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Langmuir–Blodgett resist films for microlithography by exposure to a scanning electron microscope

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Abstract

Ultrathin (20–100 nm) polymethylmethacrylate (PMMA) films prepared by Langmuir–Blodgett (LB) techniques have been explored as high resolution electron beam resists. A Hitachi S-450 scanning electron microscope has been modified for a high resolution electron beam exposure system. The lithographic properties and exposure conditions of LB PMMA films have been investigated. 0.15 μm lines-and-spaces patterns have been achieved by using the scanning electron microscope as the exposure tool. After etching, the sample has been studied by atomic force microscopy for pinhole measurement. The results demonstrate that the etch resistance of such films is sufficiently good to allow patterning of a 100 nm aluminium film suitable for mask fabrication.

1. Introduction

With the further increase in very-large-scale integration and the requirement of devices such as the high electron mobility transistor and the surface acoustic wave device, a variety of high resolution lithography techniques with electron beams, X-rays or deep UV have been developed [1]. Electron beams have the potential for studying small samples since the beam can be focused to about 5 Å. Further, a pattern can be created under computer control without a previous step of making a mask. The major limitation on the resolution in electron beam lithography is imposed by the proximity effect caused by electron scattering, which causes a uniform incident exposure to result in a non-uniform distribution of actually received exposure in the pattern area. These resolution-limiting effects generally become more serious with increasing resist thickness. The use of ultrathin resists will reduce electron scattering within the resists and thus make proximity effect correction schemes easier to implement. Therefore, to improve the resolution in electron beam lithography, ultrathin resists (with thickness less than 300 nm) should be adopted. However, conventional spin-cast resist films seem unable to give high quality ultrathin films for ultrahigh resolution lithography, since the high pinhole density, high permeability, inadequate etch resistance, and inability to cover topographic steps increse steeply below 3000 Å. In recent years, Langmuir–Blodgett (LB) films, which are prepared form the deposition of a monolayer spread on a water surface onto solid supports such as silicon wafers, have been explored as a new type of high resolution resist to remedy the disadvantages of ultrathin spin-cast resists [2–5]. However, some problems still exist, such as low thermal and mechanical stabilities and relatively poor etch resistance.

In this work, however, we have successfully demonstrated the possibility of obtaining high resoltion, good etch resistance and thermal stability from ultrathin resists prepared by LB techniques.

2. Materials and exerimental details

2.1. Polymer and substrate

Atactic polymethylmethacrylate (PMMA), which is shown in Fig. 1(a) and was purchased from the Wuxi Institute of Chemical Industry, with a weight average molecular weight of 80 000, was used to prepare ultrathin electron beam resist films. The substrates used in our study consisted of a 100 nm evaporated aluminium film on Si⟨111⟩ wafers.

2.2. Langmuir–Blodgett film

The LB film depositions were performed using a Face Langmuir trough equipped with a microbalance for measurement of the surface pressure by the Wilhelmy plate method. For the aqueous subphase, deionized water was distilled twice in an all-glass still. The PMMA was spread on the water subphase form a very

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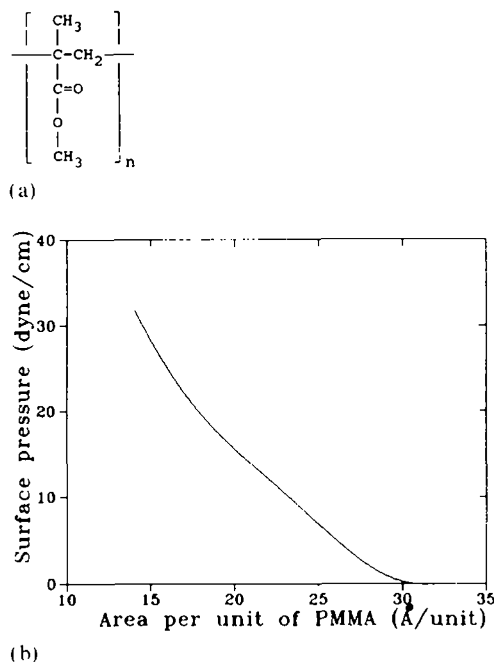

Fig. 1. (a) Structure of PMMA. (b) PMMA pressure area isotherm at 18 C.

dilute solution (0.52 mg ml^{-1}) in trichloromethane, 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 slow compression, the pressure–area isotherm for PMMA, measured at 18 °C and at a compression rate of 40 cm^2 min^{-1} with 100 μl of a 0.52 mg ml^{-1} PMMA solution, shown in Fig. 1(b) was recorded before film transfer.

The film was transferred at a surface pressure of 15 dyn cm^{-1}. At this surface pressure, the polymer chain backbones were lying parallel to the water surface [6, 7]. The dipping speed was 8 mm min^{-1}. The transfer ratio was 1.0 in both downstrokes and upstrokes, so that a Y-type LB film resulted. After the first and second layers had been transferred, the sample was baked for 4 min at 100 °C before the next stroke. In the transfer of subsequent layers, baking at 100 °C for 3 min was performed after every 10 layers. The aim of this bake process is to increase the adhesion between the first layer and substrate or subsequent layers. The thickness per layer of PMMA is 0.85 nm measured by ellipsometry [7]. Therefore the thickness of the multilayer PMMA film can be estimated easily. After transfer, the film was prebaked at 100 C for 0.5 h. The pre-baking temperature was set below the glass transition temperature T_g of PMMA (about 105 °C) in an attempt to maintain the film constructon that was induced as a result of the LB deposition procedure. All experiments were carried out at 18 ± 1 °C in an air-conditioned grade 1000 ultraclean room.

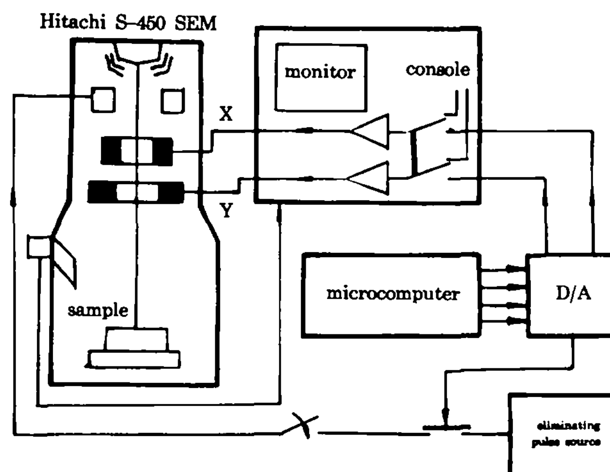

Fig. 2. Diagram of a modified scanning electron microscope for electron beam exposure system.

2.3. Electron beam exposure

The electron beam exposure tool used in our study is a modified scanning electron microscope (Hitachi S-450) controlled by a computer for high resolution electron beam lithography, developed by the Nanjing Electronic Device Institute in cooperation with Southeast University, illustrated in Fig. 2. The electron beam scanning in the X and Y directions is controlled by a microcomputer (AST Premium II/40) through a 12-bit digital analogue converter. An eliminating pulse signal source controlled by the computer generates the pulse to eliminate the electron beam to avoid resist exposure while the electron beam is shifting. A sample plate which can rotate through 360 was designed and fabricated. The shifting resolution of the sample plate in X, and Y directions is 1 μm. The electron beam is a circular Gauss beam. Its minimum diameter is 7 nm. The microcomputer controls the exposure dose by controlling the scanning time. The location of this exposure system is completed through manual control of the sample plate and electron beam scanning by computer. The beam current of the electron beam was measured by a ZC 36 type microcurrent meter through a Faraday cup. The beam diameter was measured by the edge measurement method [8]. The exposure dose can be calculated easily from beam current, beam diameter and scanning time.

To measure the exposure characteristics of LB PMMA resist films, the exposure was performed at 30 kV accelerating voltage, 1.7 × 10^{-10} A beam current, 20 nm beam diameter and 35 MHz address rate. Figure 3 shows the characteristic exposure curve of a 59.5 nm (70 layers)LB PMMA film.

The exposures of the LB PMMA film were performed in point scanning mode, with a magnification of 1000 ×, 30 kV accelerating voltage, 200 Å beam diameter and

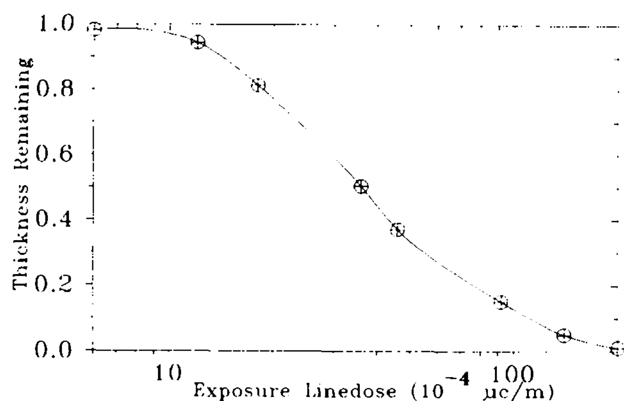

Fig. 3. Characteristic exposure curve of an ultrathin LB PMMA film.

1.7×10^{-10} A beam current, and with line doses ranging from 0.06 μC m^{-1} to 1.56 μC m^{-1}.

2.4. Development

After exposure, the PMMA was developed in a 1:3 solution of methyl isobutyl ketone (MIBK):isopropyl alcohol (IPA) for 15 s at 23 °C. Post-baking at 80 °C for the resist films was performed for 40 min after developing.

The developing characteristics of PMMA have been studied in detail by Greneich [9]. Figure 4 shows the developing characteristics of LB PMMA films. 120-layer PMMA LB films were deposited on Si⟨111⟩ wafers. The thickness of the films was 102 nm. Then the sample was exposed to the modified Hitachi S-450 scanning electron microscope for rectangular field exposure. After exposure the sample was immersed into the MIBK:IPA = 1:3 developer at 23 °C, which was not agitated. Periodically the sample was removed and the resist thickness determined by an alpha-step instrument.

2.5. Al etching

Following the post-baking process the sample was immersed in 7:2 denionized water:phosphoric acid for

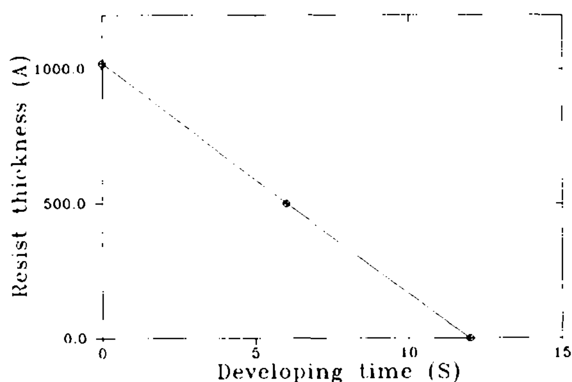

Fig. 4. Characteristic PMMA LB resist film development curve (102 nm PMMA LB film; MIBK:IPA = 1:3 developer; 23 °C temperature).

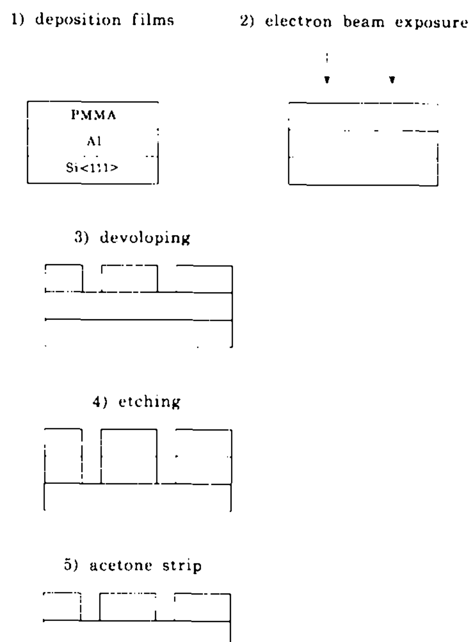

Fig. 5. Schematic diagram of the experimental process.

90 s to transfer the resist pattern to Al. After Al etching, the PMMA was stripped using acetone rinsing. The sample was then examined by scanning electron microscopy for resolution measurement and by atomic force microscopy (AFM) for pinhole density measurement. Figure 5 shows a schematic diagram for the experimental process.

3. Results and discussion

Figure 6 shows the pattern of the sample after the subsequent exposure, developing and etching processes. It was exposed at a 30 kV accelerating voltage, 20 nm beam diameter, 1.7×10^{-10} A beam current and magnification of 1000 ×. The lines were written with a single pass of the electron beam. The white lines in Fig. 6 represent the etched lines. The narrow lines were exposed with a line dose of 0.06 μC m^{-1}. Also, the line scanning time of the wide lines was approximately twice the time of the narrow lines. Correspondingly they were exposed with a dose of 0.13 μC m^{-1}. The width of the narrow lines is 0.15 μm. The width of the wide lines is 0.25 μm. As a result, Fig. 6 shows 0.15 μm lines or 0.25 μm lines with a 0.6 or 1.67 mark-to-space ratio respectively.

The results demonstrate that LB ultrathin resists permit etching of underlying aluminium and have potential for high resolution lithography in the deep submicron regime. In our experiments, examining the developed sample with an Olympus optical microscope, we judged that the resists of exposed lines had been

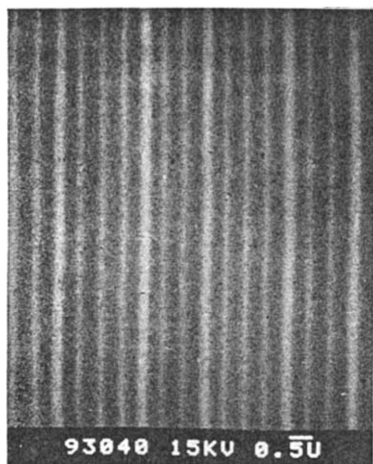

Fig. 6. Pattern etched in a 100 nm thick Al film evaporated on an Si wafer with 80-layer LB PMMA film as resist, exposed with a modified Hitachi scanning electron microscope operating at 30 kV acceleration voltage, 20 nm beam diameter and 1.7×10^{-10} A beam current. The narrow lines and the wide lines in this pattern were exposed with a line dose of 0.06 μC m^{-1} and 0.13 μC m^{-1} respectively.

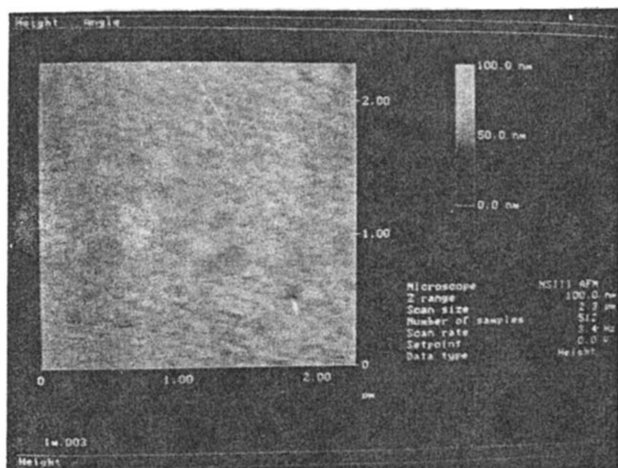

Fig. 7. The pinhole after etching as measured by AFM.

developed thoroughly (under the exposure conditions). After etching, we did not find any apparent large pinholes with a Nanoscope III atomic force microscope manufactured by Digital Instruments Inc. The pinhole indicated by an arrow in Fig. 7 is one of the larger pinholes, and is less than 15 nm in diameter. This indicates that the PMMA ultrathin films prepared by the above-mentioned methods had high quality and good etch resistance for the acid etching solution. It has solved the problem that PMMA has a relatively bad etch resistance for reactive ions and alkaline etching solution in optolithography. In addition, compared with other amphophilic molecules for electron beam resist (ω-tricosenic acid [2], manganese sterarate [3], N-octadecylacrylamide [5], α-octadecylarylic acid [10] and diacetylene 10,12-pentacosadyinoic acid [11]), PMMA does not have a long hydrophobic chain. As a result, LB PMMA films have higher robustness. Through comparing different samples, we found that the baking process in the film deposition process is crucial. The process could increase the adhesion between films and substrate so as to increase the etch resistance of the resists. In the exposure process, the results demonstrate that the pattern resolution changed from 0.45 μm to 0.15 μm following the changes in dose, as is shown in Fig. 8. Furthermore, it is uncertain that our exposure conditions were most optimal because of the restraint of the exposure system.

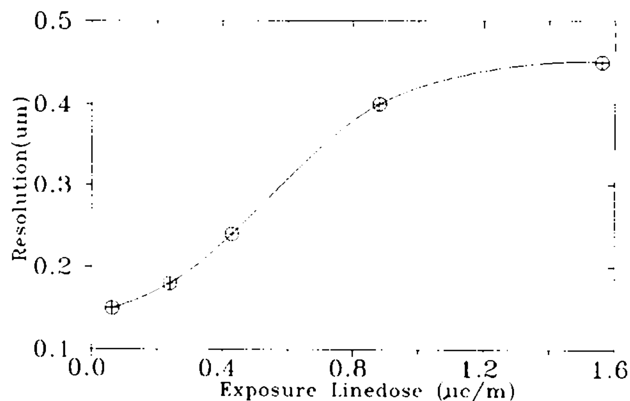

Fig. 8. The curve of the dose resolution relation.

4. Conclusions

We have prepared high quality PMMA ultrathin films with high robustness and low pinhole density using LB techniques. The films had good etch resistance and 0.15 μm resolution has been obtained through exposure with a modified scanning electron microscope. The results demonstrate that the system has potential for applications in mask fabrication or study of some special device in the laboratory.

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