Influence of Substrate Materials on Deposition of Plasma-polymerized SiO:CH Particles

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Particles of silica with organic functional groups (SiO:CH) were synthesized by plasma-enhanced chemical vapor deposition with a trimethylmethoxysilane reactant, and the influence of substrate materials on deposition behaviors of the particles were investigated. The deposited films consist both of a uniform SiO:CH layer deposited on the substrates and of the SiO:CH particles or their aggregates on the layer surfaces. The spherical shape of the particles indicates that they are polymerized through a homogeneous nucleation process in vapor phase. Averaged particle diameters are almost same on any type of the substrate materials. On the other hand, the area densities of the particles on gold-coated glass or silicon substrates are much higher than that on a glass plate. Averaged particle number of an aggregate is also higher on the gold-coated substrates. These behaviors of the SiO:CH particles can be explained by electrical properties of the substrate materials.

Keywords: Chemical vapor deposition, SiO:CH particle, Self-organized structure

1. Introduction

Silica materials with organic functional groups (SiO:CH) has attracted much attention because of its hydrophobicity, flexible bonding states, and low dielectric constant for the applications such as water-repellent surfaces [1-2], gas-barrier coatings [3-4], and insulating layers in microelectronic devices [5-6]. These properties can be improved when the SiO:CH films have microstructures with appropriate size and shapes. The authors have found that nano- and micro-sized SiO:CH particles can be synthesized by plasma-enhanced chemical vapor deposition (PECVD) with organosilicon reactants at higher pressures than conventional PECVD processes for preparation of uniform SiO:CH layers [7-9]. The SiO:CH particles are polymerized in the plasma and the deposits have self-organized microstructures which can be suitable for the above-mentioned applications. However, control of synthesis and deposition of the SiO:CH particles in PECVD have not been established. In this paper, we report on the influences of substrate materials on the deposition of the SiO:CH particles polymerized in plasma.

2. Experimental

The SiO:CH samples were deposited by using a capacitively-coupled RF PECVD system which consists of a vacuum chamber, a rotary pump, parallel-plate stainless steel electrodes with the diameter of 200 mm, and a RF power supply (SEREN, R301MK II, frequency : 13.56 MHz). We used glass, Si (100), Au-coated glass, and Au-coated Si(100) plates (25 mm sq.) as substrates, which were placed side by side on the center of the upper grounded electrode. The Au layers with a thickness of 100 nm were deposited by a sputtering system (Hitachi, E-1030). After the chamber was evacuated to ~10^-2 Pa, trimethylmethoxysilane (TMMOS: Si(CH3)3OCH3) and Ar gases were introduced into the chamber as described in the previous paper [10]. Then a glow discharge was generated by applying a RF power into the lower electrode. The total pressure, the flux ratio of TMMOS/Ar and the RF
power were kept at 200 Pa, 1/3 and 50 W, respectively. The deposition time was 10 min. We characterized microstructures and chemical bonding states of the deposited films by a scanning electron microscope (SEM, Hitatchi S-3000N) and a Fourier transform infrared spectrometer (FTIR, JASCO FT/IR-4000), respectively.

3. Results and discussion

Figure 1 shows a photograph of the RF plasma between the electrodes during deposition. We can recognize a uniform plasma generation along the electrodes. Optical emission spectroscopy revealed that the emissive species are CO, CH, C₂, H₂, Ar and H as shown in Fig. 2. The existence of C₂ and H₂ evince that they are formed by many times of dissociation and recombination of the TMMOS molecules and their fragments. Figure 3 shows an IR absorbance spectrum of the film deposited on a Si(100) substrate. The films on the other substrates were not characterized by FTIR due to the opacity of glass and Au. The film have Si-X-Si (X=O, CH₃) frameworks with a plenty of -H and -CH₃ terminations, which indicate that the film shows typical chemical bonding states of SiO:CH. From the broad shape of the C-H band, we suppose that the film consists of not only the Si-X-Si but also hydrogenated amorphous C-C frameworks.

As described in the previous paper [10], the sample surfaces had an interference color, which means that a SiO:CH film with a uniform thickness is deposited on each substrate. The surface morphology of the samples was observed by SEM as shown in Fig. 4. We can see the particles and their aggregates on each substrate. Any single particle has a spherical shape, which exhibits that the particles are synthesized through a homogeneous nucleation process in vapor phase. The aggregates have a neck structure among the single particles as shown in the magnified images in Fig. 4. This neck structure indicates that the particles keep isotropic growth after cohesion of these particles in vapor phase.

We estimated the averaged particle diameters on each substrate as shown in Fig. 5, and found that the values are almost same for all the substrates. It is not surprising, because the particles are formed in the common vapor phase. On the other hand, the averaged area densities, averaged aggregation numbers (particle number in an aggregate) and distributions of the aggregation number are strongly dependent on the substrate materials as shown in Fig.
6, 7 and 8. Clearly greater amount of particles and aggregates with larger aggregation number are deposited on the Au-coated substrates than the non-coated ones.

These results can be explained by the electrical properties of the substrate materials as followings. The plasma activation starts the growth of the continuous SiO:CH films on the substrates as well as the particle nucleation in vapor phase. The substrate surfaces, therefore, begin to take charging on the insulating SiO:CH films, and the surface potential during deposition must become negative. Since the SiO:CH particles in vapor phase are also charged negatively, the particles cannot deposit on the substrate surfaces during deposition. After the plasma off, the surface negative charges can be diminished due to both the flow of positive ions in the afterglow around the surface and the charge leakage through the conductive Si or Au layers. Because the amount of the positive ions is not enough to compensate both the charges on the substrate surfaces and the particles, the surface on the glass substrate and the SiO:CH particles in vapor phase remain in negatively charged, while the charges on the other substrates can be leaked through the conductive materials. Because the resistivity of the Si(100) substrate (~100 Ωcm) is much higher than the Au layer, the charge on the Si(100) surface flows much slower than that on the Au-coated substrates. The surface potential values after plasma off, therefore, must be qualitatively in the following order:

glass << Si(100) < Au/glass ≤ Au/Si(100).

Because the particles and aggregates in vapor phase are vacuum out in a certain rate, the area density of the particles should be in the same order consequently. The larger aggregates contain higher negative charges, so that they are repulsed from the glass and Si(100) substrate surfaces which are still negatively charged.

4. Conclusions

We investigated the influences of the substrate materials on the behaviors of the SiO:CH particles polymerized by PECVD from TMMOS reactant molecules. The electrical properties of the substrate materials have been found to take a significant impact on the SiO:CH particle deposition. The results of this study will contribute to control of the particle area density and the aggregation number.

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