

Fabrication of 5–7 nm wide etched lines in silicon using 100 keV electron-beam lithography and polymethylmethacrylate resist

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The present limit of around 10 nm for the width of lines fabricated by *e*-beam lithography using polymethylmethacrylate (PMMA) resist on silicon substrates has been overcome. 5–7 nm wide etched lines in bulk Si substrates have been produced. A 65 nm thick layer of PMMA was exposed with an 80 kV electron beam of diameter smaller than 5 nm. After exposure the resist was developed in 3:7 cellosolve:methanol with ultrasonic agitation. The pattern in resist was transferred to the Si substrate with reactive ion etching. Lines of width varying between 5 and 7 nm were recorded using an S-900 scanning electron microscope which has a resolution of 0.7 nm.

Polymethylmethacrylate (PMMA) has the highest resolution among conventional organic electron beam resists and lines around 10 nm wide have been patterned in PMMA. Broers¹ first studied the resolution of PMMA on a thin Si₃N₄ membrane substrate with 50 kV electron beam lithography and concluded that the smallest line width that could be made satisfactorily on PMMA was about 15 nm. Craighead *et al.*² reported similar results on thick substrates using higher electron energy. So far, lines significantly narrower than 10 nm have not been made satisfactorily in PMMA resist.

This letter reports the exposure of significantly narrower lines in PMMA on a Si substrate and the subsequent fabrication of 5–7 nm etched lines in the Si substrate using the resist as a mask. This result has been obtained by using a relatively thick resist layer compared with the width of the line and by developing the exposed resist rapidly with ultrasonic agitation. The resist pattern was transferred to the Si substrate using reactive ion etching.

A high voltage (100 kV), high resolution electron beam lithography machine—Nanowriter,³ which was designed to explore the resolution limit of electron beam lithography, was used to expose a single layer of PMMA resist. The layer, nominally 65 nm thick and of 1100 k molecular weight PMMA, was spin coated onto a bulk Si substrate. After the resist was spun on, the samples were baked at 180 °C for several hours before being exposed with an electron beam of diameter smaller than 5 nm and acceleration voltage of 80 kV. It is impossible to measure the beam size precisely at this level and it may be that the beam size is significantly smaller than 5 nm. An estimated value obtained with the backscattered electron signal from a resolution test sample is about 3 nm. After exposure, the samples were developed in 3:7 cellosolve:methanol solution in an ultrasonic bath for times around 5 s and rinsed in IPA and then blown dry with pure nitrogen. A Hitachi S-900 scanning electron microscope (SEM) which has a resolution of 0.7 nm was used to examine the samples. The magnification was calibrated with a standard test sample (layered structure grown by MBE) to limit errors to < ±5%. Line width was measured on micrographs of the pattern. For 5 s development and 7.4 C/m² dose, the mean

linewidth was 6.1 nm and the standard deviation was 1.5 nm for 200 measurements. Figure 1 shows 5–7 nm wide lines in PMMA resist with a 10 nm thick AuPd layer on top of the resist. The grain size of the AuPd layer is of about the same size as the line width and masks the edge quality of the resist lines which appeared to be better in direct examination of the resist surface.

The resist pattern was transferred to a Si substrate using reactive ion etching with PMMA as the mask. An STS-320 reactive ion etching machine, from Surface Technology Science Ltd., U.K., was used for etching. The etching gas was a mixture of 20 sccm SiCl₄ and 10 sccm CF₄. The samples were etched for 5 s with 20 mTorr chamber pressure and 400 W etching power and were kept at 15 °C during the etching to reduce the heating of the resist. After etching the samples were cleaned immediately with acetone and IPA in an ultrasonic bath to remove any residual reactive gas. The samples were again examined in the S-900 SEM. Figure 2 shows that the linewidth of the etched lines

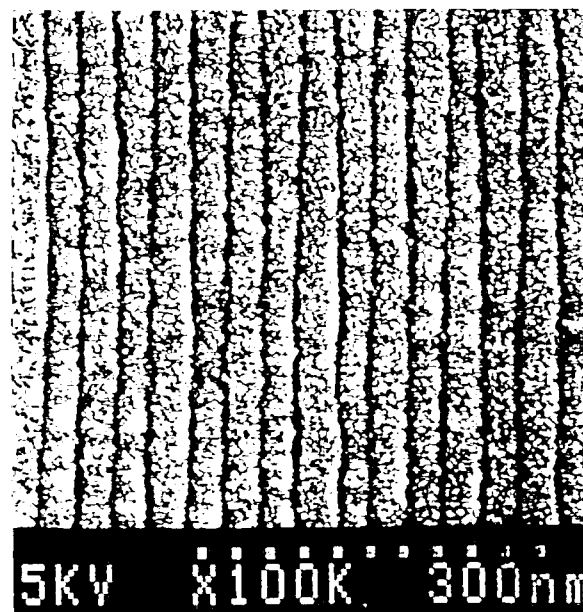


FIG. 1. 5–7 nm wide lines in PMMA resist.

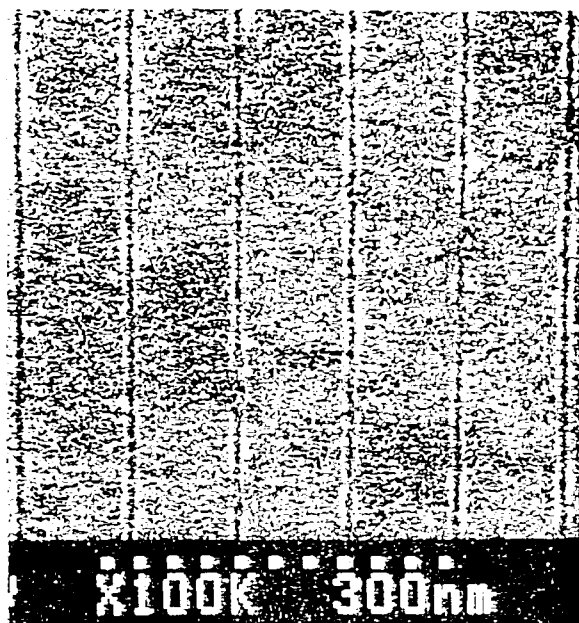


FIG. 2. 100 nm wide etched lines in Si substrate.

is between 5 and 7 nm. The etched linewidth was examined as a function of exposure dose for 5 s development. The etched lines were discontinuous for a dose of 7 C m⁻². For an increase in dose by 20% the etched lines became 10 nm wide. Between these two experiments, lines less than 10 nm in width were fabricated consistently. Samples were also made using different development times with ultrasonic agitation for a fixed dose of 7.4 C m⁻². No etched lines were observed in samples developed for 4 s. For 5–7 s resist development, lines significantly less than 10 nm were etched and no significant difference in linewidth was observed. However 10 and 15 s development widened the etched lines.

As is well known, PMMA resist is exposed by all electrons with energy above 5 eV, which include the incident electrons, the forward and backscattered electrons and the secondary electrons generated remotely by inelastic interaction between high energy electrons (either incident or scattered) and resist atoms. Because a very high accelerating voltage and a relatively thin resist layer are used in our experiments, the effect of forward and backscattering is not very important. The range of secondary electrons and the incident electron beam diameter will determine the exposed linewidth. Broers¹ suggested that it was the secondary electrons that set the resolution limit. Generally, the range of the secondary electrons that are generated is not known precisely and the measured exposure range of low energy electrons is believed to be much shorter than 10 nm.⁴ All previous results^{1–4} including recent experiments by ourselves with conventional development methods and resist layers of less than 55 nm thick have shown that there is a limit of 10 nm in the minimum achievable linewidth in PMMA resist, but with ultrasonic agitation and thick resist, lines narrower than 10 nm are obtained.

We believe that reconsideration of the development process can explain our improved results. We know that

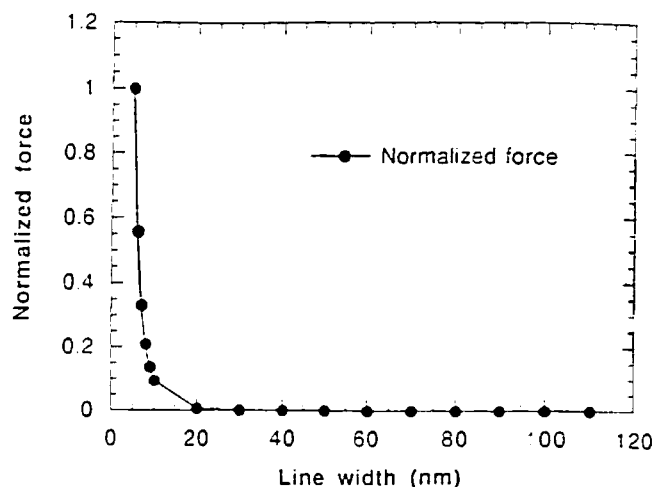


FIG. 3. Intermolecular force as a function of linewidth.

PMMA is a Van der Waals solid and the intermolecular force is important in determining its properties. When the exposed lines become smaller and are comparable with the molecular size which for PMMA is around 2 nm, the intermolecular force, which is usually expressed in the form of an intermolecular potential, becomes significant in the development process. For PMMA molecules, the Lennard-Jones potential, can be used. It has the form

$$U = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where σ is the molecule separation at which the potential energy is zero, ϵ is the minimum energy, known as the well depth, and r is the separation between two interacting molecules. These parameters can be determined by forcing agreement between the experimental data for a physical property and the calculated value for the potential. After normalization, ϵ disappears from the equation and for a value of σ , that is smaller than the linewidth, the intermolecular forces have the characteristics where the force suddenly rises when the linewidth is smaller than 10 nm. The force on exposed resist molecules from unexposed molecules for an infinitely long line as a function of linewidth is shown in Fig. 3, where only the attractive part of the force is considered.

When linewidth decreases to below 10 nm, the intermolecular force increases rapidly and the exposed resist molecules are trapped in the potential well of the unexposed molecules and are no longer dissolved into the developer solution. Conventionally, in order to develop the resist, the dose has to be increased, and so does the linewidth, until the linewidth becomes such that the exposed molecules are able to be dissolved. In these circumstances a 10 nm wide line is usually obtained. Ultrasonic agitation during development raises the potential of the molecules and helps them to dissolve into the developer. For wider lines, the intermolecular force is relatively small so the dose needed to open the resist is not much different for ordinary development from that with ultrasonic agitation, but for lines with smaller width, the forces are much larger

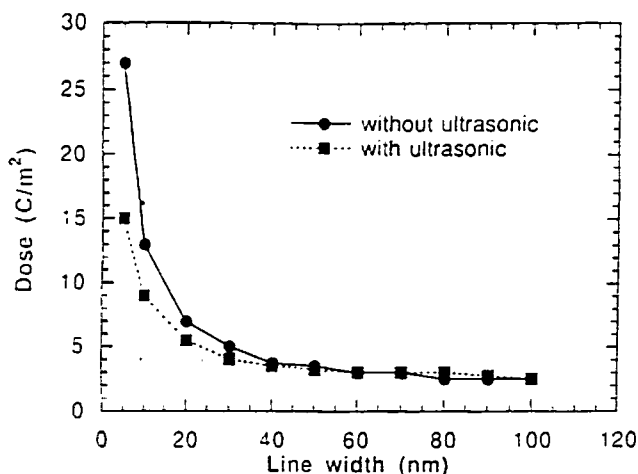


FIG. 4. Dose variation with linewidth for ultrasonic and ordinary development.

so that the dose required for ordinary development is significantly higher than that for ultrasonic development. Figure 4 compares the dose variation for ordinary and ultrasonic development and the importance of intermolecular forces is clearly seen in these results.

An alternative explanation for our results is the virtual elimination of resist swelling with ultrasonic development. During resist development there are two competing mech-

anisms that determine the developed linewidth in resist, dissolution which makes the lines widen and swelling which tries to close the gap. The swelling is determined by development time and solvent diffusion speed. The solvent diffusion speed is higher for resist with lower molecular weight and electron beam radiation reduces the molecular weight of resist, so that the higher the dose resist receives, the quicker the solvent diffuses and the faster the resist swells. For the same development time, samples developed with ultrasonic agitation need a much lower dose hence the swelling is much less serious than for those developed conventionally.

In conclusion, we have made 5–7 nm wide nanostructures such as etched lines in a Si substrate which are the smallest recorded linewidths by a factor of about two when the PMMA resist is used with electron beam lithography.

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