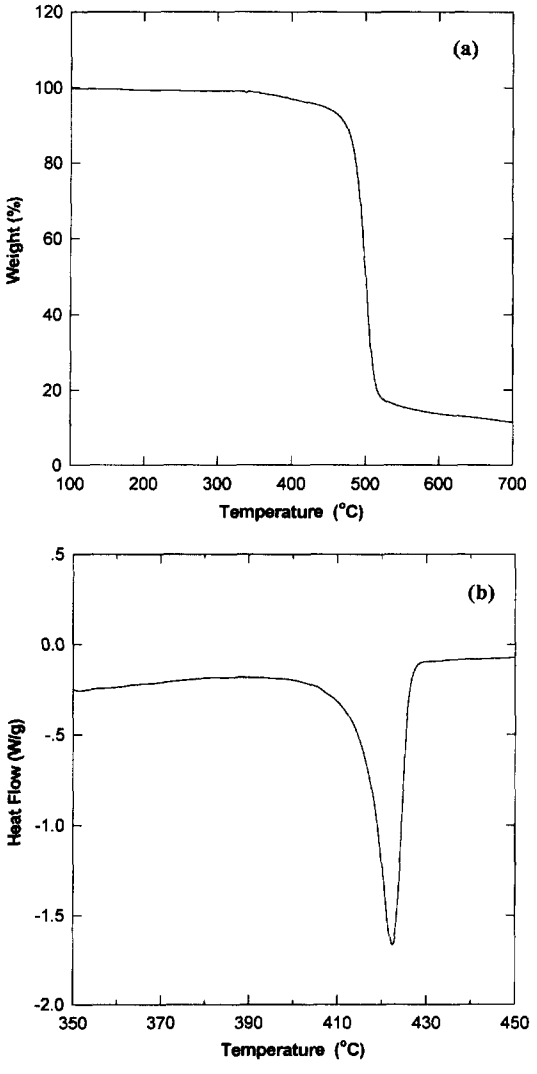

Fig. 4. Thermal behavior of deposited PA films: (a) TG thermogram in nitrogen and (b) DSC thermogram in nitrogn.

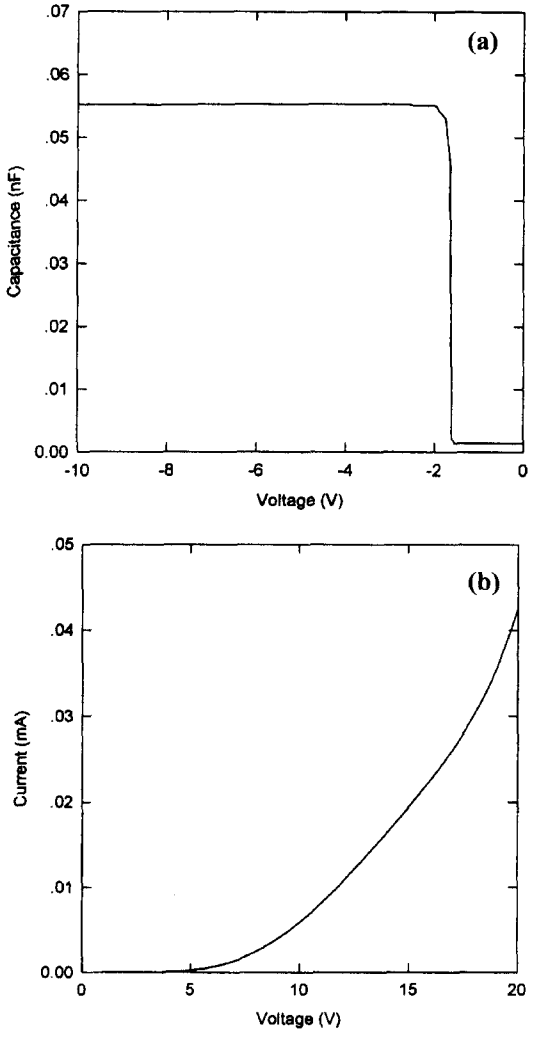

Fig. 5. C-V and I-V plots obtained on MIS capacitor incorporating PA film: (a) C-V curve and (b) I-V curve.

of the deposited PA film is about 420°C. This value is in good agreement with that obtained by Gorham and Niegisch [10]. Typical C-V and I-V curves for the PA film obtained from the base conditions are depicted in Fig. 5. The dielectric constant (ε_r) of the PA film is obtained by the following expression

$$\varepsilon_r = dC/\varepsilon_o S \quad (1)$$

where d is the PA film thickness, C is the capacitance, ε_o is the permittivity of free space [=8.8544×10^{-12} $N^{-1}m^{-2}C^2$], and S is the electrode surface area. From the results of Fig. 5, the dielectric constant of the PA film was found to be 2.66 and the dielectric strength was in excess of 2×10^5 V/cm.

3.3. Growth Rate

As far as we know, no study has been reported about variations of growth rates with experimental conditions. In the present work, dependence of the growth rate on operating conditions was explored such as precursor decomposition temperature, pressure, and substrate temperature.

The effect of precursor decomposition temperature (tube furnace temperature) on growth rate is depicted in Fig. 6. Gorham [4] found that the precursor decomposes completely into PX monomers at temperatures above 600°C. As seen in Fig. 6, the growth rate becomes a maximum at 600°C. It is interesting to note that the growth rate is relatively low below 600°C. In addition, it was observed below 600°C that some precursors which had not decomposed in the tube reactor condensed on the substrate surface. This result indicates that the precursor decomposition is incomplete at temperatures below 600°C. We see in Fig. 6 that the growth rate is slightly decreased from 49 Å/min to 42 Å/min as the precursor decomposition temperature is raised from 600°C to 750°C. It was found that at 750°C considerable particles were formed on the substrate surface, thus yielding rough films. This may be because the gas phase reaction leading to particle formation becomes significant at a high temperature of 750°C and some of particles generated in the gas phase stick to the substrate surface. Furthermore, the consumption of the PX monomers by the gas phase reaction for the particle generation results in a small decrease in growth rate.

The influence of pressure on growth rate is illustrated in Fig. 7. It is seen that as the pressure is raised from 0.37 Torr to 4 Torr, the growth rate increases from 23 Å/min to 56 Å/min. As previously noted in Fig. 3b where the diluent gas flow rate and precursor vessel temperature are fixed, the precursor concentration in the gas phase is increased with increasing pressure, resulting in an increase in growth rate. In Fig. 7 the growth rate rapidly increases as the pressure is raised up to 1 Torr and

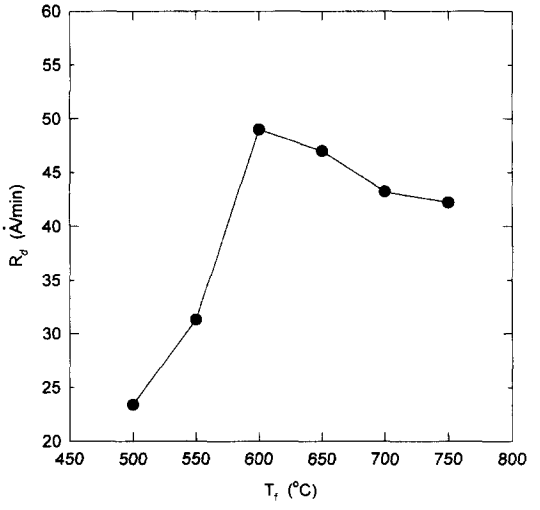

Fig. 6. Effect of precursor decomposition temperature on growth rate. T_p = 110°C, T_s = 1°C, F_{Ar} = 50 sccm, and P = 1 Torr.

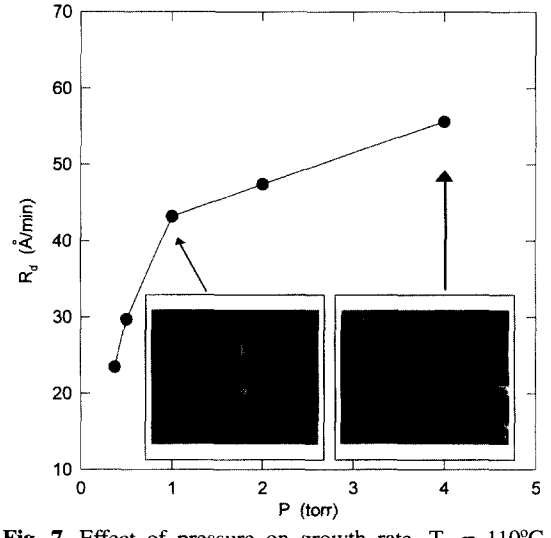

Fig. 7. Effect of pressure on growth rate. T_p = 110°C, T_s = 1°C, T_f = 700°C, and F_{Ar} = 50 sccm.

then it slowly increases with a further increase in pressure above 1 Torr. SEM photographs show that as the pressure is increased from 1 Torr to 4 Torr, the size of the particles formed on the substrate surface becomes large. Below 1 Torr the film surface looked smooth by a naked eye. These results imply that the particle generation becomes pronounced as the pressure is increased. Thus, the film surface became rougher at higher pressures. A slow increase in growth rate above 1 Torr may be partly because more PX monomers are consumed in the gas phase at higher pressures.

The effect of substrate temperature on growth rate is shown in Fig. 8. It is important to note that as the substrate temperature is raised from –4°C to 20°C, the growth rate considerably decreases from 66 Å/min to 16 Å/min. The growth rate usually increases as the substrate temperature is raised in most chemical vapor deposition (CVD) processes. Gorham and Niegisch [10] reported that the growth rate in the PA deposition diminishes with increasing substrate temperature. In our experiments, the temperature of the reactor wall was maintained above 100°C, and no deposition was observed on the reactor wall, whereas the deposition took place only around the susceptor which was maintained below room temperature. The color of the substrate surface was changed more rapidly with time at lower substrate temperatures, implying that more films are deposited on the substrate. Also thick films were formed on the wall of the cold trap immersed in the liquid nitrogen. These observations are consistent with the results shown in Fig. 8. As previously mentioned, the dimer is pyrolyzed into PX monomers which condense on the substrate surface and polymerize to produce PA films. According to Gorham and Niegisch [10], polymerization proceeds by a free radical mechanism and consists of three steps: an initiation, propagation, and termination step. Polymerization is initiated by two or more PX monomers adsorbed on the substrate surface reacting to form a diradical. In the propagation step, film growth occurs at both sides of the diradicals. The termination step consists of the radicals being buried so far into the film that monomers cannot reach the polymer chain radicals, therefore living polymer still exists throughout the bulk of the film. As the film thickens, the centers of growth become buried in the polymer matrix and the PX monomer supply to them is virtually impossible due to the slowness of monomer diffusion so that the number of the radicals exposed to the surface is decreased. However, new centers of growth are continually formed as the PX monomers are supplied from the gas phase. Eventually, a steady state will be established when the rate of formation of the centers becomes equal to the rate of their loss by the burying process. As the substrate temperature is raised, the polymerization rate increases, whereas the amount of condensation of PX monomer decreases. Therefore, the substrate temperature affects the growth rate in a different way depending on the magnitude of condensation and polymerization rates. From the results of Fig. 8, the rate-determining step of the deposition of PA films seems to be the condensation of monomer onto the substrate surface. Propagation reaction of monomer addition to the polymer chain is quicker than the initiation reaction. As the substrate temperature is lowered, there is an increase in growth rate but a decrease in the propagation rate, thereby causing a lower molecular weight polymer to be formed. This will bring in a degradation of the PA films, which needs a further study.

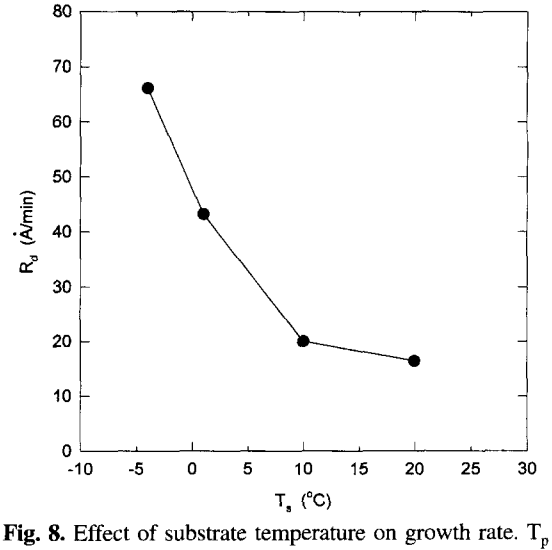

Fig. 8. Effect of substrate temperature on growth rate. T_p = 110°C, T_f = 700°C, F_{Ar} = 50 sccm, and P = 1 Torr.

IV. Conclusions

In this study, PA films have been deposited from

[2.2]paracyclophane by the Gorham method. The diluent gas (Ar) flow rate ranged from 20 to 80 sccm, the precursor vessel temperature from 80 to 110°C, the precursor decomposition temperature from 500 to 750°C, the pressure from 0.5 to 4 Torr, and the substrate temperature from −4 to 20°C. The PA film thickness measured was 3,500-12,000 Å and the growth rate was 20-70 Å/min. The dielectric constant of the deposited PA films was 2.66 and the dielectric strength was greater than 2×10^5 V/cm. It was shown that the growth rate became a maximum at a precursor decomposition temperature of 600°C. The precursor decomposition was incomplete at temperatures below 600°C. The growth rate decreased with increasing substrate temperature, implying that the condensation of a PX monomer on the substrate surface is a rate-determining step in the growth of the PA films. At a precursor decomposition temperature of 750°C or at a pressure above 1 Torr the film surface became rough, which indicates that gas phase reaction leading to particle formation becomes significant at higher temperatures and pressures.

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