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Surface modification of Si-containing polymers during etching for bilayer lithography

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Abstract

Surface modification of polydimethylsiloxane (PDMS) under O₂ plasma exposure is studied by XPS and real time ellipsometry. Results show the conversion of the PDMS surface into a SiO_x-like material. Total layer thickness and extension of the SiO_x layer are controlled by the sample bias. We suggest that surface and line edge roughness defects occurring when using PDMS as top layer in bilayer lithography are intimately related to the rapid kinetics of conversion and to the formation of SiO_x hard micromasks on the surface. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PDMS; XPS; Pattern roughness; Bilayer lithography

1. Introduction

The next generation of microelectronic circuits will require minimum characteristic dimensions below 100 nm, a task achievable through the adoption of 193- and 157-nm lithography as the next industrially preferred steps in optical lithography. However, the high absorbance of carbon-based polymers at 157 nm [1] makes the use of bilayer resist schemes more attractive than before. For such applications, the pattern is imaged in a thin layer (~100 nm) of Si-containing photosensitive polymer, lying on top of a thick planarising resist, and the pattern transfer to the bottom layer is performed by plasma etching (plasma development). Si-containing polymers, such as polydimethylsiloxane

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(PDMS), which exhibit low absorbance ($< 4 \mu\text{m}^{-1}$) at these wavelengths [1,2], are candidate top layer resist materials for bilayer lithography. The etching resistance of Si-based polymers to oxygen plasmas has been studied and related primarily to their Si-content [3]. However, formation of surface and/or line-edge roughness (SR, LER) during plasma development is a severe drawback that should be waved away. Recent studies have shown that a breakthrough step in fluorine-containing plasma can strongly reduce SR and LER [4–6], in contrast with most studies which concern etch rates and pattern transfer [4,7] in various plasma conditions. This article is focused on the investigation of the chemical modification of the PDMS surface in oxygen plasma with the aim to understand the origin of SR and LER.

2. Experiment

We used the commercial PDMS obtained from Aldrich (average molecular weight 120 000). Samples consist of Si wafers coated with a bilayer resist: a hard-baked novolac (AZ5214 by Clariant) for the bottom resist layer and a PDMS film, 100 nm thick, for the top resist layer. Etching reactor used during this study is equipped with an Alcatel ICP (inductive coupled plasma) source operating at 13.56 MHz. The plasma diffuses in the process chamber where the wafer is located. A second rf generator (13.56 MHz, 600 W) allows to bias the substrate independently. The temperature of the sample is controlled by cooling the sample holder at 20 °C using a cryostat (HUBERT unistat 385). Heat transfer between the sample and the holder is achieved by mechanically clamping the wafer to the holder and by injection of helium at the backside of the wafer. In situ multiwavelength ellipsometry is used to measure in real time the evolution of the top layer thickness. Chemical modification of the surface after plasma exposure is investigated using quasi in situ XPS. Plasma conditions used are: top power 800 W, pressure 10 mTorr, flow rate 40 sccm, bias voltage has been varied from 0 (0 W) to -100 V (50 W).

3. Results

3.1. Etch rates

Fig. 1 compares the top layer thickness versus plasma exposure time for three different bias voltages. At plasma ignition, a strong consumption of the material is observed, then the etch rate drops rapidly and reaches a rather stable value for $t > 60$ s. However, the value depends strongly on the bias voltage, from 0.3 nm/min at 0 V to 7 nm/min at -100 V bias. At -100 V, i.e. typical dry development condition, the etch rate of AZ5214 is 630 nm/min leading to a selectivity of 90. Fig. 1 also reports the thickness variation for thermal oxide layer under the same conditions. In this case, constant etch rate are observed.

3.2. Surface analysis

After plasma exposure, XPS analysis shows the presence of oxygen, carbon, silicon and fluorine. The presence of fluorine is attributed to breakthrough steps, carried out in previous experiments. Fig.

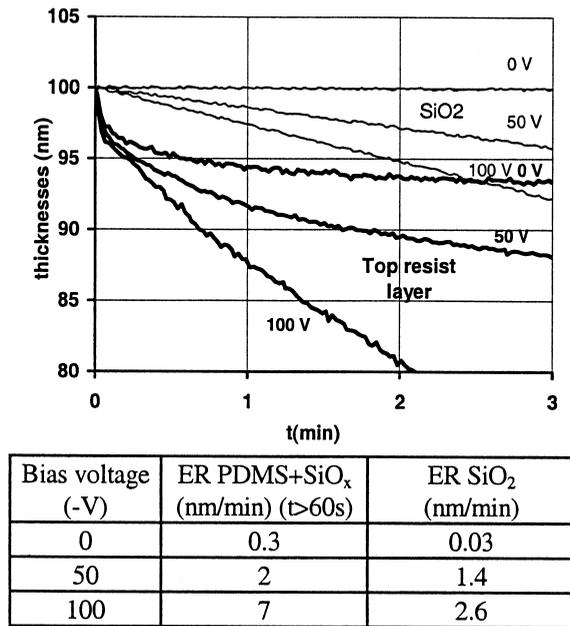


Fig. 1. Evolution of the top resist layer thickness during O₂ plasma at different bias.

2 shows the atomic percentage that are calculated from the area under the various peaks corrected with their respective atomic sensitivity factors. The fluorine content, which is not plotted in Fig. 2, remains stable (around 10%) and thus its presence does not influence the other percentage evolution. Silicon atomic percentage is independent of time and bias, it remains constant around 20%, a value corresponding to PDMS before plasma treatment. On the other hand, oxygen and carbon percentage depend strongly of bias and time. A decrease in carbon concentration is accompanied by an increase in oxygen concentration. XPS analysis of PDMS prior plasma exposure reveals a single component for the Si_{2p} spectrum (Fig. 3). Location at 102.1 eV is in a good agreement with what one can expect from the polymer formula and from binding energy shifts: ~1.0 eV per O and ~0.3 eV per C bound to Si. Upon exposure to oxygen plasma the Si_{2p}(PDMS) component decreases in intensity and is

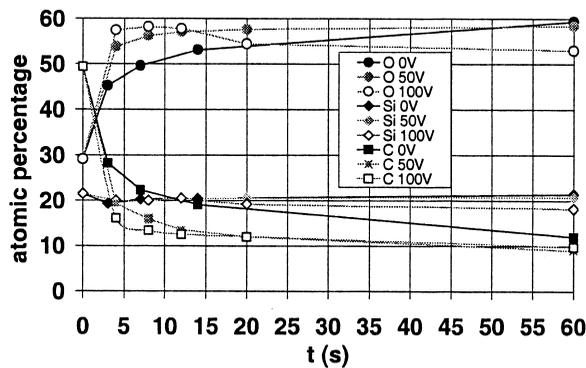


Fig. 2. Silicon oxygen and carbon quantification of PDMS versus time as a function of bias.

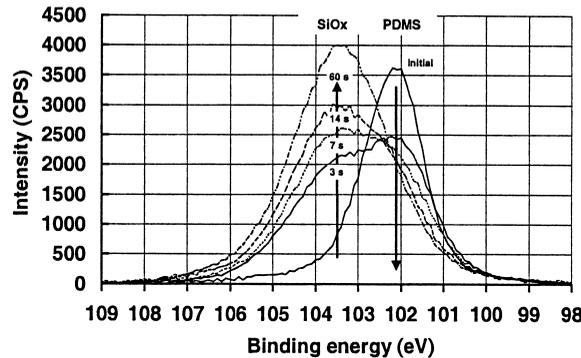


Fig. 3. Si_{2p} distribution versus etching time in O_2 plasma (no bias).

gradually replaced by a SiO_x type component (103.5 eV). Fig. 3 reports data obtained without sample bias. Results for -50 and -100 V bias show the same behavior, the major difference being that the larger the bias, the faster the spectrum evolution. Thus, these results suggest conversion of the organosilicon species to SiO_x -like species, as observed in atomic quantification. Combination of XPS analysis performed at various exposure times with XPS angular analysis allows to precise that the chemical modification of the PDMS material, i.e. its transformation into SiO_x -type material, concerns only a shallow surface layer. Assuming a simple two-layer model: a thin homogeneous layer above the PDMS layer separated by a sharp interface, one can estimate the thickness of SiO_x layer from the Si_{2p} (PDMS) and Si_{2p} (SiO_x) peak intensity, using the classical expressions:

$$I_{\text{PDMS}} = I_{\text{PDMS}}^{\infty} \exp\left(-\frac{z_{\text{SiO}_x}}{\lambda \cos(\theta)}\right) \quad (1)$$

$$I_{\text{SiO}_x} = I_{\text{SiO}_x}^{\infty} \left\{ 1 - \exp\left(-\frac{z_{\text{SiO}_x}}{\lambda \cos(\theta)}\right) \right\} \quad (2)$$

Where I_{PDMS}^{∞} and $I_{\text{SiO}_x}^{\infty}$ are the intensities obtained for a bulk sample of these materials, θ is the XPS angle and λ is the Si_{2p} photoelectron mean free path. As the λ value in the SiO_x -like layer is not known, we have used for the calculation an approximate value of 30 Å. In any case, the thickness evolution reported in Fig. 4 will be similar for a different λ value, unless λ should change sharply with exposure time or sample bias.

It should be noticed that the evolution of the SiO_x layer thickness with time and bias is in good agreement with the variation of the oxygen percentage. Indeed, for $t > 8$ s, i.e. when the oxygen concentration is nearly stable ($\sim 55\%$), the SiO_x thickness for -100 V is almost constant (~ 6 nm), whereas it continues to increase for 0 and -50 V bias.

4. Discussion and conclusion

Ellipsometric and XPS analysis give some complementary information on the PDMS modification mechanism. In particular, the optical constant of the PDMS and SiO_x -type compound are very similar.

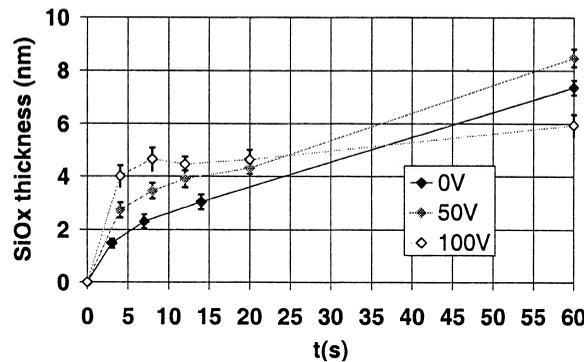


Fig. 4. SiO_x layer thickness versus time for three biases.

As a consequence, the top-layer thickness given in Fig. 1 and determined by ellipsometry, is the thickness of a PDMS + SiO_x layer.

At the beginning of the process ($t < 5$ s), the SiO_x layer grows rapidly—the larger the bias, the faster the growth—and the PDMS thickness decreases quickly. Above 60 s, the top-layer resist etch rate becomes constant. The difference between these two steps can be explained by the following proposed mechanisms:

Oxygen species present in the plasma play two roles. On one hand, they form with carbon some volatile compounds and on the other hand they oxidize silicon. Thus, the SiO_x layer grows as the PDMS is consumed. At the same time, the SiO_x layer is sputtered away under the effect of energetic ion bombardment. Indeed, silicon cannot form any volatile compounds with oxygen or carbon, so the only possibility to remove silicon is sputtering. Consequently, the SiO_x thickness depends on both the ion bombardment and the chemical reaction at the interface between SiO_x and PDMS. Moreover, the formation of this layer controls the oxygen concentration at the SiO_x–PDMS interface and this concentration can be assumed to be larger when the SiO_x layer is thinner. Therefore, we suggest that the short initial step is strongly dominated by PDMS chemical etching. Then, once the SiO_x surface concentration is large enough to make a ‘protective layer’ ($t > 60$ s) the etch rate observed mainly reflects the sputtering rate of the SiO_x layer. However, this material is less plasma resistant than thermal SiO₂.

At -100 V, after a few seconds, the SiO_x thickness is constant. So both processes (sputtering and PDMS conversion) occur at the same rate and the PDMS is consumed at 7 nm/min. When the substrate is not biased, first, formation of volatile compound and oxidation occurs, but since the SiO_x thickness is not limited by the bombardment, the conversion of PDMS into SiO_x at the interface will probably continue as long as the local oxygen concentration is large enough. But the total layer thickness remains typically constant (ER < 0.3 nm/min). Intermediate bias voltage lead to an intermediate situation: for example, at -50 V and $t = 60$ s an effective etch rate is measured but the growing SiO_x layer does not seem to have reached its final thickness.

The very quick conversion of PDMS at its surface into SiO_x material in typical dry development condition (bias ~ -100 V) results in the revealing and stabilization of the latent SR and LER. These hard SiO_x features then act as micromasks throughout the dry development. The possibility to reduce or suppress the latent SR and LER by using a breakthrough step in etching conditions strongly

suggests that the latent roughness is confined in a very shallow region at the surface of the PDMS pattern.

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