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Surface and line-edge roughness in plasma-developed resists

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Abstract

Silicon-containing, plasma-developed resists are characterised by surface (SR) and line-edge roughness (LER) measurements as functions of the exposure dose and plasma development conditions. Specifically, bilayer siloxane-based resists of different molecular weight distributions, and single-layer silylated chemically amplified resists are evaluated with measurements of SR and LER, while the results are compared with those of solution-developed chemically amplified resists. We show that plasma-developed systems can have low LER provided the resist material, the resist chemistry, and the processing conditions are chosen appropriately. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Plasma; Surface Roughness; SR; Line-edge roughness; LER; Bilayer resists

1. Introduction

Currently, the lithographic processes are facing the demands for characteristic dimensions in the sub-100-nm range, imposing strict requirements for smoother line-edges. At such small dimensions, it is suspected that even the size of polymer chains and the conformation of a single segment of a chain can affect roughness. Because of its importance, the roughness problem has been discussed in several publications in the last few years and various measurements are proposed to fully characterise roughness [1–8].

SR and LER are material and process dependent properties of patterned resists with the final roughness being a convolution of the roughness induced by each process step. Such steps include solution and/or plasma development of the resist and the subsequent etching steps for the substrate. For the solution development process, LER has the same origin as SR [1] with the additional element of its dependence on the details of the latent image, while for the plasma development process, SR and LER may differ in origin.

Our work presented here includes an experimental study of SR and LER for plasma-developed and solution-developed resists, since it is usually believed that plasma-developed resists suffer from high

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(or at least higher) LER compared to solution-developed systems. We present our first experimental results for a class of bilayer Si-containing resists based on siloxanes, since siloxane polymers are transparent enough at 157 nm radiation [9], to justify their use as copolymers in resists for lithography at 157 nm and below. The results will be compared to SR data for a negative-tone, solution-developed CAR. Low LER values are demonstrated for the plasma-developed resists.

2. Experimental

For the study of SR and LER of bilayer resists, we have used the siloxane resists as model materials which could be useful for both e-beam and 157-nm lithography provided they are co-polymerized with polymers capable of aqueous base development. In particular, a commercial material PDMS (from Aldrich) with a broad molecular weight distribution ($M_w/M_n = 2$), and a material synthesized at the polymer synthesis laboratory of the University of Athens having a very narrow molecular weight distribution ($M_w/M_n = 1.01$) were used. The average molecular weight was the same for both polymers ($M_w = 120\,000$), but obviously M_n is smaller for the Aldrich material. The materials were used as bilayer resists on top of hard-baked novolac resist (AZ5214 from Clariant) coated on silicon wafers at a thickness of 500 or 1000 nm. After an initial bake at 90°C for 90 s, the novolac resist was baked at 200°C for 15 min. The final bottom-resist thicknesses after the hard bake were 400 or 800 nm. Subsequently, 100-nm thick siloxane films were spin-coated on the bottom layer. For the exposures, e-beam lithography was used, since 157-nm tools are not widely available. The resist was exposed to a 50-keV e-beam, solution-developed in MIBK, and plasma-developed in an oxygen plasma (RIE) at a pressure of 10 mTorr. Two plasma development conditions were tried: without and with a breakthrough step (BTS, with a mixture of 20% SF₆/20% CHF₃/60% O₂ for 6% of the total development time) before the main etching process (in pure oxygen).

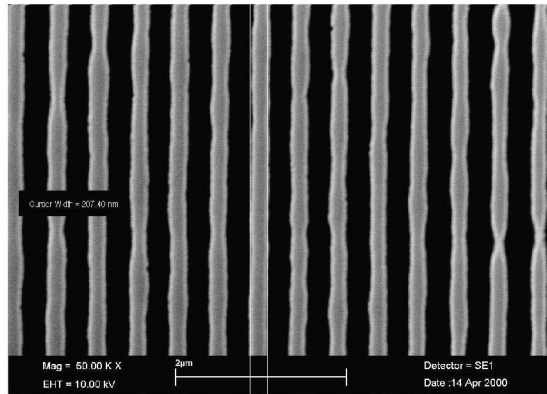
For comparison purposes, an epoxy novolac-based resist (EPR), a very sensitive chemically amplified negative tone resist [10], was selected as a solution-developed resist. EPR with 1% photoacid generator (PAG) content was used, it was prebaked and post-exposure baked at 110 and 90°C, respectively, to form a film of a final thickness of 4500 Å. The same resist was used with silylation and plasma development [11], as a plasma-developed (positive tone) resist. For the plasma development of the silylated EPR, a mild BTS etch was used (with a mixture of 5% SF₆/5% CHF₃/90% O₂ for 5% of the total development time).

In all cases, LER was observed on lines/spaces with SEM (LEO 440), and SR was measured on 300 × 300-μm pads with AFM (a Topometrix TMX 2000 system and a Digital Instruments Nanoscope III system) in the non-contact mode.

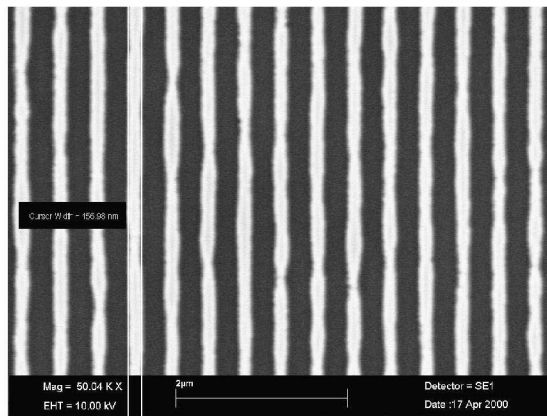
3. Results and discussion

3.1. Siloxane polymers

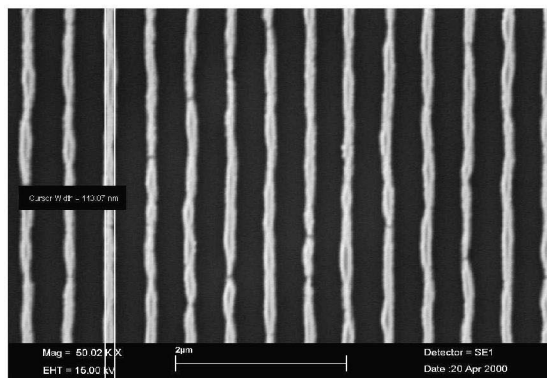
In order to prove the resolution capabilities of the siloxane materials, we show in Fig. 1 SEM images of various lines/spaces fabricated after exposure with a 50-nm diameter, 50-keV e-beam, solution development of the top PDMS layer, and finally plasma development of the bottom novolac



Line-size: 0.25 μm , Dose: 5 $\mu\text{C}/\text{cm}^2$



Line-size: 0.15 μm , Dose: 8.75 $\mu\text{C}/\text{cm}^2$

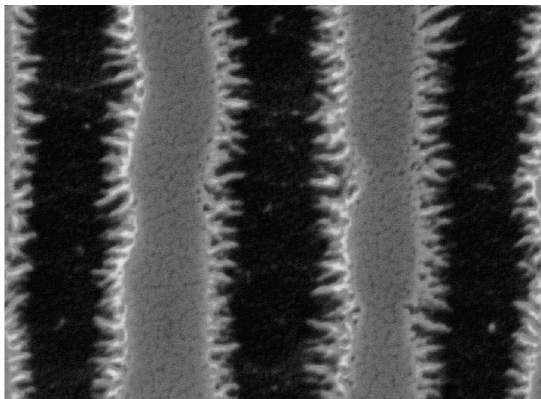


Line-size: 0.10 μm , Dose: 12 $\mu\text{C}/\text{cm}^2$

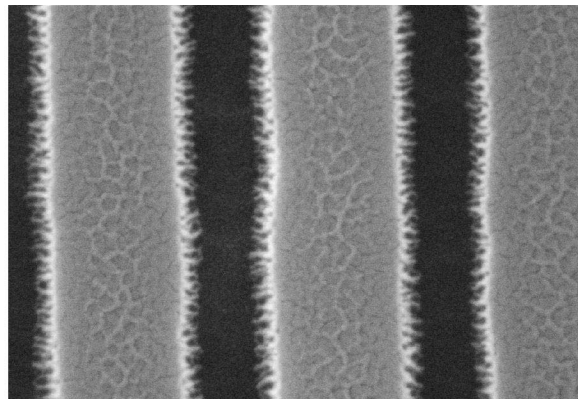
Fig. 1. SEM images of nominal 0.25- μm (1:1), 0.15- μm (1:2), 0.10- μm (1:3) lines fabricated with siloxane (PDMS by Aldrich) as the top material of a bilayer scheme. The plasma development included a BTS etch.

resist (BTS etch was included). Although some waviness was observed for fine lines, due to the relatively large beam diameter and partly due to swelling induced by the use of organic developer, lines in the sub-100-nm range were obtained. Both materials (of different molecular weight distributions) exhibited very good resolution, suggesting that such materials could be prepared as 157-nm lithography resists, provided that aqueous development is established.

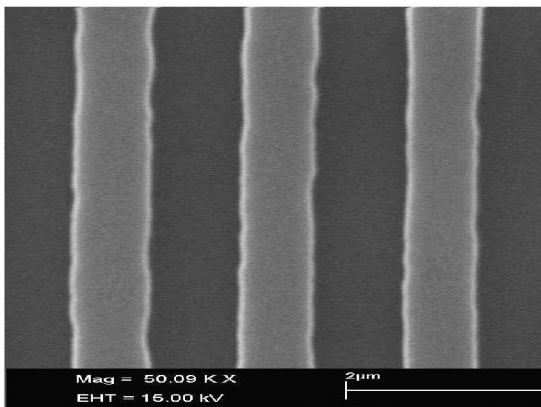
Fig. 2 shows top-down SEM images of lines/spaces (nominal dimensions: 0.5 μm , 1/1) obtained without (top) and with (bottom) BTS for the synthesized PDMS material (University of Athens). Similar results were obtained with the commercial material (Aldrich) [12]. Without BTS, the observed high LER and SR for most doses are due to the incomplete solution-development of the top layer for this bilayer system. Apparently, some residues remain after solution development, which, given the



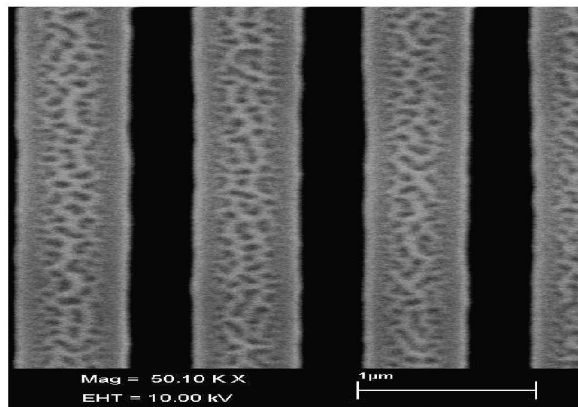
Dose: 4.2 $\mu\text{C}/\text{cm}^2$



Dose: 5.4 $\mu\text{C}/\text{cm}^2$



Dose: 4.25 $\mu\text{C}/\text{cm}^2$



Dose: 7 $\mu\text{C}/\text{cm}^2$

Fig. 2. SEM images of 0.5 μm 1:1 L/S patterned on 100-nm thick synthesized PDMS material e-beam exposed and solution-developed on top of a hard baked novolac resist, O_2 plasma-developed: (top) without BTS and (bottom) with BTS etch.

high Si content of the siloxane and the high selectivity of the etching process, caused a roughening of the surface in the subsequent O_2 plasma development step. The SR is observed as LER at the edges of patterns since the residues at the edges of the lines will cause LER. At high doses, LER is reduced, however, SR increases due to the high extent of crosslinking of the overexposed siloxane film. This increase in SR is confirmed by AFM observations [12] and shows that LER and SR may not behave similarly. With a BTS etch, LER is greatly reduced. Surface roughness is again high at high doses, due to strong crosslinking.

In Fig. 3, SR after 1 min oxygen plasma development without and with a BTS step is shown as a function of dose for the synthesized material (the commercial material shows an analogous behavior). To avoid damaging the AFM tip, we did not measure SR after full development, but only after partial development, i.e. 1 min etching instead of 4 min needed for etch end point. In addition to SR data, the contrast curve is displayed without BTS (BTS slightly increases the contrast value, but the contrast curve is not shown to avoid cluttering Fig. 3). AFM measurements show a minimum of SR at useful doses, and a high SR at high doses. It is worth-noting the significant reduction of SR at small doses by including a BTS in the plasma development, which removes the Si-containing residues from the top of the novolac layer. Thus, Fig. 3 helps to explain the relation between SR and LER and the role of BTS, as follows: Assuming an ideal square-wave exposure profile at useful doses, the SR on the lines is close to the minimum, while the SR on the spaces is high without a BTS. As one crosses from the lines to the spaces, the SR increases, i.e. LER is present. On the contrary, after appropriate BTS etch, the SR in the spaces is very small, and thus the transition from lines to spaces is rather smooth, i.e. low LER is observed.

However, even with a BTS etch, SR reaches a maximum at doses between 0.7 and $2 \mu C/cm^2$, as

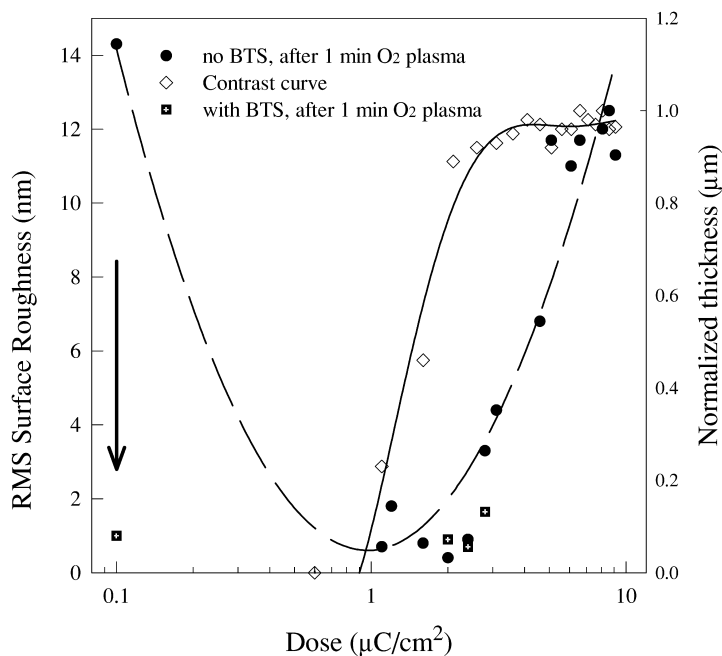


Fig. 3. Surface roughness (RMS value) as a function of the exposure dose and the contrast curve for the synthesized PDMS material, after 1-min development in O_2 RIE plasma, without (filled circles) and with (filled squares) a BTS etch.

the siloxane film gets disrupted by the plasma, and the regions of the bottom layer exposed to the O_2 plasma are etched away. Exact measurements of SR (RMS) in this region were not possible, since the surface is non-uniform, consisted of rather smooth regions of siloxane disrupted by holes deep in the novolac resist. Estimations of the maximum z variation of the AFM tip were however possible, and were found reasonable of the order of 100–150 nm, i.e. the thickness of the novolac resist etched away in 1 min.

3.2. Comparison with solution-developed and plasma-developed silylated EPR

For a first comparison between plasma and solution-developed resists, the epoxy novolac-based resist EPR, a very sensitive chemically amplified negative-tone resist [10], was selected. SR was studied after exposure to different doses and solution development. Fig. 4 shows the SR curve as a function of the exposure dose and the contrast curve for EPR, similarly to Fig. 3 for the PDMS material. The first observation is that SR goes through a maximum that is seen to exist at the onset of the contrast curve. The maximum is sharp and drops quickly as the dose increases to give full thickness of the resist film. The reduction of SR with the dose is due to the increase of crosslinking in the negative tone resist, and thus to the reduction of polymer chain aggregate removal.

The surface roughness of the plasma-developed silylated EPR as a function of dose, and the contrast curve, are shown in Fig. 5. The figure reveals that the SR of the unexposed–silylated areas is comparable to that of the highly exposed–unsilylated areas and below 2 nm (etching included a mild BTS).

Comparison of the results in Figs. 3–5 indicates that, for both plasma- and solution-developed resists, a maximum in the SR versus dose curve exists at small doses (corresponding to small

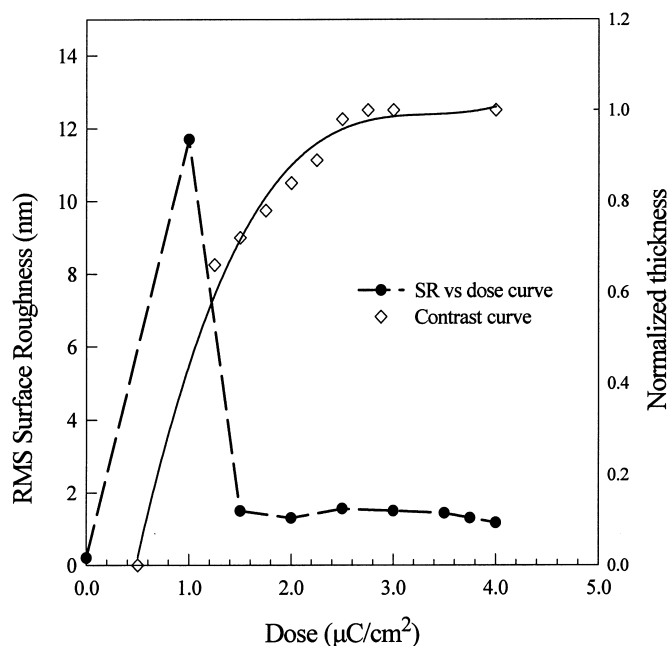


Fig. 4. Surface roughness of solution-developed EPR (negative tone) as a function of exposure dose. The contrast curve is also shown.

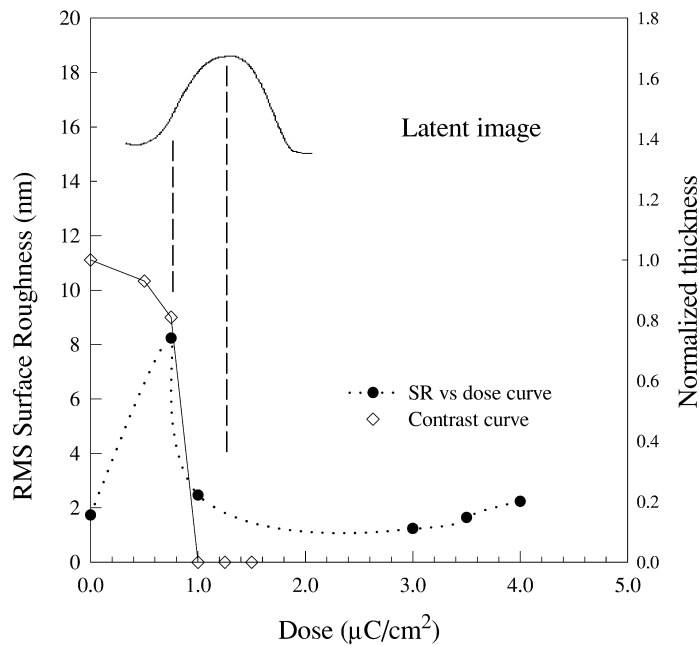


Fig. 5. Surface roughness of plasma-developed silylated EPR (positive tone) as a function of dose and the contrast curve. Schematic of the latent image is also shown to indicate how SR climbs up towards its max value, as the exposure dose drops to zero at the edges of the image, thus increasing LER.

remaining thickness). At useful doses, both type resists can have similarly low values of SR, provided the appropriate BTS etch is performed for plasma-developed resists.

The behavior of SR presented in Figs. 4 and 5 agrees with literature results [3,4], where a rather universal characteristic of the SR versus dose curve has been observed: SR goes through a maximum as one crosses from very small to useful doses. The position of the maximum in the SR vs. dose curve can explain the relation between SR and LER: If the latent image were ideal (square wave), LER would be the average between the corresponding SR at the same dose and that at zero dose. However, since the latent image is usually far from ideal, LER could be climbing up to the maximum of the SR curve. Thus, the closer the maximum in roughness is to the clearing doses, the more LER will be present in the system. For example, the maximum in SR for the plasma-developed silylated EPR is very close to the lithographically useful doses (clearing doses), as shown in Fig. 5. Thus, it is expected that the plasma-developed silylated EPR will have somewhat higher LER than the solution-developed EPR, which we verified experimentally. We speculate that if a sufficiently drastic BTS etch were employed in the plasma development of silylated EPR, LER could be reduced, as the max in SR would be moved to smaller doses (further away from the clearing doses), and equally good results would be obtained for the wet and dry process.

4. Conclusions

Siloxane-based resists were evaluated as potential materials for fabrication of lines in the sub-100-nm range, by measurements of SR and LER as functions of the exposure dose and plasma

processing conditions. Comparison with solution-developed resists showed that plasma- and solution-developed resists can have similar values of SR at useful doses, provided an appropriate BTS etch is performed for plasma-developed resists.

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