Plasma-polymerized Particles from Organosilane Molecules and Microstructure of Their Deposits

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1. Introduction

Plasma-enhanced chemical vapor deposition (PECVD) using organosilicon reactants is one of the superior processes for deposition of silica films at low temperatures with excellent step coverage. Recently, silica-based films with organic functional groups (SiO:CH) deposited by PECVD have been intensively studied for various applications such as low-k layers in semiconductor devices [1], gas barrier films [2-3], water-repellent surfaces [4-5], etc. The PECVD with organosilicon reactants can synthesize not only uniform films but also microparticles at relatively higher pressure due to polymerization of the reactants in plasma phases [6-10]. The highly rough surface of the films consisting of the microparticles also have various potential applications such as ultra-water-repellent surfaces. However, control of synthesis and deposition of the microparticles in PECVD has not been established. This study investigated the size, dispersion and agglomeration of the microparticles deposited by PECVD.

2. Experimental

The SiO:CH samples were deposited by using a capacitively-coupled PECVD system (Fig. 1) which consists of two face-type stainless steel electrodes with the diameter of 200 mm. We used Si (100) plates as substrates, which were placed on the grounded upper electrode. After the PECVD apparatus was evacuated to ~10^-2 Pa, trimethylmethoxysilane (TMMOS : Si(CH3)3OCH3) and Ar gases were introduced into the reaction chamber through a dispersion ring located at the bottom of the chamber, and the gas inlet at the hatch, respectively, as illustrated in Fig. 1. Then a glow discharge was generated by applying an rf power into the lower electrode. The flux ratio of TMMOS/Ar and the rf power were kept at 3/1 and 50 W, respectively. The total pressure was varied in the range of 100~400 Pa. We characterized microstructures and chemical bonding states of the films by SEM and FTIR, respectively.

Fig. 1. Schematic diagram of the PECVD system.

3. Results and discussion

From the visual observation, the films deposited at 100~200 Pa had uniform interference color,
while the films deposited at higher pressure showed milky turbidity, which was partially quite strong on the film deposited at 400 Pa. In spite of the different appearances of the SiO:CH films, as shown in Fig. 2, the chemical bonding states of the films were not strongly influenced from the deposition pressure. The films synthesized in this study have Si-X-Si (X=O, CHx) frameworks with -H and -CH3 terminations. Figure 3 shows the SEM image of the film deposited at 300 Pa. It is clear that the turbidity of the film is due to the visible light scattering by the microparticles. From the SEM image, we notice that the SiO:CH film consists of a uniform film and agglomerates of the microparticles, and any particle is not buried in the uniform film but attached on it.

![IR absorption spectra of the SiO:CH films.](image)

**Fig. 2.** IR absorption spectra of the SiO:CH films.

![A cross-sectional SEM image of the SiO:CH film deposited at 300 Pa.](image)

**Fig. 3.** A cross-sectional SEM image of the SiO:CH film deposited at 300 Pa.

Figure 4 shows the dependences of in-plane particle dispersion on the deposition pressure. The non-uniformity of the particle position on the films deposited at 400 Pa is much larger than that prepared at 300 Pa.

![Dependences of in-plane dispersion of the SiO:CH microparticles on the deposition pressure.](image)

**Fig. 4.** Dependences of in-plane dispersion of the SiO:CH microparticles on the deposition pressure.

**References**