Wavelength dependence on the formation of SiO$_2$ films by ultraviolet-laser-induced photochemical deposition using silicone rubber

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Abstract. We have proposed a novel method which permits to grow silicon dioxide (SiO$_2$) films on various substrates at room temperature using silicone rubber. In the method, two F$_2$ laser (157 nm) beams are used. One is used for generation of source gases from the silicone rubber (1st laser). Another is used for illumination of a substrate to deposit the films (2nd laser). We study on characteristics of the deposited films using laser beams which have longer wavelengths than the F$_2$ laser beam. When a fourth harmonics of Nd:YAG laser (266 nm) is used as the 1st laser, SiO$_2$ films with no carbon contaminants are grown as same as the case that an F$_2$ laser is used. The films are consisted of granular structures and the grain size become small as the laser fluence of 2nd laser beam increase. When an ArF laser (193 nm) is used as the 2nd laser, the deposition rate of the films is very low and the films have carbon contaminants. It shows that the 2nd laser beam plays an important role not only in the growth of the films but also in the prevention of carbon contaminants being mixed into the film.

1. Introduction

There is considerable interest in low temperature techniques for depositing silicon dioxide (SiO$_2$) films because in this way one can reduce dopant redistribution and defect generation for microelectronic devices, and fabricate micro-optical components on heat-sensitive material such as polymers. Various low temperature fabrication methods have been proposed for preparation of SiO$_2$ films, including plasma-enhanced chemical vapor deposition (PECVD), photo-CVD (PCVD), and pulsed laser deposition (PLD) [1-4]. The PCVD has also a potential for eliminating surface deterioration by the impingement of high-energy particles and has been applied to the preparation of SiO$_2$ films. For example, a transparent thin film was obtained at room temperature by Xe excimer lamp radiation using tetraethoxyorthosilicate (TEOS) as a raw material [2]. A rapid and patterned deposition was carried out at low temperature using an ArF laser [1]. However, these methods require source gases and a substrate heater. In addition, these SiO$_2$ films often contained contaminants such as carbon.

Recently, we proposed a simple method for growing SiO$_2$ films on various substrates at room temperature [5]. In this method, an F$_2$ laser beam with a wavelength of 157 nm at a low laser fluence simultaneously irradiates silicone rubber (polydimethylsiloxane, [SiO(CH$_3$)$_2$]$_n$) and a substrate. The SiO$_2$ films can be grown by combining Si in the ejected gaseous molecules from the silicone rubber with the excited oxygen [O(1D)] atoms generated by F$_2$ laser irradiation. This method makes it possible to grow very smooth and pure SiO$_2$ films at locally selected area on any substrates at room
temperature without any source gases.

In the present work, we investigate characteristics of the SiO$_2$ films which are fabricated by using the fourth harmonics (FH) of Nd:YAG laser beam with a wavelength of 266 nm or ArF laser beam with a wavelength of 193 nm. The surface morphology and chemical composition of the films are compared with those of the deposited films using an F$_2$ laser. Then we consider the role for the laser beams of illuminating the substrate and irradiating silicone rubber in the formation of the SiO$_2$ film.

2. Experimental

In the experiment, it was necessary to use two laser beams. One was for generating the gas and another was for depositing the film. Two prominent types of experiment were performed. In the first experiment, two beams with same wavelength originated from one laser system were used. The details have been reported elsewhere [5]. In the second experiment, two wavelengths from two different laser systems were used. An F$_2$ laser and an ArF laser were used as a light source and the results were compared. The F$_2$ laser fluence on a Si substrate and silicone rubber was 13 mJ/cm$^2$. The ArF laser fluence was 33 mJ/cm$^2$ which was adjusted to provide almost same photon number in the silicone as that of F$_2$ laser illumination. Both of the laser fluences were below the ablation threshold for silicone rubber (140 mJ/cm$^2$, 180mJ/cm$^2$) [6, 7]. The pulse repetition rate was kept to 20 Hz.

The experimental apparatus of the second experiment is illustrated in figure 1. The Nd:YAG laser beam irradiated silicone rubber and the F$_2$ laser beam illuminated the Si substrate. The substrate and silicone rubber lied at right angles to each other in the vacuum chamber (27 Pa). The F$_2$ laser beam and the Nd:YAG laser beam were introduced through the MgF$_2$ window and CaF$_2$ window, respectively. The two laser beams were synchronized using digital delay/pulse generator with a pulse repetition rate of 20 Hz. The timing of the two laser beams were adjusted to get the highest deposition rate. The laser fluence of the Nd:YAG laser beam was 100 mJ/cm$^2$ which provided almost same deposition rate as that of F$_2$ laser irradiation. The laser fluence was below the ablation threshold for silicone rubber (200 mJ/cm$^2$) [7].

3. Results and discussion

Figure 2(a) shows the AFM image of the film surface grown by ArF laser illumination for 15 min. A rough-textured surface was observed. For comparison, a film grown by F$_2$ laser illumination for 5 min is shown in figure 2(b). The growth rate of the films fabricated by ArF laser illumination was lower than one quarter of that fabricated by F$_2$ laser illumination.

A FT-IR transmittance spectrum of the film grown by ArF laser illumination is shown in figure 3. The thickness of the film was 30 nm. The spectrum of the film grown by F$_2$ laser illumination is also shown in the figure. The film thickness was 45 nm. The spectra were corrected by subtracting the effect of IR absorption of the substrate. There was not much difference between the two. The IR absorption of the Si-O-Si stretching mode was existed at 1000-1100 cm$^{-1}$. Since the IR peaks of Si-CH$_3$ at 1260 cm$^{-1}$ and CH$_3$ near 2900 cm$^{-1}$ were not seen, the formation of the film did not result from the ablation of the silicone rubber.

A depth profile of chemical elements (Si, O, and C) was analyzed by XPS with repeated Ar ion sputtering. Atomic concentration was calculated using the peak area in the spectrum and the sensitivity
The atomic concentration of C averaged close to 3% in the depth direction until Ar ion etching reached the substrate. An ArF laser beam is not absorbed by O₂, and the photon energy (6.4 eV) is lower than that (7.9 eV) of F₂ laser beam. Therefore, the film is considered to have carbon contamination and lower deposition rate because the O(1D) is not generated.

A thin film with the thickness of 130 nm was grown on a substrate when the Nd:YAG laser beam irradiated silicone rubber and an F₂ laser beam (18 mJ/cm²) illuminated the substrate for 15 min. No film was grown at un-illuminated area of the substrate with the F₂ laser beam. The FT-IR transmittance spectrum of the film was the same as that of the film grown by F₂ laser irradiation of silicone rubber. The chemical composition ratio of O to Si obtained from the XPS depth profile was approximately 2 to 1. The ratio was almost constant in the depth of the film. No carbon peaks were observed. Therefore, we can suppose the film is SiO₂. However, the refractive index of the film was 1.448 and was lower than that (1.452) of the film grown by F₂ laser irradiation of silicone rubber. Figure 4(a) shows the SEM image of the film surface. The surface morphology was grainy compare with that (figure 4(b)) of the film grown by F₂ laser irradiation of silicone rubber. It is supposed that the lower refractive index of the film was caused by the grainy morphology.

The photon energy (4.6 eV) of a Nd:YAG laser beam is lower than that of an ArF laser beam. Although O(1D) atom is not generated by Nd:YAG laser, the film had no carbon contaminants. Thus, the high photon energy of an F₂ laser beam illuminating the substrate could have an effect on elimination of carbon in growing the film. The grainy morphology of the film could result in the presence of inadequately-decomposed low molecular weight (LMW) silicone gases. This is probably due to the lower photon energy of the Nd:YAG laser beam.

Figure 5 shows the relation between the deposition rate and the fluence of F₂ laser illuminating the substrate. The fluence of Nd:YAG laser irradiating the silicone was constant. The deposition rate increased until a laser fluence of approximately 240 mJ/cm², followed by decrease. The SEM images of the film surfaces for the F₂ laser fluence of 80, 240, and 670 mJ/cm² are shown in figure 6(a), 6(b), and 6(c), respectively. The laser beam was irradiated for 15 min for film growth. The film surfaces for
80 and 240 mJ/cm² were smoother than that (figure 4(a)) for 18 mJ/cm². As much as the photon number increased, the same could decompose the LMW silicone on the substrate. Thus, the film was dense and the surface was smooth. Since more O(1D) atoms were generated by an increase of F₂ laser fluence on the substrate, the deposition rate could increase. However, when the F₂ laser fluence became close to the ablation threshold (approximately 1 J/cm²) for SiO₂ [9], the film surface became rough shown in figure 6(c), and the deposition rate decreased.

4. Conclusions

A novel method, which permits to grow SiO₂ films at room temperature without source gases, was demonstrated. In the method, it was necessary to use two laser beams. One was for generating source gases and another was for depositing the films. When the FH of Nd:YAG laser was used as the first laser beam, SiO₂ films with no carbon contaminants were grown as same as the case that F₂ laser was used. The films were consisted of granular structures and the grain size became small as the laser fluence of second laser increased. When the ArF laser beam was used as the second laser, the deposition rate of the films was very low and the films had carbon contaminants. It showed that the second laser beam illuminating the substrate played an important role not only in the growth of the films but also in the prevention of carbon contaminants.

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