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Study of Thin Polymeric Film Deposited by the PECVD Process for use at 193 nm

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A plasma enhanced chemical vapor deposition (PECVD) reactor was used to deposit thin polymeric films with high absorption at 193 nm. The reactor is suitable to deposit uniform and pinhole free thin polymeric films with conformality over 95%. Conformal films with thickness as low as 200 Å have been deposited on silicon, glass, and quartz substrates, as well as silicon oxide, silicon nitrate, and aluminum films. Deposited films had variations in thickness of 3 to 5% over an area of 8 inches in diameter. Thin films deposited on silicon substrates under varying levels of RF power were scanned using the AFM technique. The measurements show increasing surface roughness of the scanned samples as the RF power increases.

Keywords: polymeric films; plasma enhanced chemical vapor deposition

1 Introduction

Polymers are increasingly being used in numerous technological applications, due to their low weight, ease of fabrication into desired shapes or forms, favorable mechanical, optical, and electrical properties, as well as low cost. The performance of polymeric materials can be further enhanced by low pressure plasma deposition of inorganic or organic coatings, which can satisfy one or more functions, including optical antireflective coatings, optical filters, decorative coatings, barriers against gas and vapor permeation for packaging, as well as hard/protective coatings against harsh terrestrial and/or space environments (1). Polymeric thin films are being investigated for their use in semiconductor devices (2), optical waveguides (3), telecommunication devices (4), low-k dielectric materials (5), and display devices (6).

The process of plasma polymerization of organic compounds, which is carried out under vacuum, is quite different from the conventional polymerization (7). Plasma polymerization is a solvent-free, room temperature process that can be used to rapidly deposit thin polymer films onto a wide variety of substrates. Plasma enhanced chemical vapor deposition (PECVD) is a dry process wherein a material is excited into the plasma state by high frequency electronic pulses and forms an ionized gas that deposits and polymerizes on a substrate, as the gas flows through a vacuum chamber. Polymer forming materials must easily evaporate or sublime into the gas phase and have low ionization energy. These characteristics allow for a reasonable rate of thin film growth on the substrate. In this regard, PECVD shows considerable potential benefits over spin-on materials such as low waste and improved uniformity and conformality. Thin films deposited by PECVD are being actively studied for solar cells (8), waveguide devices (9) and biomaterials (10).

Deposition of organic polymeric materials by PECVD is less common than deposition of inorganic thin films. We have recently reported organic, polymeric antireflective coatings (ARCs) deposited by PECVD (11). Also, we described a novel method to deposit organic thin film from a mixture of monomers with different boiling points using an injector-apparatus attached to a PECVD reactor (12). In this article, we report results obtained from polymeric thin films for bottom anti-reflection (BARC) application., and the use of a atomic force microscopy (AFM) technique to describe the effect of radio frequency (RF) power on surface roughness of thin organic polymeric films deposited on silicon substrate by the PECVD process.

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2 Experimental

2.1 Materials

To test the performance of PECVD reactor, monomers such as styrene (A) and 2-fluorotoluene (B) were selected (Figure 1). These monomers where purchased from Aldrich and used without further purification. The chosen monomers have low boiling points, which allow film deposition without heating the monomer reservoir. This is important when building an automated reactor for high output, because it results in one less parameter to control, making the process more manageable. However, when a chosen monomer has a high boiling point (>180°C), then heat must be applied to the monomer reservoir, as well as to the mass flow controller, valve, and the pipe which leads the monomer gas into the quartz bell jar.

2.2 Optical Characterization

Using a Varian Cary 500 spectrophotometer, the ultraviolet-visible absorption spectrum as a function of wavelength was measured for styrene and 2-fluorotoluene thin film deposited onto quartz slides. The thickness of both materials was around 1000 Å (Figure 2).

2.3 PECVD Reactor

A PECVD reactor was used for deposition of organic materials for both anti-reflection coating applications with strong absorption at 193 nm and 240 nm wavelengths and applications, where thin and conformal coating is needed. The substrate is positioned inside the aluminum chamber on top of a turntable in the downstream of the plasma (Figure 3). In the near afterglow reactor, the samples are not immersed in plasma where ion and electron bombardment can occur, instead they are placed 8 inches away from the bottom of the quartz bell jar where the plasma is initiated. Since the wafer is placed away from the end of the quartz bell jar, less charge will be collected from the plasma. Therefore, when processing wafers with gate oxide, less charge will flow to the gate oxide. The accumulation of charge on the small area of the gate oxide can exceed the breakdown voltage, where tunneling effects can occur, resulting in device failure. The process is fully automated for all deposition parameters, such as RF power, pulsing period, operating pressure, as well as gas flow may be programmed to guide film deposition. This automation feature results in consistency from deposition to deposition. The monomer gas entering into the quartz bell jar passes through a mass flow controller. Electromagnetic energy provided by a coil wrapped around the quartz bell jar is fed into the neutral gas monomer to generate ions, electrons, and excited particles, etc. The pressure inside the reactor chamber is kept at some desired pressure by the throttle valve. The RF power and the pulse duration are parameters that depend on the monomer used in the film deposition process. The energy of individual particles can increase with increasing absorbed power and decreases with increasing gas pressure (collisions). Particle collisions act as a balancing factor limiting particle energies, and are therefore a crucial parameter in the thickness and quality of the deposited polymeric film.

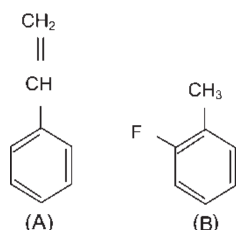

Fig. 1. Chemical structures of styrene (A) and 2-fluorotoluene (B).

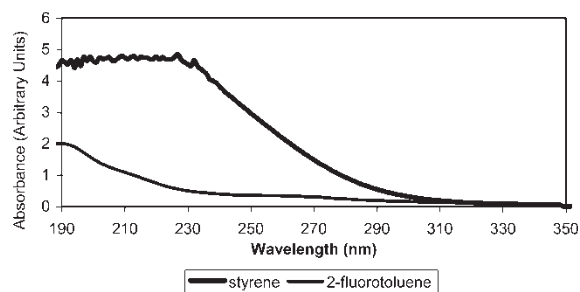

Fig. 2. Absorbance spectra for styrene and 2-fluorotoluene.

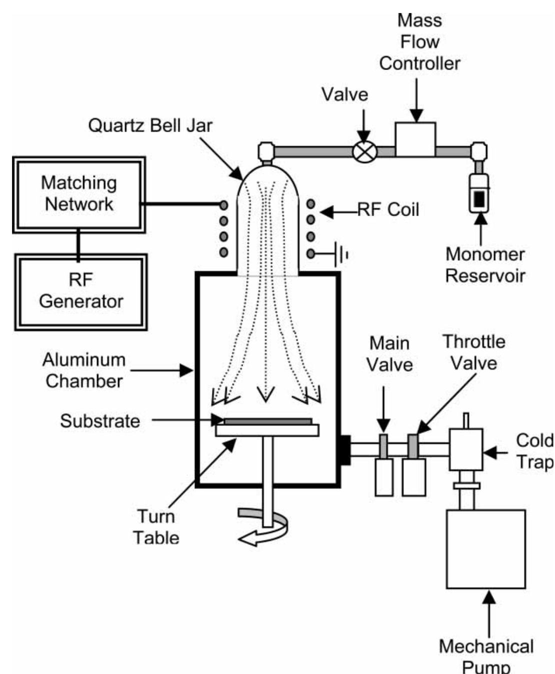

Fig. 3. Schematic diagram of the PECVD reactor.

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Table 1. Monomer deposition conditions

Monomer	RF power (W)	Pressure (mTorr)	Gas flow (sccm)	Deposition time (sec)	Film thickness (Å)	Pulsing ON/OFF (msec)
2-Fluoro-toluene	110	30	25	120	350	220/50
	120	30	25	120	360	220/50
	130	25	30	180	450	280/30
	150	30	25	120	320	220/50
Styrene	110	30	25	120	400	190/50
	120	25	25	120	510	200/30
	130	30	25	120	440	170/50
	150	30	25	120	440	150/50

3 Results and Discussion

Films were deposited using a 13.56 MHz inductive-coupled RF glow discharge. During deposition, the RF generator was operated in the pulsed mode. An ON-OFF power routine was used to control the film thickness. The application of RF power also dictates the degree of polymerization of the deposited film. The film deposition parameters for 2-fluorotoluene and styrene are shown in Table 1. The values of film thickness were obtained from a quartz micro balance thickness monitor.

Figure 2 shows the absorbance for styrene as a broad peak around 5 for wavelengths ranging from 190 to 230 nm, and for 2-fluorotoluene the peak is around 2 at 190 nm. The measured optical densities of styrene and 2-fluoro-toluene were 11 and 5.7, respectively. An optical density higher than 5/μm at the desired wavelength would make the polymer film ideal for ARC applications. Styrene has a higher absorption at 193 nm than 2-fluorotoluene, but both materials can be used for this application. Table 2 gives the thickness of the deposited films, the measured values of the real part of the refractive index (n) and the imaginary part of the refractive index (k) at 193 nm. These parameters were measured on a J. A. Woollam Variable Angle Spectroscopic Ellipsometer (VASE).

Table 2. Optical properties of deposited film for varying levels of RF power

Monomer	RF power (W)	n at 193 nm	k at 193 nm	Thickness (Å)
2-Fluoro-toluene	110	1.8302	0.4961	313.72
	120	1.7885	0.4742	344.55
	130	1.7399	0.6819	495.34
	150	1.7602	0.4425	373.36
Styrene	110	1.7005	0.7486	418.22
	120	1.6873	0.7243	448.57
	130	1.6999	0.7465	431.69
	150	1.6915	0.7338	432.44

After optimization of the parameters, deposition pressure, monomer gas inflow, and pulse duration, the variations in the thickness of the deposited polymeric films were consistently better than 5% over the entire surface area of an 8 inch diameter silicon wafer. A Filmetrics F20 spectroscopic reflectometry measurement system from Filmetrics, Inc. was used to measure and map film thickness uniformity across the wafer. The deposition rate was kept at 1–2 Å/sec. Slow film deposition results in smooth surface film. Topography

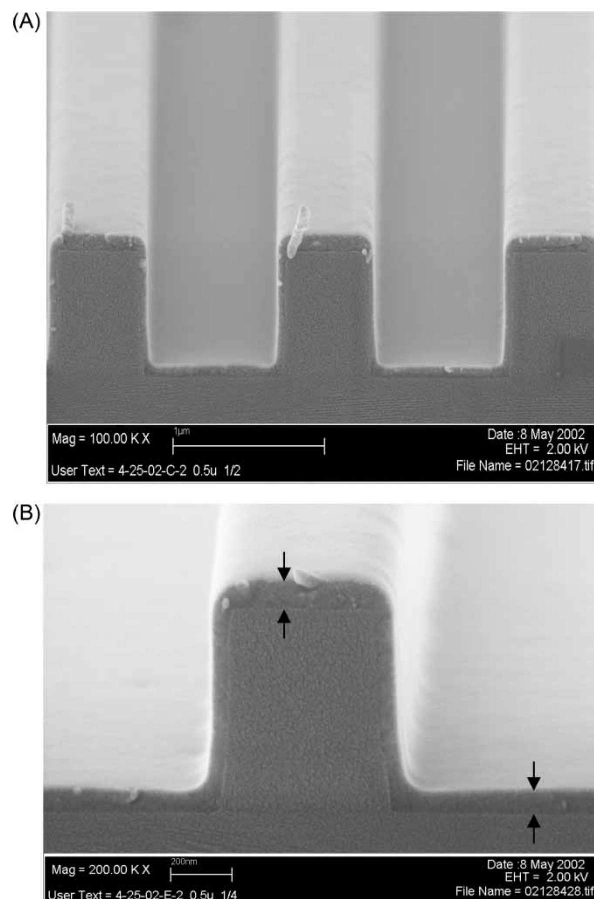

Fig. 4. 2-fluorotoluene; RF power 125 Watts; 7000 Å step height; magnification: 100,000 X (A) and 200,000 X (B).

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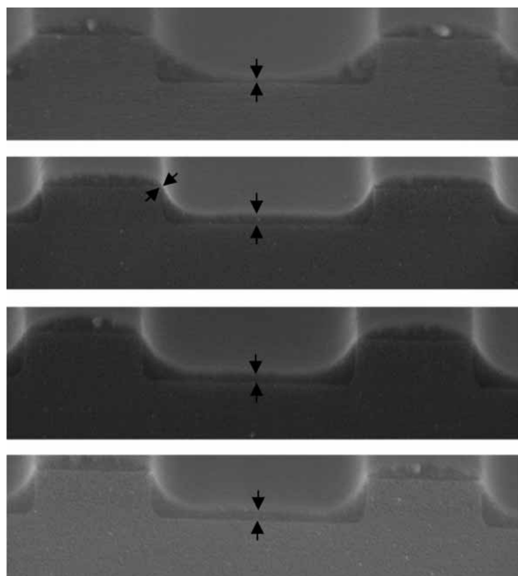

Fig. 5. This figure shows a sequence of SEM pictures of styrene film deposited onto 1000 Å high steps etched on silicon. The RF power levels used to deposit these films from the top to bottom pictures were 110, 120, 130, and 150 Watts. The etching process at the sharp edges of the steps can be clearly seen in these pictures.

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silicon wafers with 7000 Å step height were used to test the conformality of the deposited films. Conformality is defined as the ratio of the film thickness coated on top of the topography vs. thickness at the bottom of the structures. Film conformality was tested by depositing 2-fluorotoluene and styrene thin films onto topography silicon wafers previously patterned by plasma etching. The conformality of the 1000 Å thick 2-fluorotoluene thin film was over 95%, as shown in Figure 4. Also from these pictures, one can see the smooth surface of the deposited films. These materials showed good adhesion to various substrates like silicon, glass, and quartz, as well as to silicon oxide, silicon nitrate, and aluminum films. The adhesion tests of thin films deposited on these substrates and films were performed using the ASTM tape peel test.

The RF power used to deposit polymeric films can affect the surface characteristics of the films. In our process, the RF power is used not only to ionize the monomer gas in the quartz bell jar, but also to facilitate uniformity of the deposited films. Nonetheless, energetic ions, when impinging upon the surface of the polymer film, can etch away film of certain materials when they are deposited onto the top of sharp edges as shown in Figure 5. Figure 5 shows a 300 Å styrene film deposited onto a 1000 Å high step patterned on silicon wafer. RF power of 110, 120, 130, and 150 Watts were used to deposit these films. As one can see from these pictures, the flat part of the film is consistently very uniform. However, at the sharp edges on top of the structure the styrene film has been etched away. Also, one can see an excess of material deposited at the bottom corners of each

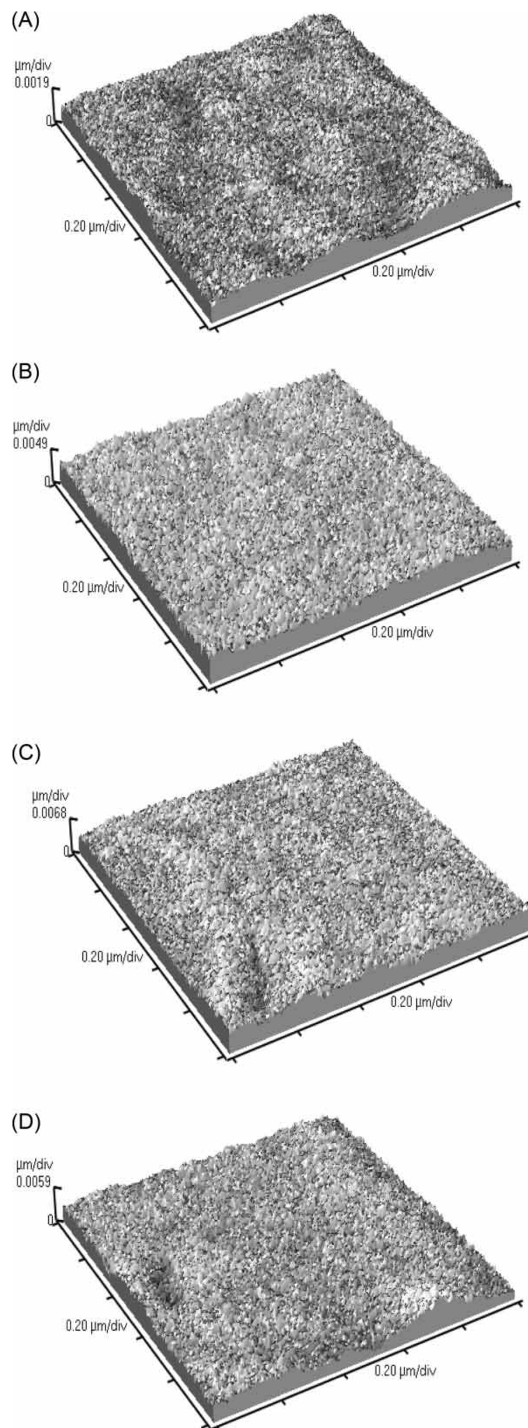

Fig. 6. Figures (A) through (D) are AFM topographic figures of 2-fluorotoluene thin film. The RF power levels used during the deposition of these films are 110, 120, 130, and 150 Watts, respectively.

of the steps. This sequence of pictures also shows an increase in film thickness as the RF power increases. Although styrene is an excellent material to be deposited in our PECVD reactor, where it covers plain 8-inch silicon wafer with thin film of excellent uniformity, it may not be

Table 3. Measured RMS and average surface roughness values

Monomer	RF power (W)	RMS roughness (Å)	Average surface roughness (Å)	Surface area $(\mu m)^2$
2-Fluoro-toluene	110	1.91	1.48	1
	120	4.16	3.26	1
	130	4.68	3.54	1
	150	4.96	3.89	1
Styrene	110	3.84	2.99	1
	120	4.33	3.3	1
	130	5.74	4.51	1
	150	5.95	4.67	1

suitable for deposition on wafers where features may be present. The thickness of the film at the sharp edge is thinner than film deposited on the flat surface of the silicon wafer. However, films of 2-fluorotoluene deposited under the same conditions were not etched away (Fig. 4). Therefore, the etching process depends on the monomer being deposited.

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To study the effect of processing conditions on the surface topography of thin film samples of different monomers deposited by the PECVD process using varying levels of RF power, the AFM technique was used to measure surface roughness of the deposited films. AFM is a very sensitive tool for measuring the three dimensional morphology of thin films, and directly measures the surface roughness, as well as feature height and width through the use of a very fine, sharp probe that is swept across the sample surface while a very small force is applied.

AFM was carried out on a Thermomicroscopes (PSI) Autoprobe CP instrument. The scan area was restricted to $1.0\ \mu m \times 1.0\ \mu m$ and the scan rate was set to 1 Hertz. The imaging was done in regular contact mode. Gold-coated contact microlevers with a cantilever force constant of the order of 0.03 N/m were used for all measurements. Typical force values used were in the range of 3 to 10 nanoNewtons. The images obtained were flattened using a third order exponential fit in the fast scan direction. Both root mean square and average roughness were calculated over the entire area of the scan using the Proscan image processing and analysis software.

Figure 6 shows the topography images of 2-fluorotoluene film deposited by the PECVD process. These images were used to compare the effect of film deposition conditions, such as RF power used in film deposition, on the surface characteristics of deposited films. The average surface roughness (ASR) values were measured using the line profile measurement on the topography of the deposited film. The software used to obtain the sample profile was supplied with the AFM. Using this technique, we placed a horizontal line at different points on the top of the topographic images and the height profile of the film was measured. The scale of the z-axes in Figure 6 A, B, C, and D are 0.0019, 0.0049, 0.0068, and 0.0059 μm/div, respectively. Although, Figure 6 A appears rougher than Figure 6 D, its z-axis scale has been magnified almost by a factor of 3 when compared with the z-axis scale of Figure 6 D. The results of the measurements are shown in Table 3. Although one can notice variations in the ASR of the surfaces of the deposited film for both monomers, the change in 2-fluorotoluene is more accentuated from 110 to 120 W, while for styrene the most pronounced change occurs from 120 to 130 W.

4 Conclusions

The PECVD deposited films from monomers styrene and 2-fluorotoluene proved to be of excellent quality, and were uniform and pinhole free. SEM pictures of 2-fluorotoluene thin film deposited onto a patterned silicon wafer with 7000 Å steps demonstrate conformality exceeding 95%. Although the deposition process is a downstream type (i.e. the substrate is positioned away from the plasma source), the styrene thin film deposited onto a patterned silicon wafer was etched away on the sharp edges of the pattern. However, films of 2-fluorotoluene deposited under the same conditions were not etched away. Therefore, the etching process depends on the monomer being deposited. To understand more about the effect of the deposition process on the film surface, the AFM technique was used to measure the surface roughness of polymeric thin film deposited by the PECVD process and it was observed that the measured roughness of the deposited films increases as the RF power increases.

We want to emphasize that although the roughness of the surface increases with RF power, the PECVD process still results in very smooth film for all practical applications. Thickness variation of a 1000 Å thick film deposited on a 8-inch silicon wafer was about 25 Å.

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