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Ultrathin polymer films for microlithography

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Ultrathin (14–22 nm) poly(methylmethacrylate) (PMMA) films prepared by both spin casting and Langmuir-Blodgett (LB) techniques and novolac films prepared by spin casting have been explored as high-resolution electron beam resists. One-eighth micron lines-and-spaces patterns (equal to the smallest beam diameter available) have been achieved by using a Perkin Elmer MEBES I pattern generation system as the exposure tool, and the definition of 45-nm features has recently been achieved by using a high-resolution electron beam lithography system. [J. H. Newman, K. E. Williams, and R. F. W. Pease, J. Vac. Sci. Technol. B 5, 88 (1987)]. The etch resistance of such films is sufficiently good to allow patterning of a chromium film suitable for photomask fabrication. The most surprising result has been that the pinhole densities in 14.3-nm LB PMMA film and 22-nm spin-cast novolac film are only a few per cm², considerably lower than the density in spin-cast PMMA films of comparable thicknesses.

I. INTRODUCTION

Thin polymer films have been used as resist materials for lithography in microelectronic technologies since the 1960s. In optical lithography, resist thicknesses and minimum feature sizes in state-of-the-art manufacturing are about 1 μm. The resolution is limited by resist absorption, light diffraction, and rheological effects related to the resist development process. In electron beam lithography, the resist thickness and minimum feature sizes in the current electron beam mask making process are about 0.5 μm. The major limitation on the resolution is imposed by electron scattering (proximity effect), which causes a uniform incident exposure to result in a nonuniform distribution of actually received 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.

The advantages of ultrathin resists are manyfold. In optical lithography, they offer improved exposure and focus latitude and alleviate the problem of absorption in conventional resists such as novolac, especially for deep ultraviolet (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) 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. 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 in conjunction with the use of ultrathin polymer films as resist materials.

Despite these advantages, three drawbacks of ultrathin resists have been perceived: (i) high pinhole density, (ii) inadequate etch resistance, and (iii) inability to cover topographic steps. As a result, few studies have been reported to date in this area. In this work, however, we have successfully demonstrated the possibility of obtaining surprisingly low pinhole density and good etch resistance from ultrathin resists. The step coverage problem can, in principle, be overcome by using multilayer resist systems and will not be addressed in this paper.

In this study we particularly chose a resist thickness in the 20 nm regime for two reasons. First, from the scientific point of view, 20 nm is about the size of a polymer coil. Therefore, the configuration of the polymer chains should strongly influence certain macroscopic properties (e.g., lithographic properties). Second, this is thin enough to allow the penetration of tunneling electrons. As a consequence we can use the STM as a low-voltage and small beam diameter exposure tool to explore lithography in the nanometer regime.

Two different techniques have been used to prepare uniform ultrathin polymer films. The first is spin casting, which is a common technique for preparing uniform resist films in the current integrated circuit processes. In general, the thickness T of the spin-cast film depends on spin speed (ω) and solution viscosity (η) in the following manner:

\[ T \sim \omega^{-0.5} \eta^{0.33} \]

Thus, dilute solutions (< 2%) and high spin speed (> 5000 rpm) have been used to prepare ultrathin resist films. The second method is the Langmuir-Blodgett technique. Conventional Langmuir-Blodgett (L-B) films formed from amphiphilic monomers, such as long-chain fatty acids, have relatively poor thermal and mechanical stabilities, which are crucial properties for resist materials. To circumvent these problems, two approaches using more stable and robust polymeric materials have been proposed. Cemel et al. have explored the possibility of forming L-B films from suitable monomeric materials, such as unsaturated fatty acids (e.g., ω-tricosenoic acid, vinyl stearate, and diacetylene derivat...
An alternative approach employed by Tredgold et al. was to prepare L-B polymer films directly from suitable amphiphilic polymers such as derivatives of styrene-maleic anhydride. We have adopted a similar approach but with a better characterized polymer, monodisperse poly-

(methylmethacrylate) (PMMA).

In this procedure a two-dimensional solid film is formed on the water surface and transferred layer by layer to the substrate. Using the L-

B technique to prepare resist materials, the layered structure of the resist films is expected to be more ordered than that of the conventional spin-cast films. The Langmuir–Blodgett and spin-casting techniques will produce ultrathin polymer films with different polymer chain configurations, and it is of interest to compare the lithographic performance between these two types of film using the same material.

II. EXPERIMENTAL

A. Polymers

Two different polymers have been used to prepare ultrathin resist films. The first is atactic-PMMA [Fig. 1(a)] obtained from Pressure Chemical Company with a weight average molecular weight (\(M_w\)) of 188,100 and \(M_w/M_n < 1.08\), where \(M_n\) is number average molecular weight. The PMMA films have been prepared by both spin-cast and L-B techniques. The second material is a conventional novolac [Fig. 1(b)] optical resist, AZ 5206, supplied by American Hoechst Corp., and only spin-cast films have been prepared.

B. Substrates

The substrate used in this study consisted of 50-nm evaporated chromium (Cr) films over 100-nm thermally grown silicon dioxide on silicon wafers. The Cr and oxide layers provide an excellent contrast for evaluating etched Cr patterns with both optical and scanning electron microscopes (SEM).

C. Spin-cast films

In order to prepare ultrathin spin-cast polymer films, very dilute polymer solutions and high spin speeds have been used. Spin-cast PMMA films with a thickness of 14 nm (measured by ellipsometry) on Cr were prepared by spinning 0.75 mg/ml chlorobenzene solution at 8000 rpm for 30 s. The solution was filtered by a 0.2-\(\mu\)m filter. After spinning, the film was prebaked for 8 h at 170 °C. Prebaking at temperatures above the glass transition temperature \((T_g)\) of PMMA \((~105 °C)\) for 8 h was performed to evaporate residual solvent and to anneal any stresses that might be induced into the film during spinning.

Spin-cast novolac resist films with a thickness of 22 nm were cast from a 1:10 diluted AZ 5206 solution and spun at 5000 rpm for 15 s. The prebake condition was 90 °C for 20 min.

D. Langmuir–Blodgett films

The L-B film depositions were performed using a Joyce–Loebel Langmuir Trough IV equipped with a microbalance for measurement of the surface pressure by the Wilhelmy plate method. To eliminate the contamination of metal ions arising from the standard glass trough, a specially designed quartz trough was used. Filtered deionized water with a pH of 7 was used for the subphase. The PMMA was spread on the water subphase from a very dilute solution (0.5 mg/ml) in chloroform, and the solvent was allowed to evaporate. The hydrophilic C–O groups are expected to be directed toward the water phase with the chain backbone lying parallel to the water surface. After several slow (50 cm²/min) compression and expansion cycles a pressure–area isotherm was recorded before film transfer.

The pressure–area isotherms for PMMA, shown in Fig. 2, were measured at 20 °C and at a compression rate of 50 cm²/min with 0.1 ml of a 0.5 mg/ml PMMA solution. Curve 1 (0–30 dyne/cm) was the first compression and curve 2 (30–0 dyn/cm) the subsequent expansion to the original maximum area. Curve 3 (0–15 dyn/cm) was the second compression followed by an expansion (curve 4, 15–0 dyn/cm) to the original area. Stroeve et al. have suggested that the hysteresis in curves 1 and 2 is due to a portion of the polymer being ejected from the two-dimensional polymer Langmuir film during the compression and being pulled back to the Langmuir layer at a slower rate during the expansion. The film was transferred at the surface pressure of 15 dyn/cm, which is just below the pressure at which hysteresis oc-

![Fig. 2. Pressure-area isotherm for poly(methylmethacrylate) at 20 °C.](image-url)
curred. The area occupied by each repeat unit of poly(methylmethacrylate) has been calculated to be $0.156 \text{ nm}^2$ from the pressure-area isotherm; this value suggests that polymer chain backbones were lying parallel to the water surface.

The surface of the evaporated Cr was hydrophilic (measured by water contact angle) due to a very thin layer of native Cr oxide. In order to have a hydrophilic (Cr oxide) and hydrophilic (C=O) interaction between the substrate and the first monolayer PMMA film, the substrate was immersed into the subphase water before the PMMA was spread on the water. The first monolayer of PMMA was transferred during the first upstroke of the substrate, at the speed of 2 nm/min. During the transfer the Cr and water interface formed a very sharp line indicating that the transfer was very uniform across the wafer. The area decrease of the interface formed a very sharp line indicating that the transfer was very uniform across the wafer. The area decrease of the monolayer film on the water surface was recorded on an area-time recorder. After the first layer had been transferred, a 20-min oven bake at $100 \text{ °C}$ was performed prior to the next downstroke. This bake process was found to be crucial for the subsequent depositions and lithographic performance of the films as will be discussed later. After baking, 16 more layers were transferred continuously. Deposition occurs during both downstrokes and upstrokes, so that the structure of the film is Y type. Values of deposition ratio defined as the area decrease of the monolayer film on the water surface divided by the area of the wafer passing through the water, are about 1.0 for all the upstrokes and about 0.8 for all the downstrokes. The thickness of the 17-layer PMMA film is 14.3 nm, as measured by ellipsometry, corresponding to $0.85 \text{ nm}$ per layer, with an excellent thickness uniformity over the deposited area (less than 1% variation across a 100-mm wafer). The film was prebaked at $100 \text{ °C}$ for 8 h after the deposition was completed. The prebaking temperature was set below the $T_g$($\sim 105 \text{ °C}$) of PMMA in an attempt to maintain any ordering of the polymer molecules that was induced as a result of the L-B deposition procedure.

E. Electron beam exposure

Spin-cast PMMA (14 nm) and novolac (22 nm) films and L-B PMMA (14.3 nm) film were exposed with a modified Perkin Elmer MEBES I pattern generation system and a high-resolution electron beam lithography system. The MEBES exposures were performed at 20-MHz address rate, 10-kV accelerating voltage, $\mu \text{m}$ beam diameter and address size, and 6 nA beam current giving a dose of $2 \mu \text{C/cm}^2$ per scan. Equal line-space patterns with nominal feature sizes from 1.25 down to 0.125 $\mu \text{m}$ and patterns with 2 $\mu \text{m}$ for the characteristic exposure measurement were written. The dose ranges for this study were 1-200 $\mu \text{C/cm}^2$ for PMMA and 1-20 $\mu \text{C/cm}^2$ for novolac resist; only positive resist behavior has been observed over these ranges. Figure 3(a) shows the characteristic exposure curves of 14-nm spin-cast PMMA film and 14.3-nm L-B PMMA film. There is no observed difference between these two films. Figure 3(b) shows the characteristic exposure curve of 100-nm-thick spin-cast novolac resist film.

The high-resolution electron beam lithography system was designed and built at Stanford for the fabrication and study of microstructures. A novel single bore objective lens provides a minimum beam diameter of $<5 \text{ nm}$. The exposures in this work were done with a 12 nm beam diameter and a 3 pA beam current. Lines were written with a single pass of the electron beam with doses ranging from 0.5 nC/cm ($\sim 100 \mu \text{C/cm}^2$) to 4.0 nC/cm.

F. Developing

After exposure, the PMMA was developed in a solution made of 3:7 cellosolve: methanol for 13 s. Cellosolve was chosen because it is strong enough to dissolve the exposed PMMA but not the unexposed material. For novolac, KLK PPD-401 developer diluted 1:1 with deionized water was used. The developing time for 22-nm novolac film was 30 s. Postbaking at $90 \text{ °C}$ for both PMMA and novolac films was performed for half an hour after developing.

G. Cr etching

Following the postbaking process the samples were immersed in a Cr etching solution (Cyantek CR-14) for 30 s to transfer the resist pattern to Cr. After Cr etching, the
PMMA was stripped using acetone rinsing. Acetone was also used for stripping novolac resist films; however, residue was left around the patterns and was stripped by further immersion in sulfuric acid. The samples were then examined with a scanning electron microscopy (SEM) for resolution measurement and with an optical microscope for pinhole density measurement.

III. RESULTS

Figure 4 shows the patterns in Cr film with a 14-nm spin-cast PMMA film as a positive electron beam (e-beam) resist. The film was prebaked at 170 °C for 8 h and exposed with a dose of 200 μC/cm². The patterns on the far right region are 0.25-μm nominal lines and spaces. There are two 0.25-μm pinholes and several pinholes <0.1 μm in size in the area shown, and these are the typical sizes and frequency in this sample. Figure 5 shows patterns in Cr, with a 14.3-nm L–B PMMA film as a positive e-beam resist. The film was prebaked at 100 °C for 8 h and exposed with a dose of 30 μC/cm². Figure 6 shows an overetched pattern in Cr with a 22-nm novolac film as a positive resist. The film was prebaked at 90 °C for half an hour and exposed with a dose of 10 μC/cm². The resolution shown in Figs. 4–6 is limited by the smallest spot diameter available on MEBES I (1,um) and is much better than the resolution obtained on thicker resist (>100 nm) for the same exposure conditions. Recently, we have exposed 14.3-nm L–B PMMA films with a high-resolution electron beam exposure system with a minimum beam diameter <5 nm. Lines down to 72 nm wide have been patterned in 50-nm Cr with a 14.3-nm L–B PMMA film as a positive resist (Fig. 7). When using 20-nm-thick Cr, the smallest linewidth in Cr was 45 nm. These results demonstrate that ultrathin resist films (both PMMA and novolac) have satisfactory etch resistance for transferring the pattern from the resist to a 50-nm layer of Cr using wet etching.

The blue color of 100-nm silicon dioxide layer provides an excellent contrast against Cr for examination under the reflection optical microscope. This contrast has been used to measure the pinhole density resulting from the ultrathin resist films. A total of twenty 4-in. wafers prepared under various conditions were immersed in the Cr etching solution for 30 s to simulate the etching in photomask fabrication. As summarized in Table I, the difference between spin-cast and L–B films is dramatic. The 14-nm spin-cast PMMA films that were prebaked at 170 °C for 8 h exhibited a pinhole density of about 10⁴ pinholes/cm², three orders of magni-
tude higher than the few per cm$^2$ obtained with 14.3-nm L-B PMMA film and with 22-nm spin-cast novolac film. Samples prebaked at 100 °C for 8 h show less etching resistance to chromium etching and have the same order of magnitude of pinhole density as samples prebaked at 170 °C. Five wafers with spin-cast PMMA and five with novolac have been examined and more than ten wafers have been examined for L-B PMMA films; for each wafer, the area examined exceeded 10 cm$^2$.

The 20-min bake at 100 °C after the first monolayer of PMMA has been transferred in the L-B trough is crucial. L-B PMMA films without the bake exhibited a pinhole density as high as that in the spin-cast PMMA film. Residual water that remains on the hydrophilic Cr surface after transferring the first PMMA layer may be causing poor adhesion between Cr and PMMA. This hypothesis is further supported by the fact that, without baking after the first layer no transfer will occur during the next downstroke and a Z-type structure will be formed in the first four layers.$^{24}$ More extensive studies on the effect of baking are in progress.

The pinhole densities of spin-cast novolac films with various thicknesses on a different substrate, 80-nm Cr on glass wafers, have also been examined using a transmission optical microscope for an area about 10 cm$^2$. These are plotted in Fig. 8 as a function of resist thickness. The pinhole densities of the ultrathin novolac films are surprisingly lower than expected. The difference in pinhole density between spin-cast PMMA and novolac films suggests that different polymers with different molecular weight (novolac has lower molecular weight) will have very different lithographic properties.

### IV. DISCUSSION

We have investigated the lithographic properties of ultrathin spin-cast PMMA films (14 nm), L-B PMMA films (14.3 nm) and spin-cast novolac films (22 nm) as electron beam resists. We demonstrated that the ultrathin resists have potential for high-resolution lithography in the nanometer regime and permit etching of underlying chromium. The resolution achieved in these ultrathin resist films is much better than that in thicker resists ($>200$ nm) for the same exposure conditions. As we expected, the lithographic performance of the ultrathin polymer films depends strongly on the film preparation methods, materials, and process conditions.

There is no obvious explanation for the thousandfold difference in the pinhole density between spin-cast and L-B PMMA films with the same material and film thickness. However, it does not appear that this low pinhole density is unique to L-B PMMA films because 22-nm thick novolac film formed by spin casting also demonstrated the low pinhole density ($<10$/cm$^2$). To try to understand this we are performing studies such as fluorescence spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning tunneling microscopy to investigate the structure of a variety of ultrathin polymer films formed both by spin-casting and by the L-B techniques. The existence proof of remarkably low pinhole frequency, better resolution and adequate etch resistance with a resist thickness at least thirty times thinner than that used presently suggests that we should seriously consider the use of much thinner imaging layers than has been common practice.
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