Analysis of Chemical and Morphological Changes of Phenol Formaldehyde-based Photoresist Surface caused by O_2 Plasma

D. A. Shutov

Department of Electronic Devices & Materials Technology, Ivanovo State University of Chemistry & Technology, 7 F. Engels st., 153000 Ivanovo, Russia

Seung-Youl Kang, Kyu-Ha Baek, and Kyung Soo Suh

IT Convergence & Components Laboratory, ETRI, 161 Gajeong-dong, Yuseong-gu, Daejeon 305-700, Korea

Nam-Ki Min and Kwang-Ho Kwon[a]

Department of Control and Instrumentation Engineering, Korea University, Jochiwon-eup, Yeongi-gun, Chungnam 339-700, Korea

[a]E-mail : kwonkh@korea.ac.kr

Chemical and morphological changes of phenol formaldehyde-based photoresist after O_2 radiofrequency (RF) plasma treatment depending on exposure time and source power were investigated. It was found that etch rate of photoresist sharply increased after discharge turn on and reached a limit with increase in plasma exposure time. Contact angle measurements and X-ray photoelectron spectroscopy (XPS) analysis showed that the surface chemical structure become nearly constant after 15 sec of the treatment. Atomic force microprobe (AFM) measurements were shown that surface roughness was increased with plasma exposure time.

1. INTRODUCTION

Stripping of photoresist in oxygen discharge is one of the oldest plasma-chemical techniques used in the semiconductor microelectronic industry[1,2]. In this process, the discharge is substantially a source of oxygen atoms which attack the organic polymer and convert it in an isotropic etch reaction into the final volatile products such as H_2, H_2O, CO, and CO_2[1-4].

Characterization of photoresist films before and after the treatment is of great importance for understanding the complicated chemical reactions and such an understanding may lead to the development of efficient photoresist stripping processes. At the same time, the O_2 plasma is normally used for the isolation process for organic thin film transistor (OTFT). In the process, it is well known that the O_2 plasma degrades the performance of OTFT devices[5]. That phenomenon is very similar to that occurred at O_2 plasma stripping in the photoresist. Accordingly, a careful investigation of the O_2 plasma effect on the polymer surface is required.

In this study, we investigated the characteristics of the photoresist surface which was exposed to O_2 plasma for various time durations and source power using XPS, AFM and surface energy measurement.

2. EXPERIMENTAL

Positive photoresist SS03A9 (Dongwoo Fine-Chem Co., Ltd.), which is prepared on the basis of phenol-formaldehyde resin, have been chosen because they have been widely used in microelectronics and are readily available. Photoresist processing on silicon wafers for this work included a spin-coating of a layer which was about 1 μm in thickness.

The wafers were then plasma-treated with the use of an RF inductively coupled plasma (ICP) system. Etching experiments were performed in a planar ICP reactor used and described in our previous work[6]. The reactor consisted of a cylindrical quartz chamber with a radius of 16 cm and a 5-turns copper coil located on 10-mm-thick

horizontal quartz window. The coil was connected to a 13.56 MHz power supply. The distance between the horizontal quartz window and bottom electrode used as a substrate holder was 12.8 cm. The bottom electrode was connected to another 13.56 MHz power supply to produce a negative dc bias voltage. The temperature of the substrate holder was held at 18 °C. Oxygen was introduced into the reactor at a flow rate of 60 sccm. The total pressure in the reactor was 10 mTorr. The etching time varied from 15 to 90 s. The input power (TCP) changed from 50 to 200 W.

The etched depth of the photoresist was measured using a surface profiler (Alpha-step 500, Tencor).The surface roughness of the photoresist layers before and after the plasma etching was investigated by AFM (atomic force microscopy) of an AFM (PSI, Model-CP) with the lateral scanning method. The values of root mean square roughness on the surface were calculated from 1×1 μm^2 sized height images. X-ray photoelectron spectra were extracted using a VG Scientific ESCALAB 200R XPS (X-ray photoelectron spectroscopy) with Al (Kα) (1486.6 eV) radiation operating 260 W. The binding energy was calibrated using C 1s peak at 284.5 eV[7,8]. Narrow scan spectra of all regions of interest were recorded with 20 eV pass energy to quantify the surface composition and identify the chemical binding states. Static contact angles for water and methylene iodide were measured using the sessile drop method with a contact angle goniometer Phoenix 300 (SEO Co. Ltd) at room temperature. The so-called two-liquid method (extended Fowkes's theory) has been used in order to calculate surface free energy[9,10].

3. RESULTS AND DISCUSSION

Figure 1 shows the changes in film etch rate versus O_2 plasma exposure time at various source power. The etch rate was calculated as "decreased thickness" divided by
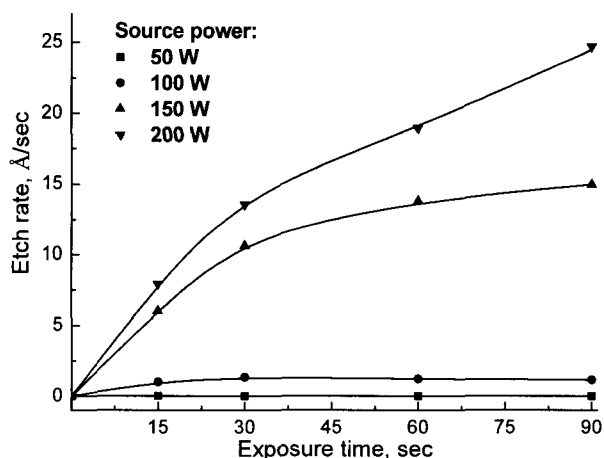
exposure time.

As can be seen in this figure, the etch rate of the film is found smaller at the beginning of the oxygen plasma exposure, up to 15 sec, after which the rate seems to become to a constant value. This is due to the fact that the surface temperature, which may affect the etch rate, changes at the beginning of the O_2 plasma exposure and then becomes stable. In addition, the surface chemical structure at the beginning of the exposure seems to be different from that of the stationary state. Moreover, the etch rate increases with increasing source power. Obviously, it is caused by the increase of the plasma active species flux on the surface. Etch rate reaches a constant value more slowly at high source power.

It is well known that the surface energy depends on the chemical state of a material surface. In order to investigate the chemical state on the photoresist surface, the contact angle was measured and the surface energy was calculated. Normally, the surface energy is divided into two components, that is, polar energy and dispersion one.

Figure 2 and 3 plots polar and dispersion components of photoresist surface energies with plasma exposure time and source power. Both the polar and the dispersion components sharply change at the first 15 seconds, after which the components seems to become constant. The increase in source power leads to the reduction of a dispersion energy and growth of a polar energy. Furthermore the polar energy of a photoresist surface treated at 100, 150 and 200 W are similar, whereas etch rates of polymer are sharply differ. It is known, that a polar component of the surface energy is closely related with the concentration of polar functional groups[11]. In turn, the concentration of polar functional groups on a surface is defined by a ratio of their formation and destruction rates. Accordingly, the increase in source power leads to not only the growth of the etch rate, but also to the increase of polar functional groups formation rate.

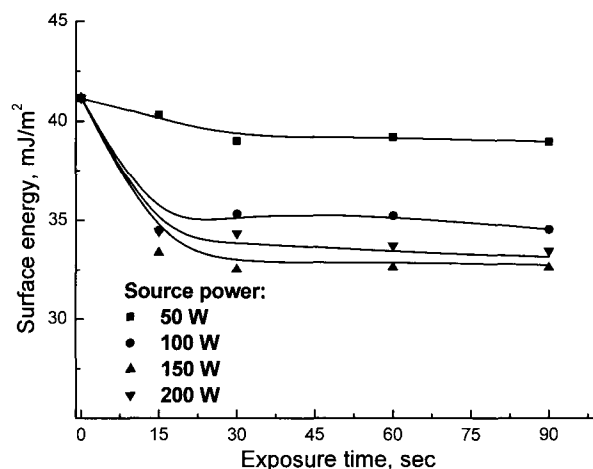Fig. 1. The photoresist etch rate as a function of the treatment time and source power.

Fig. 2. Dispersion component of surface free energy of the photoresist as a function of the treatment time and the source power.

In order to investigate binding states of the polymer, for each element XPS narrow scan analysis was carried out.

C 1s spectra before and after oxygen plasma treatment were compared. Figure 4 (a) shows the C 1s spectrum of an untreated photoresist.
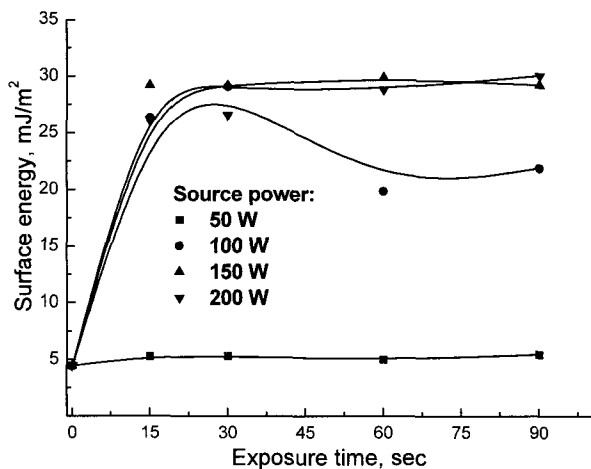

Fig. 3. Polar component of surface free energy of the photoresist as a function of the treatment time and the source power.
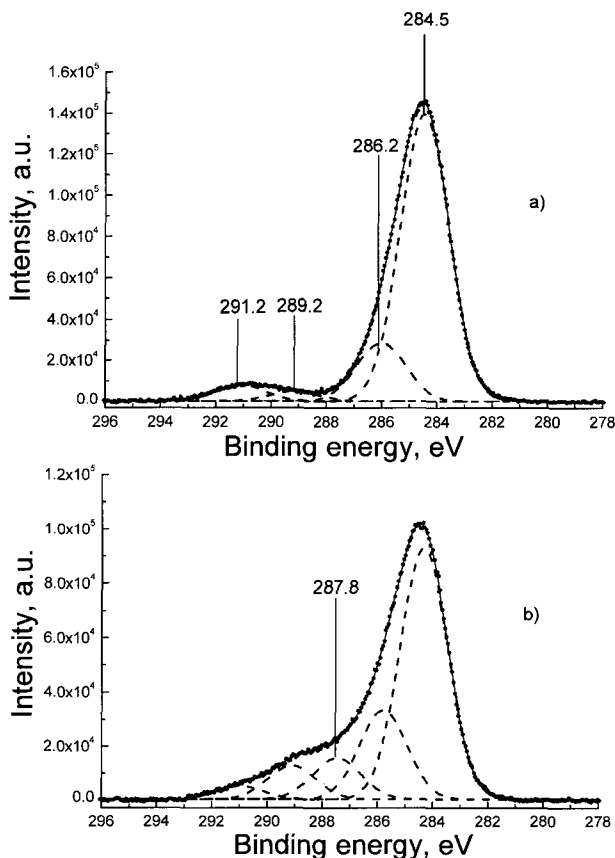

Fig. 4. The XPS narrow spectra of the photoresist: a)-before etching, b)-after 90 sec etching at 200 W.

In this figure, we can divide the spectra into four peaks. In this work, the peaks are assumed as the Gaussian distribution functions. One peak is observed at the binding energy of 284.5 eV and the others are done at 286.2, 289.2, 291.2 eV. Those first three peaks correspond to C-C/H, C-OH (in phenol), C=O (in ester or carboxylic groups) bonding states, respectively[7]. The peak at 291.2 eV corresponds to characteristic $\pi \rightarrow \pi^*$ shake-up line in aromatic compounds[7]. Meanwhile, we can observe additional peak at the spectra after treating a sample with the oxygen plasma, see Fig. 4(b). The additional peak was observed at binding energy of 287.8 eV. It is surely due to oxygen reaction. Therefore, we can assign this peak to C=O bond in aldehyde and ketone carbonyl groups[8]. This result means that after O_2 plasma treatment, the chemical composition of the photoresist surface was changed. Oxygen plasma treatment results in the reduction of carbon concentration, while the relative concentrations of oxygen atoms increase. The relative atomic ratio O 1s to C 1s on the photoresist surface with the exposure time is shown in Fig. 5. This figure shows the rapid increase of the relative atomic ratio at the first 15 second after the discharge turns on. Over the time, the ratio seems to become a constant value. Also Fig. 5 shows the area-ratio change of each carbon-oxygen bond. These behaviors reach a constant value after the first 15 seconds too.

Additionally, surface morphology of photoresist after O_2 plasma treatment has been observed. Plasma etching of photoresist caused an increase in the roughness of the surface layer. AFM images of untreated and etched photoresist surfaces are presented in Fig. 6.

The trend in variation of surface roughness with exposure time at several source powers is shown in Fig. 7. The average surface roughness of the photoresist increases with increasing both the exposure time and source power. There is not any characteristic time revealed.
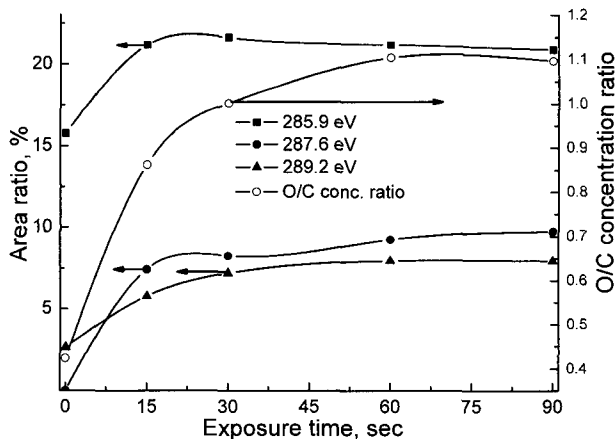

Fig. 5. The relative percentage of carbon-oxygen functional groups and relative atomic percentage of oxygen to carbon concentration as a function of treatment time. (Source power 200 W)

Any interrelation between the roughness and the chemical state of the surface is not observed. Obviously, the roughness of the surface mainly increases due to physical plasma-polymer interaction, instead of chemical reactions.

4. CONCLUSION

We have found out that during first 15-20 sec after O_2 discharge turn on, etch rate of photoresist sharply grows. Saturated etch rate and time to be reached at a constant value with the growth of source power slightly increase. Chemical state of photoresist surface does not change after first 15 sec of the treatment at the all discharge condition. Then, moderate growth of etch rate after that time in general is caused by the increase in photoresist temperature than change of a chemical structure. The increase of source power does not lead to the change of mechanisms of chemical reactions on the photoresist surface, but lead to the increase in the etch rate due to changes of plasma active species flux.

Additionally, it was found that surface roughness of photoresist increases with increasing the O_2 plasma exposure time and source power. It was assumed that the surface morphology is mainly caused by not chemical plasma-photoresist interaction.
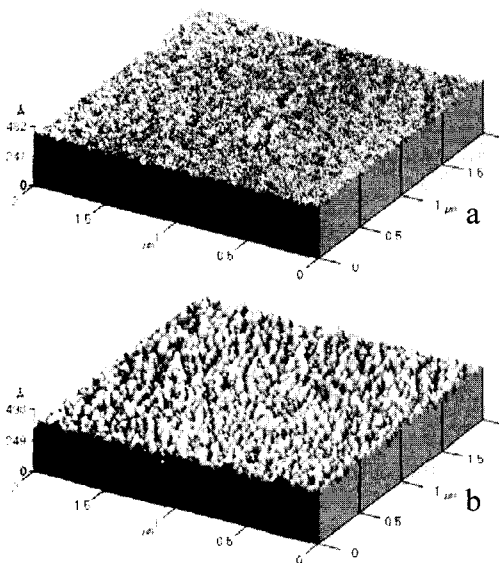

Fig. 6. AFM images of the photoresist surface: a)-before etching, b)-after 90 sec etching at 200 W.
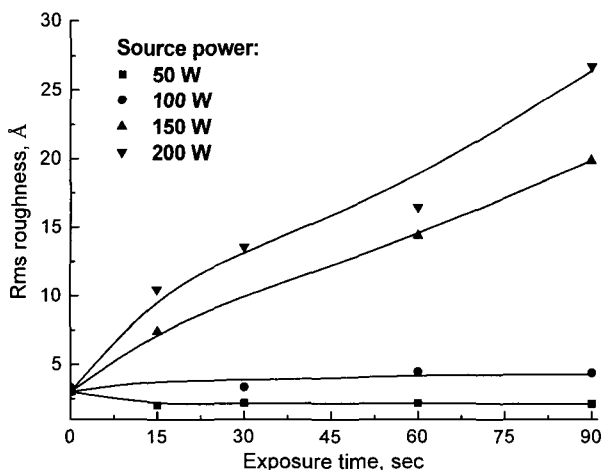

Fig. 7. The RMS roughness of photoresist as a function of the treatment time and source power.

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