Investigation of phenol phormaldehyde-based photoresist at an initial stage of destruction in O_2 and N_2O radiofrequency discharges

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Abstract: Etch rates and surface chemistry of phenol formaldehyde-based photoresist after short time O_2 and N_2O radio frequency (RF) plasma treatment depending on exposure time were investigated. It was found that the etch rate of photoresist sharply increased after discharge turn on and reached a limit with increase in plasma exposure time in both gases. X-ray photoelectron spectroscopy (XPS) analysis showed that the surface chemical structure become nearly constant after the treatment of 15 sec. Concentration of surface oxygen-containing groups after processing both in oxygen and in N_2O plasmas is similar.

Key Words: polymer, O_2 plasma, N_2O plasma, photoresist, etch rate, roughness, XPS

1. Introduction

Characterization of photoresist films before and after the plasma treatment is of great importance for understanding the complicated chemical reactions. At the same time, O_2 plasma is normally used for the patterning process for organic thin film transistor (OTFT). In this process, it is known that the O_2 plasma degrades the performance of OTFT devices [1]. Especially, this degradation is caused by damage of semiconductor and dielectric polymeric layers [2] due to the formation of oxygen-containing polar groups. Accordingly, a new etching gas chemistry for patterning process of organic materials which can allow combining relatively high etch rate of photoresist and relatively low concentration of surface oxygen-containing compounds should be investigated.

In this study, we investigated the etch characteristics and surface chemical state of the photoresist which was exposed to O_2 and N_2O plasma for various time durations.

2. Experimental

Positive photoresist SS03A9 (Dongwoo Fine-Chem Co., Ltd.) prepared on the basis of phenol-formaldehyde resin, was used in this experiment. 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 treated using an RF inductively coupled plasma (ICP) system. Etching experiments were performed in a planar ICP reactor used and described in our previous work [3]. O_2 and N_2O were introduced into the reactor with 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) was 200 W for oxygen and 400 W for N_2O.

The etched depth of the photoresist was measured using a NanoSpec 3000 spectroscopic reflectometer. X-ray photoelectron spectra were measured using a VG Scientific ESCALAB 200R XPS (X-ray photoelectron spectroscopy) with Al (Ka) (1486.6 eV) radiation operating 260 W. The binding energy was calibrated using C1s peak at 284.5 eV [4, 5].

3. Results and discussion

Fig. 1 shows the changes in film etch rates versus O_2 and N_2O plasma exposure time. The etch rates were 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 plasma exposure, up to 15 sec, after which the rate seems to become to a constant value. Etch rate of photoresist in N_2O plasma approximately is less 1.5 times than that in O_2 plasma.

Both O_2 and N_2O plasma treatments lead to similar changes in C1s XPS spectra of photoresist (Fig 2a). N 1s spectra of photoresist after N_2O plasma treatment show N atom incorporation (Fig 2b). There are no changes in N 1s spectra after O_2 plasma treatment.

We can divide C1s bond of untreated photoresist into four peaks. Main peak is observed at the binding energy of 284.5 eV (peak corresponding to C-C/H bond) and the others are done at 286.2, 289.2, 291.2 eV. Those peaks correspond to, C-OH

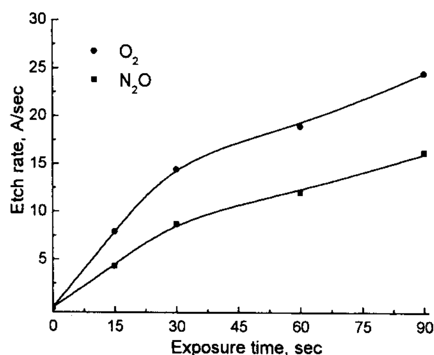

Fig. 1 The photoresist etch rate as a function of the treatment time.

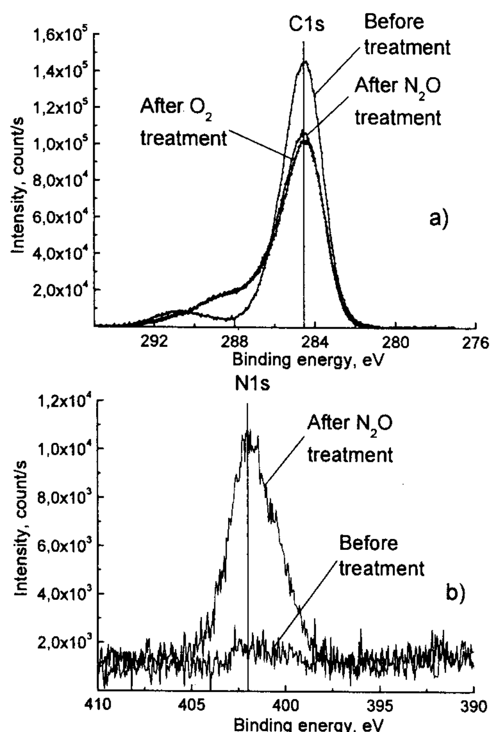

Fig. 2 The C1s (a) and N1s (b) XPS narrow spectra of the photoresist. Exposure time 90 sec.

(in phenol), C=O (in ester or carboxylic groups) and characteristic $\pi \rightarrow \pi^*$ shake-up line in aromatic compounds [4]. Meanwhile, we can observe additional peak at the spectra of the sample after treating a sample both in the oxygen and in the N_2O plasma. Additional peak was observed at binding energy of 287.8 eV. We have assumed that this peak is mainly due to oxygen reaction. Therefore, we can assign this peak to carbon-oxygen bond in aldehyde and ketone carbonyl groups [5]. Since the C 1s binding energies tend to occur in groups [6], a peaks caused by carbon-nitrogen bonds was not found out.

Both O_2 and N_2O plasma treatment result in the reduction of carbon concentration, while the relative concentrations of oxygen

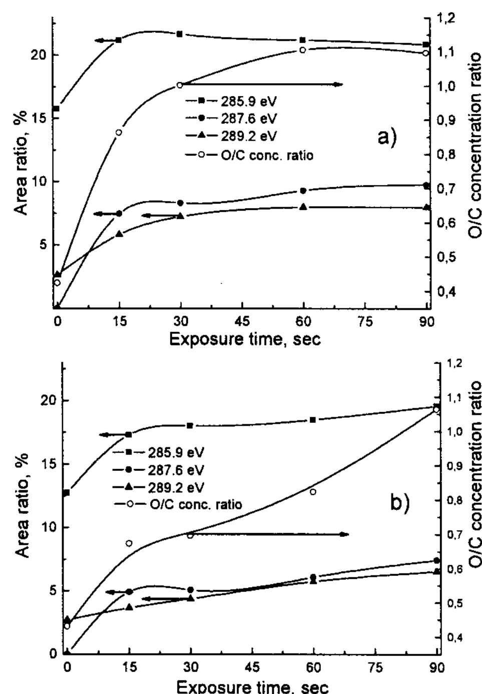

Fig. 3 Relative percentage of carbon-oxygen functional groups and atomic percentage of oxygen to carbon concentration as a function of O_2 (a) and N_2O (b) treatment time after.

atoms increase. The relative atomic ratio O 1s to C 1s on the photoresist surface with exposure time is shown in Fig. 3. Also Fig. 3 shows the area-ratio change of each carbon-oxygen bond. It can be seen that the concentration of surface oxygen-containing groups after treatment both in O_2 and in N_2O plasmas is similar.

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