ELECTRON BEAM RESISTS PRODUCED BY PLASMA-INITIATED POLYMERIZATION OF METHYL METHACRYLATE

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ABSTRACT

Ultra-high molecular weight poly(methyl methacrylate) (UHMW PMMA), produced by plasma-initiated polymerization, was tested as an electron-beam resist. One micron lines could be resolved at a dose of 3.0×10^{-7} C/cm^2. By comparison, a dose of 3.2×10^{-6} C/cm^2 was required for a commercial PMMA resist.

1. INTRODUCTION

An important step in the fabrication of integrated circuits is the transfer of the circuit pattern onto the surface of a silicon wafer. The medium into which the image is projected is usually an organic polymer, called a resist, sensitive to ultraviolet, x-ray, or electron-beam radiation. Currently, circuits with minimum line widths of 3 or 4 μm can be produced using UV lithography. E-beam and x-ray lithography are both promising techniques for the production of structures with narrower line widths, since the wavelengths of these radiatons are small, and, hence, diffraction effects can be avoided. A further advantage of e-beam lithography is that a mask is not necessary.

Previous studies have shown that poly(methyl methacrylate) (PMMA) can be used as a positive e-beam resist. This material exhibits good adhesion, contrast, and etch resistance. The principle limitation of presently available commercial PMMA resists is sensitivity. This characteristic reflects the minimum e-beam dose, expressed in C/cm^2, which, for a given resist thickness, e-beam voltage, and developoment procedure, will result in total removal of the exposed resist. For commercial production sensitivities of better than 10^{-6} C/cm^2 are needed, whereas available PMMA preparations have a sensitivity of only 5×10^{-5} C/cm^2 (1,2).

To understand what factors influence resist sensitivity, it is necessary to review briefly the theory of resist performance. The reduction in polymer molecular weight caused by electron-beam exposure can be represented by (3)

$$M_n^f = \frac{M_n^o}{1 + KGD\,M_n^o} \qquad (1)$$

where M_n^f and M_n^o are the final and initial molecular weights, K is a constant which reflects the electron energy and resist thickness, G is the number of breaks in the polymer chain per 100 eV of energy, and D is the e-beam dose. For PMMA and 10 KV electrons, KG = 2.6.

The dissolution rate, S, of a polymer can be represented by (4)

$$S = k(1/M_n)^a \qquad (2)$$

where the constants k and a depend on the polymer and solvent. Equation 2 indicates that in order to achieve a substantially more rapid dissolution of the exposed resist compared to the unexposed resist, $M_n^f << M_n^o$. The interrelationship between M_n^f, M_n^o, and D is shown in Fig. 1. Inspection of this figure shows that for a fixed value of M_n^f/M_n^o (i.e. 10^{-2}) the dose necessary for complete development decreases as the initial molecular weight increases. Thus, for example if $M_n^o > 10^7$ gm/mol, then doses of less than 10^{-6} C/cm^2 should be necessary.

Recent studies by Osada et al. (5,6) and Johnson et al. (7) have demonstrated that PMMA with molecular weights in excess of 10^7 gm/mol can readily be produced by plasma-initiated polymerization. The purpose of the present study was to explore the suitability of using such ultra-high molecular (UHMW) polymers as e-beam resists. Tests were performed to establish the sensitivity of UHMW PMMA and to compare it to a conventional PMMA resist.

2. EXPERIMENTAL

The method of preparing UHMW PMMA was similar to that described by Johnson et al. (7). A flask containing distilled and degassed MMA monomer was connected to an evacuated ampule (18 mm \ 150 mm), and the ampule was filled with MMA vapor at room temperature. The ampule was then cooled in liquid nitrogen. The cold ampule was removed from the coolant and a discharge was initiated in the MMA vapor of placing the ampule between a pair of parallel plate electrodes connected to an rf generator (13.56 MHz). The discharge was sustained at 40W for 1 min after which the ampule cooled again in liquid nitrogen. Ten milliliters of MMA were then transferred to the cold ampule. Next, the vapor above the monomer was evacuated and the ampule was sealed with a torch. At this point the monomer was thawed out and the ampule was shaken to dissolve the plasma-produced initiator, present on the ampule walls, into the liquid monomer. The ampule was then wrapped in aluminum foil and placed in a water bath at 25°C for 24 hrs.

At the end of the polymerization period, the ampule was opened, and the monomer/polymer solution (containing about 1% polymer) was spin cast onto 4-inch chromium-coated glass plates. For the sake of comparison a series of plates were also coated with PMMA resist (4% PMMA in chlorobenzene) obtained from KTI Chemicals, Inc. The loading of each polymer solution was adjusted to obtain a resist thickness of 4000 Å. The viscosity average molecular weights of the UHMW and KTI PMMA were measured to be 3.1×10^7 and 6.9×10^5 gm/mol, respectively, using a low shear viscometer.

Exposure of the coated plates was carried out either in an ETEC Autoscan scanning electron microscope or an ETEC MEBES-1 electron beam exposure system. The Autoscan system was programmed to write a sequence of equally spaced lines with a minimum width of 1 μm. The MEBES-1 system produced a test pattern consisting of equally spaced lines and closely spaced square areas. The smallest features were 0.5 μm wide and the largest were 10 μm wide. The exposed portions of the resist were developed out using a 1:1 mixture of methylethylketone and isopropanol. This composition provided a compromise between trying to keep development times short while not removing too much of the unexposed resist. The exposed portions of the chromium film were etched with Precision Glass Chromium Etchant (CR-8).

3. RESULTS

Optical micrographs of the exposed and developed plates obtained using UHMW PMMA as the resist showed that at the lowest dose, 3 × 10^{-7} C/cm^2, the 0.5 μm lines were not clearly defined but the 1 μm lines were intact. As the dose was raised to 3 × 10^{-6} C/cm^2, the 0.5 μm lines became more clearly defined but no further improvement was observed in the quality of the remaining features. It was also noted that for none of the doses used was any of the unexposed resist removed during development.

Micrographs of the test pattern obtained using the KTI PMMA resist showed that the lowest useable dose was 3.2 × 10^{-6} C/cm^2. Even at this dose, the 0.5 μm lines were not well resolved but the larger features were clearly defined. It was observed, however, that 40% of the unexposed resist was removed in the time required to remove the exposed resist. The loss of unexposed polymer also caused the exposed lines to be somewhat wider, and the spaces between the lines to be somewhat narrower than in the test pattern as written. At higher doses the definition of the 0.5 μm lines was improved but the loss of a certain amount of the unexposed resist could still be detected. Exposure at doses less than 3.2 × 10^{-6} C/cm^2 was not attempted since the loss of unexposed polymer in this case would have been excessive.

The rate of exposed resist dissolution in the developer for a given e-beam dose was determined by dividing the original resist thickness by the time required to develop out the exposed areas. A plot of resist dissolution rate versus dose is given in Fig. 2. The solid lines presented in this figure results from a fit of eqn. 2 to the data for UHMW and KTI PMMA. For doses between 10^{-6} and 10^{-5} C/cm^2 the rates of dissolution of the two resists are nearly equivalent and consequently no advantage can be attributed to the UHMW resist. The advantage of this type of resist arises from the fact that it can be used at doses less than 10^{-6} C/cm^2. Use of the KTI resist would be precluded at such low doses due to excessive loss of the unexposed polymer during development.

The data presented in Fig. 2 can be used to determine a plot of normalized resist thickness versus dose. Figure 3 illustrates such a plot for the UHMW resist, assuming a resist thickness of 4000 Å and a development time of 4 min. For this case complete development of the exposed regions would be achieved for doses of 3 × 10^{-6} C/cm^2 or more. If the development time were increased by 8 min, then the minimum dose required would be reduced to about 8 × 10^{-7} C/cm^2. These doses are substantially smaller than that normally used for KTI PMMA, 5 × 10^{-5} C/cm^2 (8,9).

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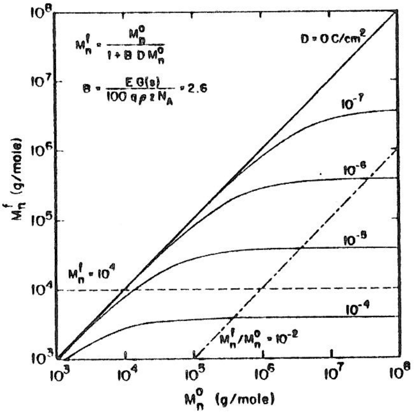

Fig. 1 Dependence of M_n^f on M_n^o and D

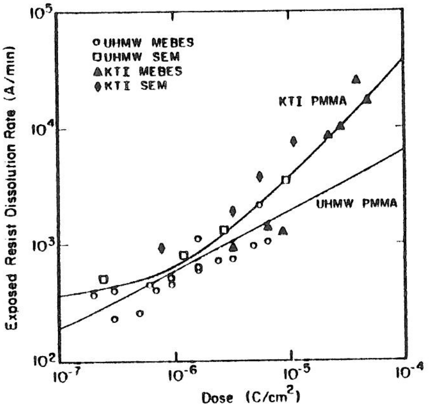

Fig. 2 Dependence of the dissolution rate on the e-beam dose

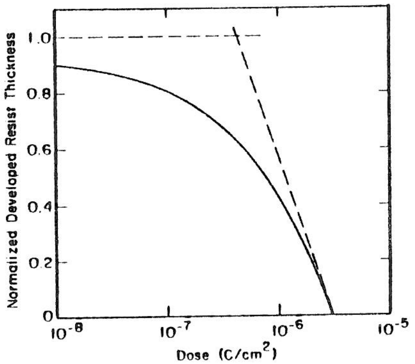

Fig. 3 Dependence of the reduced resist thickness on the e-beam dose