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Ultrathin resist films patterning using a synchrotron radiation lithography system

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Ultrathin polymethylmethacrylate (PMMA) films with a width of 17–59.5 nm have been prepared for X-ray resist by Langmuir–Blodgett (LB) technique on a trough using a steady laminar flowing subphase for monolayer compression. Using a synchrotron radiation (SR) lithography system as an exposure tool, patterns with 0.2 μm critical dimensions have been obtained, limited to the mask used. Copyright © 1996 Elsevier Science Ltd

Introduction

Conventional optical lithographies which employ standard photoresists may not be adequate for printing features with critical dimensions smaller than 0.25 μm. Because X-rays have an extremely short wavelength, they have been applied to deep submicron lithography widely. Projection X-ray lithography using wavelengths of 13–16 nm radiation is a potential technology for the mass production of ultra-large scale integration (ULSI) circuits with 0.1 μm features.[1] In this regime of X-ray wavelength, resist opacity is a serious problem and surface imaging approaches are believed to be required. In general, the opacity of conventional resist systems to soft X-ray requires the resist thickness to be reduced to smaller than 200 nm.[2] However, conventional spin-cast resist films seem unable to give high quality ultrathin films for high resolution lithography, since the high pinhole density, high permeability, inadequate etch resistance and inability to cover topographic steps increase steeply below 300 nm.[3] Trilevel resist schemes[4] have been successfully demonstrated with projection X-ray lithography at 14 nm, where 70 nm thick layers are used as imaging layers, however, the complexity and cost of this process makes it problematic for rapid acceptance in a production environment. In recent years, Langmuir–Blodgett (LB) films, which are prepared from the deposition of a monolayer spread on a water surface onto solid supports such as silicon wafers so as to result in ordered assembly construction, have been explored as a new type of high resolution resist for electron beam and ultraviolet lithography to remedy the disadvantages of ultrathin spin-cast resists.[3,5–8] In this work, we have successfully demonstrated the possibility of obtaining high resolution from ultrathin resist prepared by LB technique in X-ray lithography by using a synchrotron radiation (SR) lithography system as an exposure tool.

Experiment

Atactic polymethylmethacrylate (PMMA), purchased from Wuxi Institute of Chemical Engineering, with a weight average molecular weight of 1.8×10^5, was used to prepare ultrathin X-ray resist films. The substrates used in our study were silicon $<111>$ wafers covered with a 100 nm evaporated aluminum film. For the aqueous subphase, deionized water was distilled twice in an all-glass still. Its electric conductivity was smaller than 10^{-10} S/cm. The PMMA was spread on the water subphase from a very dilute solution, 0.5 mg/ml, in trichloromethane, and the solvent was allowed to evaporate. The properties of PMMA monolayer at air–liquid interface have been described elsewhere.[8,9] Briefly, the film at air–liquid interface, when the surface pressure was smaller than 2 dyne/cm, is a gaseous state film. While the surface pressure between 2 and 12 dyne/cm, the film is a gaseous–liquid hybrid state film. At a surface pressure of 15 dyne/cm, the hydrophilic C=O groups of PMMA are expected to be directed toward the water phase with the chain backbone lying parallel to the water surface. So the films were transferred at the surface pressure of 15 dyne/cm. The transferring process was performed using a large area Langmuir trough with steady flowing subphase, which can be used to deposit films continuously and automatically onto wafers 4 inches in diameter.[10] The dipping speed was 5 mm/min. The transfer ratio was 1.0 in both downstrokes and upstrokes, so that a Y-type LB film structure resulted. After the first and second layers had been transferred, the sample was baked for 20 min at 100°C before the next stroke. In the transfer of subsequent layers, baking at 100°C for 10 min was performed after every 10 layers. The purpose of this baking process is to increase the adhesion between the film and substrate. This baking process was set below the glass transition temperature Tg of PMMA in an attempt to maintain the film construction that was induced as a result of the LB deposition procedure. The experiment process was carried out at 14 ± 1°C in a clean room. The thickness per layer of PMMA is 0.85 nm measured by ellipsometry.[3] The layers of PMMA LB films in our study were between 20 and 70. So the thickness of PMMA LB films for X-ray exposure was about in the region of 17–59.5 nm. Atomic force microscope (AFM) studies showed that the pinholes were smaller than 12 nm in diameter with a density of about 10/cm^2,[2] three orders of magnitude lower than that of spin cast films with the same thickness.

The X-ray exposures were conducted on the beamlines of the optolithographic station at the National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China (USTC). The SR light source is an electron storage ring with a single superconducting magnet. Electrons injected from a 200 MeV racetrack microtron into the storage ring are accelerated up to 800 MeV and stored in the ring. A special exposure shutter is equipped on the beamline. Its action time is 15 ms. The vacuum in the mirror box is smaller than 5×10^{-8} Pa. The grazing angle of the installed scanning plane mirror is 20 mrad. Its horizontal accepting angle is 5.5 mrad and its oscilloscope frequency is 138 Hz. In routine operation, the stored current is 327 mA. The wavelength of the beamline we used is 16 nm. The exposure area is 30×30 mm.[2] The scanning speed of the oscillating mirror is precisely controlled in order to improve the nonuniformity. The dose uniformity within 10% is obtained all over the exposure field. The vacuum of the exposure chamber is smaller than 5×10^{-4} Pa. The X-ray mask used in this study, with critical dimensions of 0.2 μm, consists of a 1 μm thick SiN membrane on a 1 mm thick Si wafer and a 1 μm thick sputtered Au absorber.

After exposure, the samples were developed in a 3:1 solution of methyl isobutyl ketone (MIBK):isopropyl alcohol (IPA) for 10 s at 20°C. Postbaking at 80°C for the sample was performed for 40 min after developing.

Following the postbaking process the samples were immersed into 7:2 deionized water:phosphoric acid for 90 s to transfer the resist pattern to aluminum. After etching, the PMMA was stripped by using acetone rinsing.

Results and discussion

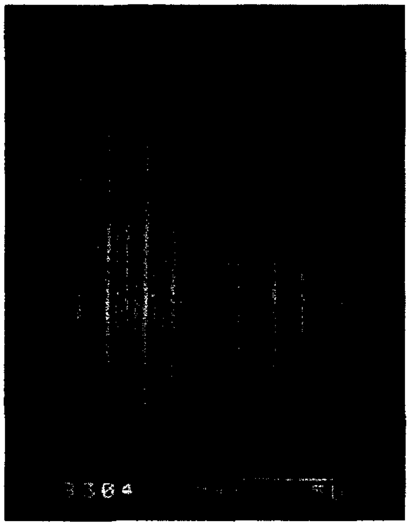

Figure 1. Scanning electron micrograph of 100 nm aluminum film on Si <111> wafer that was patterned by X-ray exposure to 80 mJ/cm^2 of 16 nm synchrotron radiation beamline at NSRL where 70-layer LB PMMA film was used as a resist.

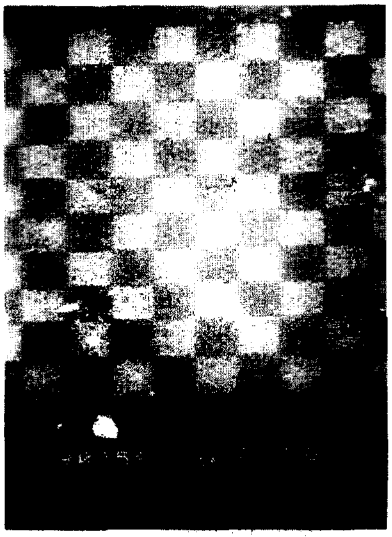

Figure 2. Scanning electron micrograph of 100 nm aluminum film on Si <111> wafer that was patterned by X-ray exposure to 50 mJ/cm^2 of 16 nm synchrotron radiation beamline at NSRL where 20-layer LB PMMA film was used as a resist.

Figures 1 and 2 show the scanning electron microscope (SEM) micrographs of the feature patterns of the samples after the subsequent exposure and developing process. Figure 1 shows that the minimum width in the grate pattern is 0.2 μm. This demonstrates that the pattern on the mask can be transferred to the aluminum layers of samples exactly. Another typical pattern is squares checkered with black and white, which is shown in Figure 2. For 20–70 layer PMMA LB film, the highest resolution pattern in mask can be successfully obtained under the X-ray exposure with a dose of 50–80 mJ/cm^2. But a dose of more than 100 mJ/cm^2 is inappropriate to such ultrathin resist films. Usually the developer for PMMA resist is a 1:3 solution of MIBK:IPA. However, in our experiment, even the developer (MIBK:IPA = 3:1) with such high solubility used, successfully obtained the transferred patterns. In other aspects, compared with other amphophilic molecules for LB film resist,[5-7,11,12] PMMA does not have a long hydrophobic chain. Moreover, for the monolayer PMMA LB film on a silicon substrate, our AFM studies on molecular level demonstrated that the PMMA polymer chain not only formed a long-range ordered orientation induced by the LB deposition process, but also twisted on itself caused by side chains effect and the scanning interaction of AFM head on it did not affect the twisted configuration of molecular chain.[13] These results give us an indication that PMMA LB films have a good robustness and mechanical stability. After the prebaking process, the adhesion between films and substrate was sufficiently good. Our wet etch experiments for PMMA LB films reported elsewhere[11] show that such resist films had a good etch resistance. The experimental results also demonstrate the sharpness of the transferred patterns with LB resist films is sufficiently good because the thickness is so thin that the diffraction effect is much weaker than that with conventional resists. All these results show that PMMA LB films have potential applications in ULSI circuits production as an X-ray resist. Especially, the LB film depositions in this study were performed on a large area Langmuir trough, in which the monolayer was compressed by steady laminar flowing subphase. So monolayers can be deposited onto large wafers up to 4 inches in diameter. The trough is useful in forming homogeneous polymeric monolayers with high surface viscosity, such as PMMA. So, even for the materials with high surface viscosity, high quality ultrathin films can be obtained by using higher pulling speed and deposition frequency, hence deposition rate. Moreover, because of its capacity for automation in all deposition processes for large area wafers, it is easier for acceptance in a production environment.

Conclusion

We successfully demonstrated the possibility of using ultrathin PMMA films as an X-ray resist. The ultrathin resist films with a thickness of 17–59.5 nm were prepared by the LB technique on a specially designed trough for compression of monolayers on the air–water interface by a steady laminar flowing subphase. Using an SR light source as an exposure tool, in the dose range of 50–80 mJ/cm^2, we obtained the patterns with 0.2 μm critical dimensions limited to the features of the mask used after etching.

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