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Polymer Chain Configurations in Constrained Geometries:  
Ultrathin Films for Microlithography

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# Polymer chain configurations in constrained geometries: ultrathin polymer films for microlithography

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## ABSTRACT

Ultrathin (0.9 nm - 15.3 nm) poly(methylmethacrylate) (PMMA) films prepared by the Langmuir-Blodgett (LB) technique have been explored as high-resolution electron beam resists. One-eighth micron lines-and-spaces patterns have been achieved by using a Perkin Elmer MEBES I pattern generation system as the exposure tool. The etch resistance of films with thicknesses greater than 4.5 nm is sufficient to allow patterning of chromium film suitable for photomask fabrication. Monolayer PMMA films containing 5 mol% pyrenedodecanoic acid (PDA) as a probe were prepared by transfer to the substrate at different surface pressures and characterized by fluorescence spectroscopy. The ratio of excimer to monomer emission intensity ( $I_e/I_m$ ) has a maximum value at  $\sim 10$  dyn/cm, which may be related to a structural rearrangement in the film. Intrinsic bilayer LB PMMA films prepared at 1 and 19 dyn/cm have also been examined by transmission electron microscopy (TEM). The wrinkle-like surface topography observed in the 19 dyn/cm sample and not in the 1 dyn/cm sample suggests that the structure of the LB PMMA film depends on the transfer pressure.

## 1. INTRODUCTION

As the dimensions of integrated circuits keep shrinking, the desired resolution will soon be beyond the limit of conventional ultraviolet (UV) lithography. Deep UV and X-radiation, high and low energy electron beams and scanning tunneling microscopy (STM) have been proposed<sup>1</sup> as possible exposure systems for the next generation high resolution lithography. In optical lithography (UV or Deep UV) the resolution is limited by resist absorption, light diffraction, and rheological effects related to the resist development process. In electron beam lithography the major limitation on the resolution is imposed by electron scattering (proximity effect), which causes a nonuniform incident exposure in the pattern area. These resolution limiting effects generally become more serious with increasing resist thickness. Therefore, to improve the resolution in both optical and electron beam lithography, the use of ultrathin resists (with thickness  $< 200$  nm) has been proposed.<sup>2</sup>

Ultrathin resists have many advantages; in optical lithography they offer improved exposure and focus latitude<sup>3</sup>, and alleviate the problem of absorption in conventional resists, such as novolac, especially for deep UV exposure. In electron-beam lithography the use of ultrathin resists will reduce electron scattering within the resists and thus make the proximity effect correction schemes (e.g. GHOST)<sup>4</sup> easier to implement. The most attractive advantage of an ultrathin resist is to allow electron penetration when the scanning tunneling microscope (STM) is used as a very low voltage exposure tool<sup>1</sup>. Because the STM is capable of creating patterns with extremely high resolution (better than 10 nm) and potentially at very high speed, it may become an important lithographic tool in the near future with the use of ultrathin polymer films as resist materials.

To prepare ultrathin polymer films on the surface of wafers, especially those of large diameter (6 or 8 inch), uniformity and defect density become important factors in determining the resist quality. The conventional spin coating method has been reported to introduce interference

striations<sup>5</sup> and high defect densities<sup>2</sup> when used to prepare ultrathin polymer films. As an alternative approach, the LB technique has been proposed to prepare more uniform ultrathin polymer films<sup>2</sup>. Using this technique monolayer polymer films can be transferred layer by layer onto the solid substrate from the water surface. An important feature of the LB technique is that the accumulation of monolayer films allows the thickness of the built-up film to be controlled in a precise manner. Consequently, extremely uniform and ultrathin polymer films can be prepared.

In order to establish a basis for rationalizing the lithographic performance of ultrathin polymer films, a better understanding of their structure at a molecular level is required. However, to date there has been very little effort in this area. Fluorescence spectroscopy and TEM have been used in this study to investigate the microstructure of ultrathin polymer films. Our first technique, extrinsic fluorescence, is capable of acting as a very sensitive probe of the polymer structure. A particular example is the use of pyrene excimer fluorescence, which has been employed in this study. The requirement for pyrene excimer formation is that two pyrene groups face each other in a sandwich arrangement at a separation distance of between 0.3 to 0.4 nm. Any structure changes on this scale will perturb the excimer forming sites and thus be detected. Our second technique, TEM, is a well known high resolution electron microscopy method for thin film microstructure studies on account of its small beam diameter (< 1 nm). Any structure changes on the order of 10 to 100 nm can be detected by TEM. In this paper we report on some recent results of fluorescence studies employing amphiphilic dyes deposited in LB monolayer PMMA films and TEM studies of intrinsic monolayer PMMA films.

## 2. EXPERIMENTAL

### 2.1. Materials

The monodisperse atactic PMMA, which was used for electron beam lithography, fluorescence spectroscopy and TEM studies, was obtained from Pressure Chemical. It had a weight average molecular weight (Mw) of 188,100 and Mw/Mn < 1.08. PDA for the fluorescence studies was obtained from Molecular Probes and used as supplied. Spectroscopic grade benzene purchased from J.T. Baker was used to prepare the PMMA solutions as a spreading solvent.

### 2.2. Substrates and LB film preparation

The substrates used in the electron beam lithography studies consisted of 50-nm chromium (Cr) films evaporated over 100-nm thermally grown silicon oxide on 4-inch silicon wafers. The Cr and oxide layers provide an excellent contrast for evaluating etched Cr patterns with both optical and scanning electron microscopes (SEM). Three-inch quartz wafers obtained from Shin-Etsu Chem. Co. were used as substrates for the fluorescence measurements. The substrates were cleaned by immersion in a 9/1- H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> solution at 120 °C for 20 min, followed by six cycles of deionized water rinsing and a final spin drying under a nitrogen ambient. The substrates used in the TEM studies were carbon films supported by copper grids purchased from Ted Pella Inc.

The LB film depositions were performed using a Joyce-Loebl Langmuir Trough IV equipped with a microbalance for measurement of the surface pressure by the Wilhelmy plate method. Filtered deionized water with a pH of 7 was used for the subphase. For the electron beam lithography and TEM studies, PMMA was spread on the water surface from a dilute benzene solution (10 mg PMMA in 20 ml benzene). For the fluorescence studies, the PMMA/PDA mixture was spread on the water surface from a dilute benzene solution (1.75 mg PDA and 8.33 mg PMMA in 20 ml benzene). Prior to compression a 20 min interval was allowed for solvent evaporation. The Langmuir film was compressed to the desired transfer pressure at a rate of 50 cm<sup>2</sup>/min, followed by a 20 minute equilibration period. The Cr-coated silicon wafers and quartz wafers were immersed into the subphase before the PMMA was spread on the water surface. The

first monolayer of PMMA was transferred during the first upstroke of the substrate, at the speed of 2 mm/min. Because of the hydrophobic property of the carbon film surface, a different procedure was used for the film transfer. In this case the copper grid supported carbon substrate was dipped into the subphase after the PMMA was spread on the water and compressed to the desired transfer pressure. The first monolayer of PMMA was transferred during the first down stroke and the second layer was transferred during the first upstroke.

### 2.3. Electron beam exposure

LB PMMA films transferred at 5, 11, 15, and 17 dyn/cm, with thicknesses 0.9 nm (1 layer) to 15.3-nm (17 layers), have been prepared and investigated as high resolution electron beam resists by exposure with a modified Perkin Elmer MEBES I pattern generation system. The MEBES exposures were performed at 20 MHz address rate, 10 kV accelerating voltage, 1/8  $\mu\text{m}$  beam diameter and address size, and 6 nA beam current giving a dose of 2  $\mu\text{C}/\text{cm}^2$  per scan. Equal line-space patterns with nominal feature sizes from 1.25  $\mu\text{m}$  down to 0.125  $\mu\text{m}$  were written. The dose ranges for this study were 1-200  $\mu\text{C}/\text{cm}^2$ . After exposure PMMA was developed in a 3:7 cellosolve:methanol solution for 13 s. Prebaking and postbaking conditions were 100°C for 2 hours and 90°C for 30 min, respectively. Following the postbaking process the samples were put in a Cr etching solution (Cyantek CR-14) for 30 s to transfer the resist pattern to Cr. The samples were then examined with a scanning electron microscope (SEM).

### 2.4. Fluorescence measurement

Fluorescence spectra were measured on a Spex Fluorolog 212 spectrofluorometer equipped with a 450 W xenon arc lamp and a Spex DM1B data acquisition station. Spectra were recorded in the front-face illumination mode using 343 nm excitation wavelength. Single scans were performed using a slit width of 1.0 nm. PDA fluorescence emission spectra were recorded from 360 to 600 nm, with the monomer and excimer fluorescence measured at 376.5 and 485 nm, respectively. Monomer and excimer peak heights were used in the calculation of the ratio of excimer to monomer emission intensities ( $I_e/I_m$ ). Excitation spectra were recorded from 300 nm to 360 nm and monitored at 376.5 and 500 nm for the monomer and excimer excitation, respectively.

### 2.5. TEM experiments

Two-layer PMMA films on the copper grid supported graphite were transferred at 1 dyn/cm and 19 dyn/cm. After transfer the films were shadowed by 2-nm evaporated Cr at a 15° angle. Shadowing enhances the surface structure to be observed. A Phillips 430 transmission electron microscope, operated at 300 keV, was used to examine the samples.

## 3. RESULTS

### 3.1. Electron beam lithography

LB PMMA films with thicknesses greater than 6.3 nm withstood the 50-nm Cr etching, allowing the patterns to be transferred from the resists into Cr films. Fig. 1 is an example of the patterns in Cr employing a 8.1 nm (9 layers) LB PMMA film, transferred at 15 dyn/cm, as a positive electron beam resist. Resist films prepared at different transfer pressures did not appear to differ substantially in their lithographic performance. Those films thinner than 4.5 nm (5 layers) proved unsuitable for withstanding the chromium etch once they had been cycled through MEBES (even though nominally unexposed).

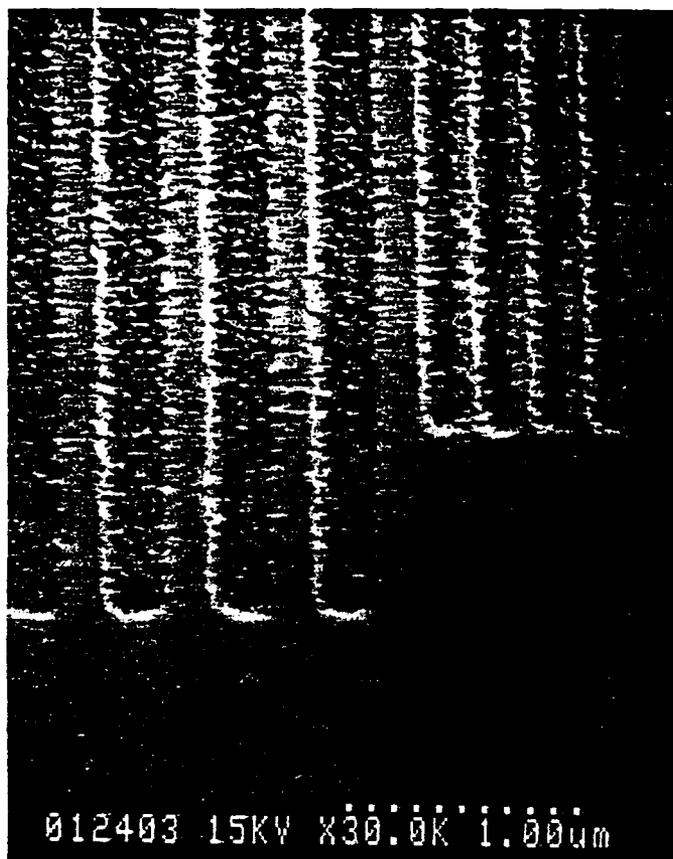


Fig. 1 Patterns in 50 nm Cr film employing a 8.1 nm (9 layers) LB PMMA film as resist, exposed with a MEBES I system at 10 kV accelerating voltage, 1/8  $\mu\text{m}$  beam diameter and address size, 6 nA beam current, and with a dose of 80  $\mu\text{C}/\text{cm}^2$ .

### 3.2. Fluorescence measurements

LB monolayer PMMA films doped with 5 mol% PDA have been prepared at surface transfer pressures ranging from 1 to 17 dyn/cm. Examples of PDA emission and excitation spectra are given in Fig. 2 and 3 respectively. The fluorescence measurements on these films have been plotted in Fig. 4 as  $I_e/I_m$  vs. surface pressure.  $I_e/I_m$  increases as the surface pressure increases, and decreases as the pressure passes some critical value ( $\sim 10$  dyn/cm). A summary of the results of the fluorescence excitation spectra are listed in Table I. The excitation spectrum, which is analogous to the absorption spectrum, is generated by monitoring the emission intensity at a specific wavelength as a function of excitation wavelength. From the excitation spectrum we can analyze the configurations of different absorbed species. All the excimer excitation spectra were red shifted ( $\sim 4$  nm) and broadened relative to that of the monomer.

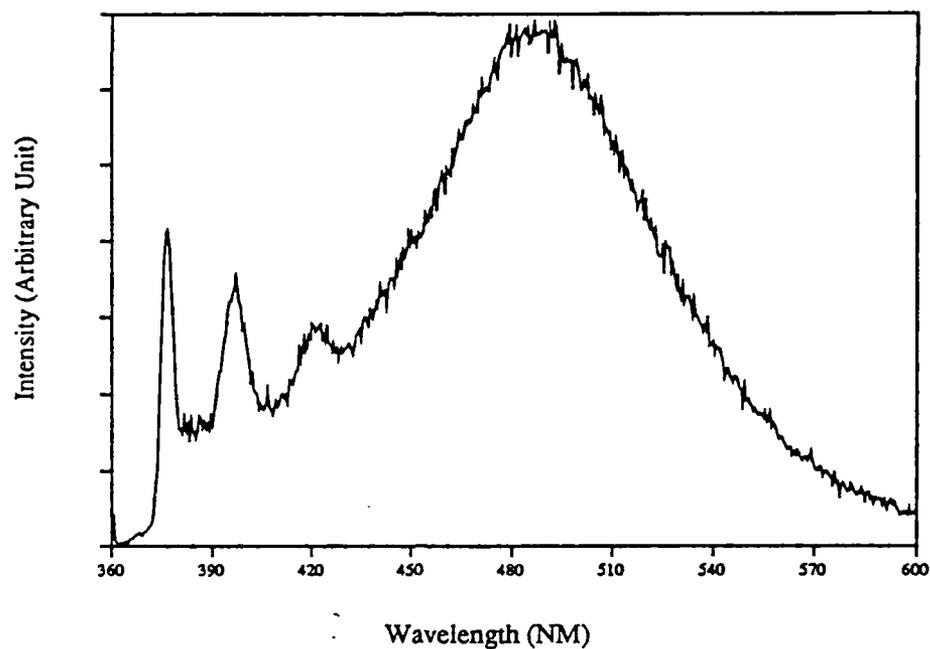


Fig. 2 Fluorescence emission spectrum of 5 mol% PDA in monolayer LB PMMA film transferred at 7 dyn/cm. The excitation wavelength is 343 nm.

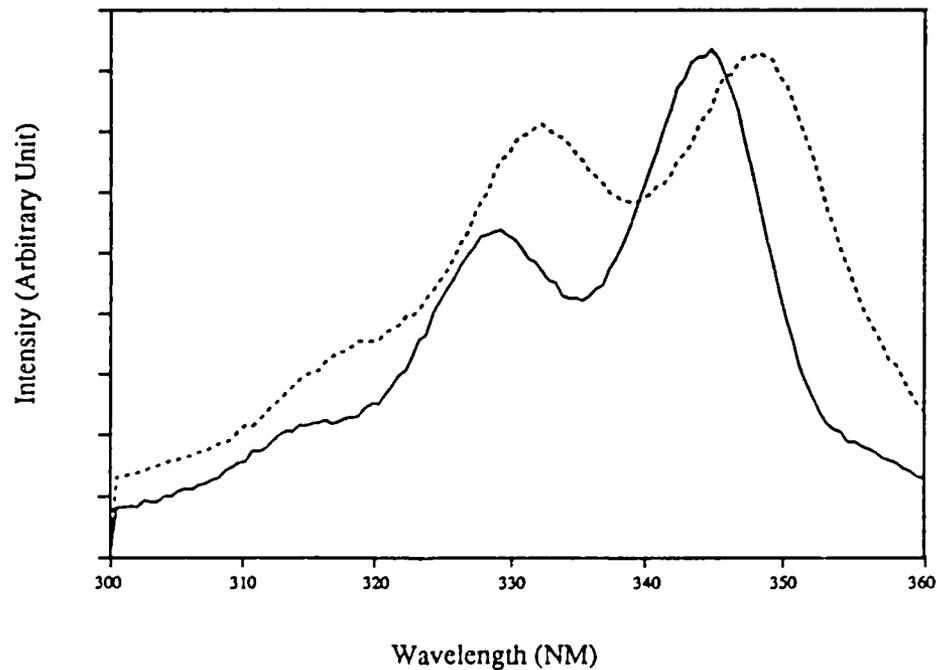


Fig. 3 Fluorescence excitation spectra of 5 mol% PDA in monolayer LB PMMA film transferred at 7 dyn/cm. The excimer excitation (dashed curve) was monitored at 500 nm and monomer excitation (solid curve) was monitored at 376.5 nm.

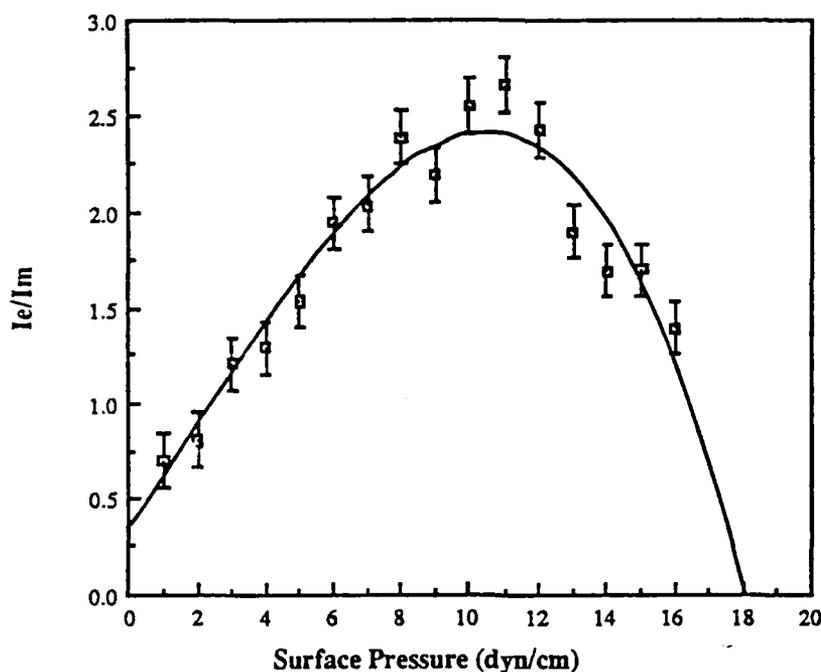


Fig. 4 Ratio of excimer ( $I_e$ ) to monomer ( $I_m$ ) fluorescence intensities of 5 mol% PDA in monolayer LB PMMA film as a function of transfer pressure.

Table I. Summary of the Results of PDA Fluorescence Excitation Spectra (188K Mw PMMA)

Surface Pressure (dyn/cm)	<sup>a</sup> $\lambda_{Max}$ (nm)		Peak Broadening <sup>b</sup>	
	Excimer Exc.	Monomer Exc.	Excimer Exc.	Monomer Exc.
2	348	344	1.18	1.69
4	348	344	1.26	1.73
6	347.5	344	1.45	2.06
8	347.5	344	1.42	1.95
10	348	344	1.49	2.14
12	347.5	344	1.38	1.95
14	347.5	344.5	1.50	2.17
16	347.5	344.5	1.51	2.26

- a.  $\lambda_{Max}$  is the wavelength at which the global maximum peak intensity of the PDA excitation spectrum occurs.
- b. Peak Broadening is defined as the ratio of the intensity of the maximum peak of the PDA excitation spectrum to the intensity of its adjacent local minimum.

### 3.3. TEM experiments

Fig. 5 and 6 are the photographs of the bilayer PMMA, prepared at 1 dyn/cm and 19 dyn/cm respectively, as observed by TEM at 180,000x magnification.

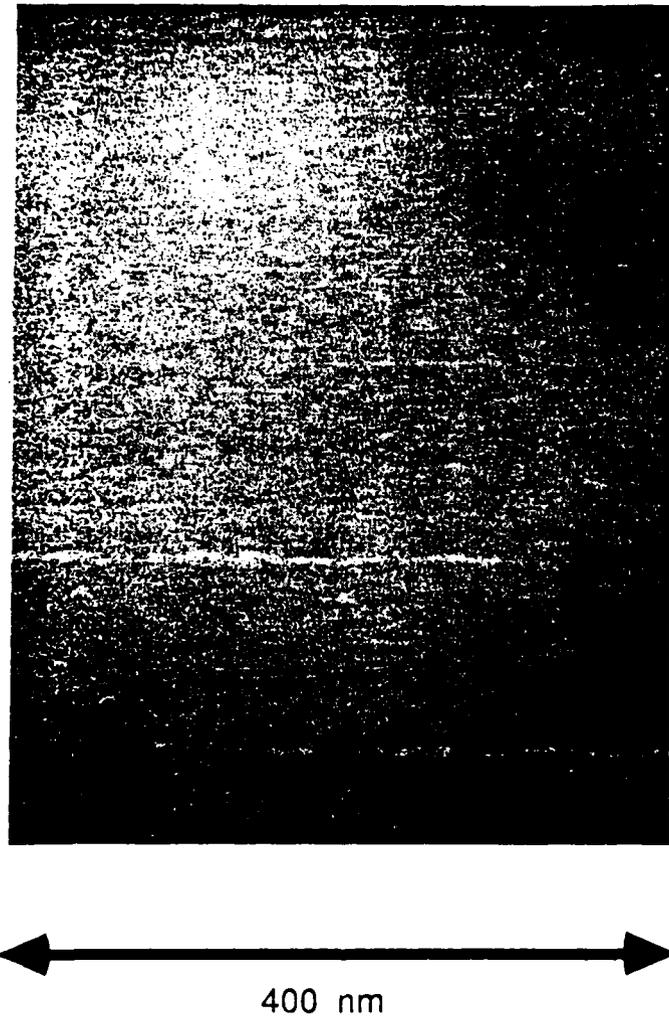


Fig. 5 TEM photograph of bilayer LB PMMA film prepared at 1 dyn/cm. The magnification of the photo is 180,000x.

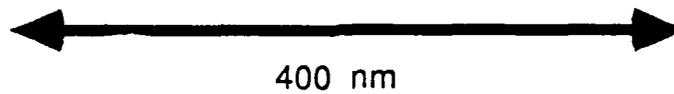
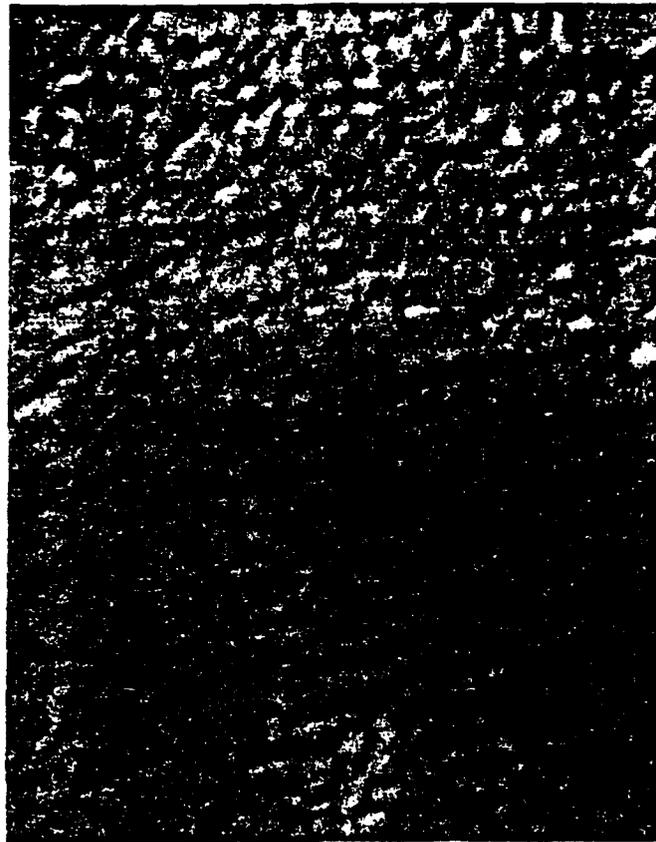


Fig. 6 TEM photograph of bilayer LB PMMA film prepared at 19 dyn/cm. The magnification of the photo is 180,000x.

## 4. DISCUSSION

### 4.1. Electron beam lithography

LB PMMA films with thickness of 6.3 nm (7 layers) are sufficient for patterning a Cr film suitable for photomask fabrication. For ultrathin PMMA films the resolution (see Fig. 1) is limited by the smallest spot diameter available on MEBES I (1/8  $\mu\text{m}$ ). However, it is not possible to obtain this resolution if a thicker resist ( $> 100$  nm) is used under the same exposure and developing conditions, which demonstrates that ultrathin resists are able to minimize the proximity effect. Also, since the radius of gyration of 188,100 Mw PMMA is about 10 nm in the bulk and since the thickness of the 7 layer film (6.3 nm) is less than 10 nm, it is reasonable to assume there must be an alteration of chain configuration in the ultrathin films. This will be particularly true when the post deposition baking temperature of the multilayer films is less than the glass transition temperature (115°C), as is the case for the present experiments. In such a case, interdiffusion of PMMA chains between the deposited layers may not achieve a configuration characteristic of the bulk.

### 4.2. Fluorescence measurements

When the PMMA/PDA mixture forms a Langmuir film, the hydrophilic C=O groups of PMMA are expected to be directed toward the water phase with the chain backbone lying generally parallel to the water surface. The COOH groups of PDA are also expected to be directed toward the water with the long aliphatic chain and pyrene groups directed upward. Upon compression of the Langmuir film, the PMMA chains presumably become more compact and finally collapse. The collapse pressure of PMMA has always been a controversial issue in the literature. This has arisen because of different definitions and methods of determining collapse pressure and different stereoregularity of the PMMA. Stroeve et al.<sup>6</sup> provide a detailed discussion of these points in which they suggest that for Langmuir layers of syndiotactic PMMA (Mw  $\sim 100,000$ ) there are two important regimes: a regime where reversible loss becomes important, at about 15 dyn/cm, and a regime where there is an irreversible collapse of the Langmuir layer, at surface pressures greater than or equal 34 dyn/cm. While the reversible loss mechanism must be associated with some of the polymer being forced out of the monolayer, this layer must be available to be pulled back into the interface upon expansion of the Langmuir layer. For the atactic-PMMA (Mw  $\sim 188,100$ ) used in this study, we have observed these two regimes from the pressure-area measurements.

5 mol% PDA was used as a probe to detect structural changes in the PMMA matrix. As the pressure increases the two dimensional surface concentration of PDA increases and thus the probability of intermolecular excimer formation increases, i.e.  $I_e/I_m$  increases. However, once the pressure exceeds 10 dyn/cm,  $I_e/I_m$  starts to decrease indicating that the structure of the excimer has been influenced by microstructural changes in the polymer matrix. The excitation spectra of PDA at different surface pressures indicate that the extent of the red shift (excimer vs. monomer), which is due to the ground state interaction of the dyes, is not influenced by the surface pressure in the range 0 - 17 dyn/cm. This suggests that the probe molecules are not unduly constricted as the inter/intra chain voids shrink in size during compression. In other words, as the pressure increases, the voids become smaller and consequently  $I_e/I_m$  increases. However, despite the fact the probes are forced to occupy a smaller area, they are not being constrained to the extent that they experience a change in ground state interaction. As the pressure surpasses  $\sim 10$  dyn/cm, the polymer chain may start to buckle and form loops that extend above the monolayer, thereby being disruptive to excimer formation in this region. No clear picture on the molecular level is presently available. However, the spirit of our concept is contained in the highly schematic representation of Fig. 7.

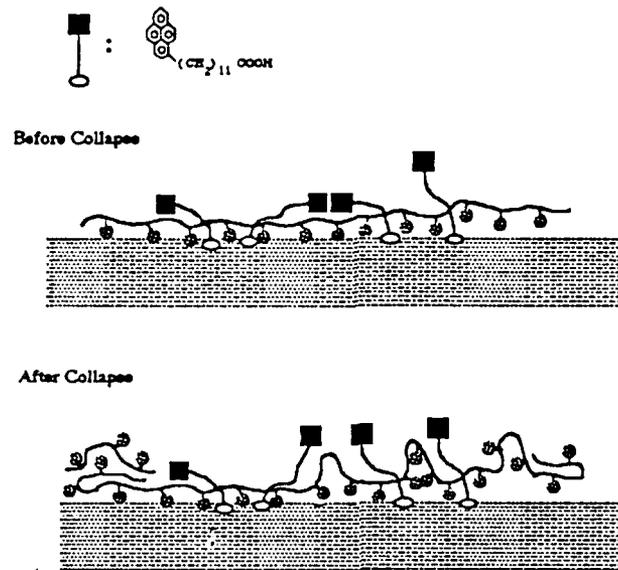


Fig. 7 Schematic of PDA dyes in monolayer Langmuir PMMA film on the water surface before and after the film collapse.

#### 4.3. TEM experiments

A bilayer LB PMMA film prepared at 1 dyn/cm (Fig. 5) shows much less surface topography than the sample prepared at 19 dyn/cm (Fig. 6) when examined under TEM. The wrinkle-like structure in Fig. 6 may be a result of macroscopic film collapse.

### 5. SUMMARY

Ultrathin LB PMMA films have been demonstrated to act as high resolution electron beam resists. Film collapse has been observed in LB PMMA films by using fluorescence spectroscopy and TEM. However, film collapse did not appear to influence the lithographic performance when seven or more layers of LB PMMA films were used as the resist. A more comprehensive study of the relationship between lithographic performance and LB film structure is currently underway.

### 6. ACKNOWLEDGEMENTS

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