Mechanism for Generation of Molecular-Level Line-Edge Roughness of ArF photoresist during Plasma Etching Processes

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1. Introduction

ArF photoresists, namely chemically amplified photoresists including photoacid generators (PAGs) [1], have been used in recent 193-nm lithography processes. However, ArF photoresists have serious problems during plasma etching processes, such as line-edge roughness (LER) [2]. LER can called be classified by pattern-size roughness, "low-frequency LER," and molecular-level-size roughness, called "high-frequency LER". High-frequency LER, in particular, is a more serious problem for wiring in ultra-large-scale integration (ULSI) devices of less than 32 nm. The generation mechanism of low-frequency LER has been already discussed in a previous paper [3]. Conversely, the generation mechanism of high-frequency LER has not yet been clarified. It is speculated that high-frequency LER is determined by molecular level structures in ArF photoresist. Namely, we must understand the relationship between irradiation species from plasma (ions, electrons, radicals, and ultraviolet/vacuum-ultraviolet (UV/VUV) photons) and molecular-level reactions on the ArF photoresist surface. Surface temperature is also important because heating is a key factor in the chemically amplified photoresist reaction process [4].

We discuss the dependence of molecular-level LER on the irradiated species from the plasma and clarify the generation mechanism for molecular-level LER to solve the problems associated with ArF photoresists.

2. Experiment

We investigated the effects of UV/VUV photon radiation, ion bombardment, and surface heating on ArF photoresists using our developed neutral-beam process. The neutral-beam source is shown in Fig. 1 [5]. It consists of inductively coupled plasma (ICP) between parallel carbon electrodes and has numerous apertures in the bottom carbon electrode through which neutral beams can be extracted. The incident energy of the beams can be adjusted by changing the voltages applied to the carbon electrodes. The apertures in the bottom carbon electrodes are 1 mm in diameter and their total area is 50% of the area of the electrode. To control the irradiation species from the plasma in this experiment, we used bottom carbon electrodes that were either 10 or 2 mm thick so they would have apertures with different aspect ratios: AR10 and AR2. Ions from the plasma were neutralized by collisions with the sidewalls of the AR10 apertures and passed through the AR2 apertures without being neutralized (Fig. 2).

Processes were performed using Ar and Cl_2 gases [ICP source power: 600 W, process-chamber pressures: 4.0 mTorr for Ar and 1.6 mTorr for Cl_2 , distance between the bottom electrode and samples: 80 mm, applied voltages: floating to the top electrode and ground to bottom, irradiation time: 5 min]. The experimental conditions are summarized in

Table 1. In these experiments we used blanket ArF photoresist polymer films. The structures of the ArF photoresist polymer and PAG we used are shown in Fig. 3. The film thickness was measured using ellipsometry. The surface roughness of the films was measured using scanning probe microscopy (SPM), and the chemical bonding states in ArF photoresist polymers were investigated by analyzing the Fourier transform infrared (FTIR) spectra normalized by film thickness.

3. Results and Discussion

A. Etching rates for ArF photoresist films

The etching rates for ArF photoresist films are shown in Figure 4. Note that the term *etching rate* here means the rate at which film thickness is reduced by etching, removal, and/or shrinkage. The etching rates increased after ion and UV/VUV-photon irradiation for both gasses. At 20°C the etching rates obtained with Cl ions was greater than that obtained with Ar ions, and at 100°C the etching rate obtained with Ar ions was much greater than the obtained at 20°C with Ar or Cl ions. Since the etching rate in Cl₂-neutral-beam irradiation was almost the same as Ar-neutral-beam irradiation, the Cl₂-neutral-beam flux can be estimated to have been comparable to Ar-neutral-beam flux. Because the energies of UV/VUV photons from both Ar and Cl₂ plasmas are high enough to break chemical bonds in ArF photoresist films, the increased etching rate observed in Cl-ion and UV/VUV-photon irradiation can be attributed to chemical reactions of chlorine. In particular, in Cl₂-ion and UV/VUV photon irradiation, chlorine might react with chemical bonds broken by UV/VUV irradiation.

B. Surface roughness of ArF photoresist films

Figure 5 shows that the Root-Mean-Square (RMS) roughness, which remained unchanged after Ar-neutral-beam irradiation at either temperature, was greater after Ar-ion and UV/VUV-photon irradiation at 20°C and was much greater after Ar-ion and UV/VUV-photon irradiation at 100°C. The difference in the surface roughness of the ArF photoresist films is consistent with the different etching rates.

C. Chemical bonding states in ArF photoresist films

To investigate the effects of irradiation species and surface temperature on the ArF photoresist polymer structure, we analyzed the chemical bonding states in ArF photoresist polymers using FTIR. We investigated peaks between 2800 and 3100 cm⁻¹ to the C-H bonds in the adamantyl groups and peaks at 1796 and 1730 cm⁻¹ that can be assigned to C=O bonds in the lactone groups and ester units.

Figure 6 shows the C-H region of the spectra obtained before and after irradiation. As shown in parts (a)-(d), the peaks in this region decreased only after Ar-ion and UV/VUV-photon irradiation at 100°C. According to these results, it is speculated that PAG-mediated deprotection in

ArF photoresist films can be amplified at high surface temperatures. Moreover, it is noteworthy that chlorine did not react with the adamantyl groups. In other words, the adamantyl groups were resistant to chemical reactions.

Figure 7 shows the C=O region of the spectra obtained before and after irradiation. The peaks assigned to the lactone and ester units slightly decreased under Ar-neutral-beam irradiation. After Ar-ion and UV/VUV-photon irradiation, these peaks were smaller than those after neutral-beam irradiation. However, there was not significant dependence on temperature with respect to the decrease in the spectra of C=O bonds. This means that the changes in C=O bonds are not caused by PAG-mediated deprotection. Furthermore, the peaks assigned to C=O bonds were smaller after Cl2-neutral-beam irradiation and after Cl-ion and UV/VUV-photon irradiation. This indicates that C=O bonds, unlike C-H bonds, react with chlorine.

4. Conclusion

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We investigated the effects of irradiation species and surface temperature on surface roughness of ArF photoresist films. The combination of UV/VUV-photon irradiation and heating induced and amplified PAG-mediated deprotection in the ArF photoresist polymers. The lactone and ester units in the base polymers were vulnerable to physical bombardment, chemical reactions, and UV/VUV-photon irradiation. The vulnerability results in changes in the base-polymer structure, which could account for the differences in the etching rates and surface roughness of ArF results photoresist films. Our demonstrated that UV/VUV-photon irradiation plays an important role for generation of molecular-level line-edge roughness.

References

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Table 1. Experimental conditions. Neutral-beam irradiation can be obtained by using AR10 apertures and ion and UV/VUV



(b)

(a)

Fig.6. FTIR spectra in the C-H region before and after (a) Ar-neutral-beam irradiation at 20°C and 100°C, (b) Ar-ion and UV/VUV-photon irradiation at 20°C and 100°C, (c) Cl₂-neutral-beam irradiation at 20°C, and (d) Cl-ion and UV/VUV-photon irradiation at 20°C.

