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Surface roughness induced by plasma etching of Si-containing polymers *

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Abstract—Interfacial properties of polymers and their control become important at submicrometer scales, as polymers find widespread applications in industries ranging from micro- and nano-electronics to optoelectronics and others fields. In this work, we address the issue of controlled modification of surface topography of Si-containing polymers when subjected to oxygen-based plasma treatments. Treated surfaces were examined by atomic force microscopy to obtain surface topography and roughness of plasma-treated surfaces. Our experimental results indicate that an appropriate optimization of plasma chemistry and processing conditions allows, on one hand, small values of surface roughness, a result crucial for the potential use of these polymers for sub-100 nm lithography, and, on the other hand, desirable topography, applicable for example in sensor devices. Plasma processing conditions can be modified to result either in smooth surfaces (rms roughness < 1 nm) or in periodic structures of controlled roughness size and periodicity.

Keywords: Silicon-containing polymers; plasma treatment; surface roughness; bilayer resists.

1. INTRODUCTION

In recent years, roughening of materials has attracted considerable attention, as surface and interface roughness controls many important physical and chemical properties of deposited films. Since roughness or the topography of surfaces, in general, often results from processing, this paper addresses the issue of the dependence of surface roughness (induced by plasma etching) on plasma processing conditions. Current literature relevant to the issue of plasma-induced roughness includes studies of the roughening of plasma-etch fronts of Si [1, 2], the evolution of

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the topography of lattice systems [3] and the formation and evolution of roughness on plasma-treated polymeric films [4, 5].

In this paper, examples are presented of surface roughness of a Si-containing polymer, poly(dimethylsiloxane) PDMS, induced by oxygen-based plasma treatments. Our work includes experimental study of surface roughness (SR), as a function of exposure dose and plasma processing conditions. The dependence of the roughness and its structure on the gas composition and electrode temperature is considered. Atomic force microscopy (AFM) was used to generate the surface images and to measure the roughness while scaling analysis was performed on the resulting images to yield the scaling characteristics of surface roughness.

2. EXPERIMENTAL

For the first study of surface roughness of bilayer resists, we used the PDMS as a model material which could be useful for both e-beam and 157-nm lithography provided that PDMS was 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 synthesized material 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. These materials were used in bilayer schemes as top layer resists on a 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 thickness after the hard bake was 400 or 800 nm. Subsequently, 100-nm thick siloxane films were spin-coated on the bottom layer.

The plasma process optimization was performed on e-beam exposed wafers. For this purpose, PDMS resists were exposed to a 50 keV e-beam, wet developed in methyl isobutyl ketone (MIBK) for the fabrication of patterns on the top layer, and finally dry developed in oxygen-containing plasmas for the pattern transfer to the bottom resist layer, as shown in the schematic of Fig. 1.

Pads of PDMS and line/space structures with submicrometer resolution were thus formed. Two plasma processing conditions were tried for the pattern transfer to the bottom resist: (a) pure O_2 plasma and (b) first a short breakthrough step (BTS) in F containing plasmas followed by the main etching process in pure oxygen.

Plasma processing was performed both in a NE 330 Nextral reactive ion etcher (RIE) and in an Alcatel high density inductively coupled plasma (ICP) etcher. Process gases included pure oxygen and dilute mixtures with F-containing gases. In the ICP reactor, the temperature of the sample holder was well controlled by thermostating the electrode, while heat transfer between the sample holder and the electrode was achieved by mechanically clamping the substrate holder to the electrode and backside helium contact. On the contrary, in the case of the RIE

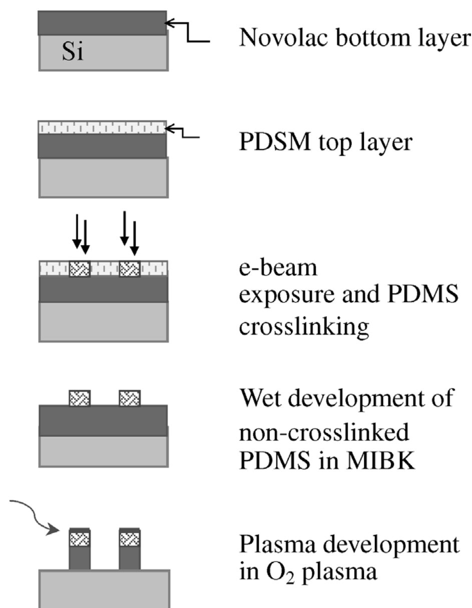

Figure 1. Schematic of the imaging process of bilayer lithography with PDMS as the top layer resist.

reactor, the samples were simply placed on the electrode without special care for providing good thermal contact with the electrode.

The etching behaviour of PDMS, used as the imaging layer in bilayer lithography, has been reported in previous work [6] in terms of line edge roughness. Briefly, it has been shown that plasma processing conditions have a significant effect on line-edge roughness, and can be appropriately optimized if small roughness is desired. This work focuses on the study of surface roughness of PDMS as a result of oxygen plasma treatment and its dependence on the plasma processing conditions.

Plasma developed PDMS lines/spaces were observed with an LEO 440 Scanning Electron Microscope. Surface roughness was measured on polymeric surfaces with a Topometrix TMX 2000 Atomic Force Microscope. The values of surface roughness reported throughout this work represent the root mean square (rms) deviation of the surface heights from an average height value, and they are calculated using the software supporting the AFM. The area of sample scanned, over which the value of roughness was determined, was usually 1×1 or 2.5×2.5 μm. Scaling analysis performed on surface images gave correlation lengths smaller than 100 nm. Thus, the scale of measurement (1 μm or higher) is not expected to affect the surface roughness values, as it is at least 10 times the correlation length [7]. Measurements were performed in the contact mode and were compared successfully to results obtained on the same samples but in the tapping mode of a second AFM instrument (Digital Instruments). The same behavior of surface roughness (e.g. the same variation with exposure dose) was observed with both instruments (and

modes). Therefore, the use of the contact mode of the AFM is reliable for our polymer samples.

3. RESULTS AND DISCUSSION

3.1. Production of smooth surfaces

The experimental results show that if plasma processing conditions are appropriately optimized, small values of surface roughness (as well as line-edge roughness) can be obtained on PDMS. This result is crucial for the potential use of these and other Si-containing polymers for sub-100 nm lithography, as far as surface or line-edge roughness is concerned. The surface roughness of the examined polymeric surfaces was found to depend mainly on the exposure dose, the processing gas composition, and the electrode temperature.

The former two factors and their effect on surface roughness are shown in the results of Fig. 2. The surface roughness for the Aldrich material is shown as a function of the exposure dose, for different plasma etching conditions (pure O_2/or BTS with SF_6/He and then pure O_2) in a high density plasma (ICP) etcher. As the figure shows, the surface roughness of the bilayer material decreases as the exposure dose increases. Notice that, for both processes, surface roughness attains values independent of dose after a threshold value, just above the lithographically useful doses. Furthermore, at high doses, a short treatment in the ICP reactor (at $T = 15°$C) with F-containing plasmas (SF_6/He) before the oxygen treatment resulted in surface roughness smaller than with the treatment in pure O_2 plasmas.

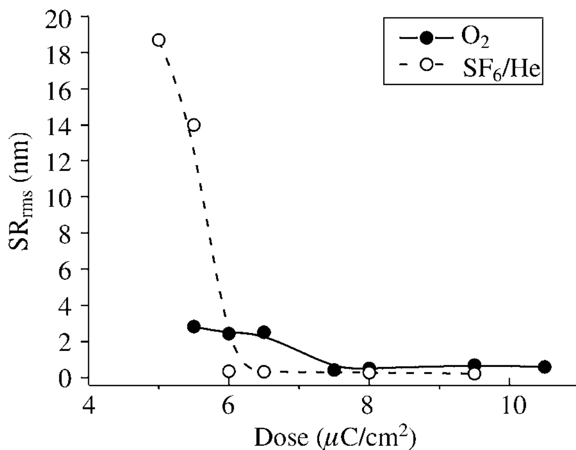

Figure 2. Dependence of the surface roughness of the bilayer scheme, with PDMS as top layer, on exposure dose in a high density plasma (ICP) etcher, after pattern transfer in two different etching mixtures: O_2 only (filled circles) and SF_6/He followed by O_2 (open circles). The transfer etching conditions were: total pressure 10 mtorr, breakthrough etching in SF_6/He plasma (500 W, 0 V bias, 6 s) and main etching in O_2-only containing plasma (600 W, −100 V bias, 2 min).

However in both cases, rather smooth surfaces with roughness values smaller than 1 nm are obtained, as shown in the AFM image of Fig. 3 (for a PDMS surface at high doses).

Although detailed discussion of the phenomena responsible for the observed behaviour of roughness is beyond the scope of this work, a brief explanation will be attempted here. It has been shown in previous work [6, 8] that exposure of Si-containing polymers to O_2-based plasmas leads to rapid oxidation of the polymer surface, transforming it to a silica-like thin ($\approx$5 nm) layer. Therefore, this layer shows an appreciable resistance to etching in pure O_2 plasmas, in contrast to the organic underlayer (AZ5214). This can explain the reduction of surface roughness with exposure dose. At low enough doses, the crosslinking of the PDMS is only partial and thus some regions of the PDMS surface get dissolved during the wet development process exposing partially the underlying polymer. As a result, when such inhomogeneous surface is exposed to O_2-based plasmas, the silica-like parts of the surface resist the treatment, while the organic parts (AZ5214) are etched down creating a surface of high roughness. At high doses, however, the PDMS is crosslinked enough to create a homogeneous layer that covers the underlayer protecting it from etching, and thus a surface of small roughness (1 nm) is obtained.

The effect of the electrode temperature on the roughness formation is not shown in detail in this work, however, experiments performed in the ICP reactor at different electrode temperatures have shown that the higher the processing temperature is, the rougher the PDMS surface becomes. More specifically, values of surface roughness as high as 4 nm are obtained for a temperature of 60°C at the processing electrode. Therefore, for smooth PDMS surfaces, ICP processing on an electrode at a temperature at or below room-temperature is necessary.

If such processing conditions appropriate for smooth surfaces are also employed for the pattern transfer from the top PDMS layer to the underlayer (AZ5214), lines of small side-wall roughness are obtained, as shown in Fig. 4. Therefore, the PDMS/AZ5214 bilayer resist may be appropriate as masking material for pattern

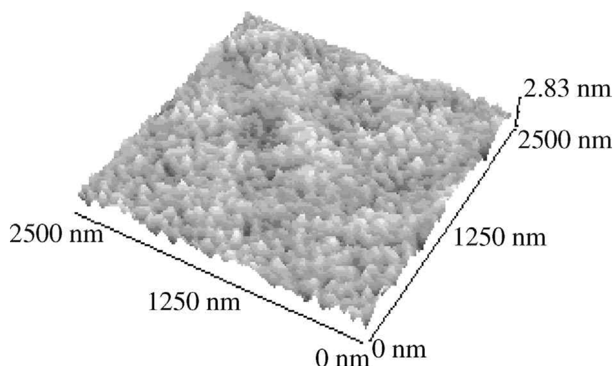

Figure 3. AFM image of the PDMS surface after pure O_2 plasma treatment in an ICP reactor (processed at $T = 15\,^{\circ}$C). Small surface roughness is obtained (RMS surface roughness = 0.4 nm, max value of the z-scale = 2.83 nm).

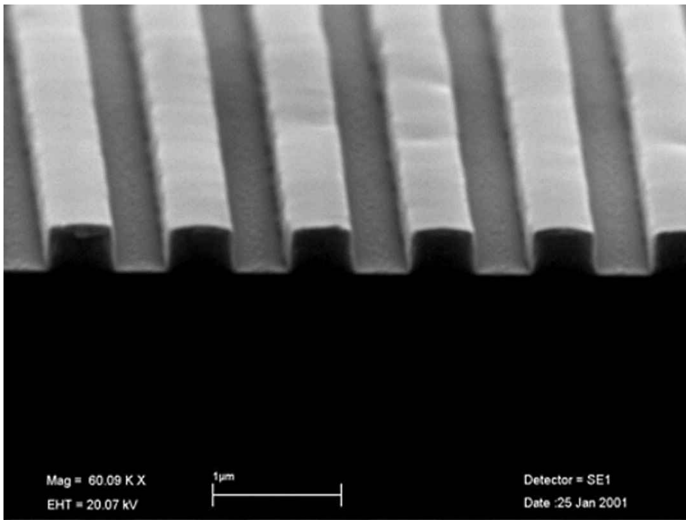

Figure 4. Cross section of 0.5 μm Lines/Spaces fabricated in a bilayer resist scheme with 100 nm PDMS as the imaging layer and 360 nm AZ5214 as the bottom underlayer. The transfer etching was performed (in ICP reactor) in an optimized first step in SF_6/He plasma (500 W, 0 V bias, 6 s) and the main etching in O_2-only containing plasma (source power 600 W, -100 V bias, pressure 10 mtorr, with a 20% overetch).

transfer e.g. to Si substrates. In fact, given the good etch selectivity ($>15:1$) of the underlayer AZ5214 over PDMS, a pattern can be transferred reliably from a 100 nm PDMS layer to an underlayer as thick as 1.5 μm. This is also guaranteed by the reasonable anisotropy of the etching, demonstrated in Fig. 4, which can be attributed to the plasma conditions (low plasma power and cooling of the sample at room-temperature) at which the dry development was performed, albeit in pure O_2 plasmas. In addition, the extremely high selectivity of the anisotropic etching of Si over resist masks, that exceeds $100:1$ in high density plasma reactors with advanced processes, shows a potential for use of the bilayer scheme with PDMS as the top imaging resist to pattern transfer as deep as 150 μm in Si, appropriate for MEMS fabrication.

3.2. Surfaces with controlled high roughness

On the other hand, when appropriate topography is desired on Si-containing polymer surfaces e.g. for application in sensor devices, plasma processing conditions can be modified to result in surfaces with high roughness. Such surfaces were obtained in our experiments by means of O_2-based treatment in a RIE plasma reactor. In this case, periodic mound structures of controlled roughness size and periodicity (rms roughness up to tens of nm, and periodicity of several hundreds nm) were obtained as shown below.

Figure 5 illustrates an AFM micrograph of the surface of the Ardrich material exposed to high dose and treated to oxygen-based RIE plasma with a breakthrough

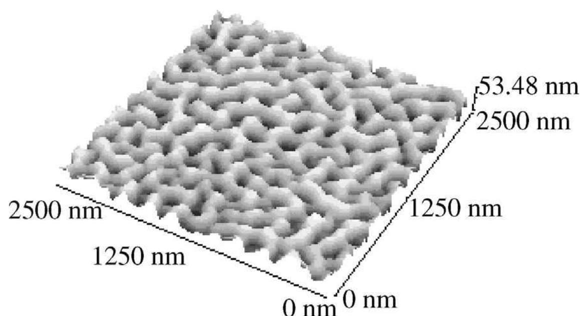

Figure 5. AFM image of the poly(dimethyl siloxane) (Aldrich) surface, e-beam exposed and treated in O_2 RIE plasma (10 mtorr, 400 W) with breakthrough step (20% SF_6 + 20% CHF_3 + 60% O_2 for 6% of the total treatment time). The e-beam exposure dose used was 8 $\mu C/cm^2$ and the measured RMS surface roughness was 8.5 nm (z-scale max = 53.48 nm).

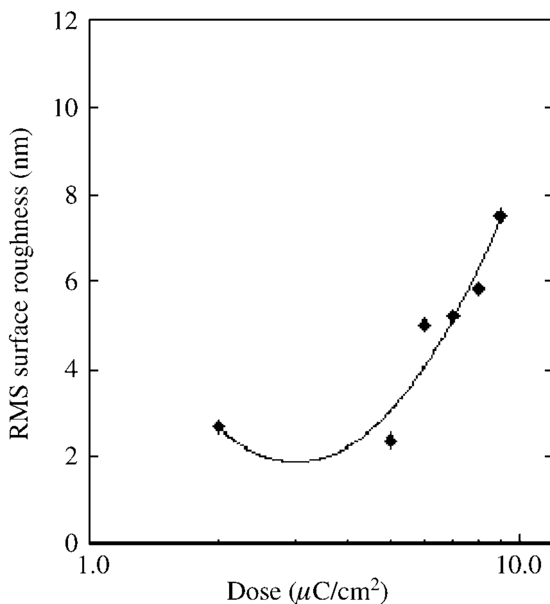

Figure 6. The surface roughness after 1 min in O_2 RIE plasma without a breakthrough step as a function of dose for the Aldrich material (processing in 10 mtorr, 400 W O_2 plasma).

step. Indeed, a surface of high roughness (rms value 8.5 nm) was obtained, while scaling analysis of the surface roughness showed a quasi-periodic surface structure with a periodicity of about 150 nm.

In Fig. 6, the surface roughness after 1 min in O_2 RIE plasma without a breakthrough step is shown as a function of dose for the Aldrich material. For the material processed in the RIE reactor, roughness is high at very low doses (not shown in the plot) as in the case of the ICP-treated PDMS of Fig. 2. However, as the dose increases, the roughness of the PDMS surface increases drastically, in contrast to the ICP-treated PDMS (Fig. 2). A similar dependence of surface

roughness on dose was observed for the PDMS material with the narrow molecular weight distribution ($M_w/M_n = 1.01$), however higher values of roughness were obtained at high doses.

The big difference in roughness values obtained for materials treated in the ICP and the RIE reactor is attributed to the different temperatures at which plasma treatment was performed in the two reactors. Specifically, the temperature of the process was well controlled in the case of the ICP reactor due to the good thermal contact of the treated sample to a temperature-controlled electrode. On the contrary, the temperature of the sample in the RIE reactor was insufficiently controlled, due to the fact that sample treatment takes place on a thick thermally insulating plate. An explanation for the effect of temperature on surface roughness will be presented briefly below.

The observed formation of high roughness on Si-containing polymers treated in the RIE reactor is related to the relief of the compressive stress, developed between the bulk of the polymer film and the silica-like thin layer (grown on the polymer surface during oxygen plasma treatment [8]), as the sample cools to room temperature following the plasma treatment. The developed stress is proportional to the temperature fall after treatment and the difference in the thermal expansion coefficients of the plasma-grown silica-like layer and the bulk polymer [9]. This can also explain the higher roughness value obtained for surfaces treated in the ICP reactor at temperatures higher than room temperature (e.g. at $T = 60^{\circ}$C, as discussed in Section 3.1). The relatively smaller roughness observed in the case of the material with the wide molecular weight distribution can be attributed to the higher mobility of the shorter polymer chains, resulting in smoother silica-like surfaces.

The results shown in this work refer to thin PDMS films on another polymer, but analogous results can be obtained for thick PDMS films. Although we report here only results for PDMS surfaces, ongoing work on silylated and silsesquioxane polymers will be reported soon from our group.

4. CONCLUSION

Oxygen-based plasma treatment of Si-containing polymers has significant effect on surface topography and roughness which can be controllably varied, depending on application requirements. The plasma processing conditions (gas composition, electrode temperature) offer a potential for control over surface topography and roughness of Si-containing polymers appropriately treated in such plasmas.

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