Regular Paper

Thin Film Deposition of Photoluminescent Silicone Rubber by Pulsed Laser Deposition

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Received xxx xx, xxxx; accepted for publication xxx xx, xxxx

Abstract

Silicone ($[SiO(CH_3)_2]_n$) rubber surface was photochemically modified into photoluminescent property by a faint beam of 193 nm ArF excimer laser, then the modified surface of silicone rubber was ablated in a vacuum chamber by the intense ArF excimer laser to deposit thin films of the photoluminescent silicone rubber on a silica glass substrate. The chemical bonding of the deposited thin films was almost identical to the photoluminescent silicone rubber as a laser target, by the Fourier-transform infrared spectroscopy. The deposited thin films emitted white light under an illumination of 325 nm He-Cd laser as same as the case of the photoluminescent silicone rubber target. Also, the photoluminescence spectra of the deposited thin films could be controllably changed by varying the single pulse laser fluence. In addition, the thin films of the photoluminescent silicone rubber area-selectively deposited in micron size gave emission of white light under the illumination of He-Cd laser as well.

Keywords: Photoluminescence, Silicone rubber, Pulsed laser deposition, ArF excimer laser, Area-selective deposition

1. Introduction

Silicone ($[SiO(CH_3)_2]_n$) rubber is chemically stable and has superior properties such as a heat-, cold- or chemicals-resistance, in addition to the high optical transparency in UV to IR region. Thus, the silicone rubber is widely used for scientific and industrial uses; it is currently used for an optical waveguide, sealing material and lens material of UV- and white-LEDs, for instance [1]. Recently, we have reported on the photochemical modification of silicone rubber using a 193 nm ArF excimer laser; the silicone rubber modified by a faint beam of the ArF excimer laser gave emission of white light under an illumination of 325 nm He-Cd laser [2,3]. The chemical bonding of the modified silicone rubber was found to be a silica-like silicone, and the photoluminescence (PL) derived its origin from oxygen deficiency centers and peroxy-centers of silica structure in the modified silicone rubber [4-6].

In this paper, we expanded the previous our work on the photochemical modification of silicone rubber; the photoluminescent silicone rubber was ablated in a vacuum chamber by the intense ArF excimer laser, and thin films of the photoluminescent silicone rubber were deposited on a substrate. In the present work, based on the compositional fidelity of PLD, thin films of the photoluminescent silicone rubber was deposited on other material except silicone rubber. The PL emitted from the deposited thin films under the illumination of He-Cd laser was measured when the single pulse laser fluence was varied.

2. Experimental method

A laser beam generated by an ArF excimer laser (Lambda Physik, EMG202MSC) irradiated the surface of 2-mm-thick silicone rubbers (Togawa Rubber, K-125) in air without a lens. The single pulse fluence of ArF excimer laser on the silicone rubber surface was 40 mJ/cm^2. The pulse duration was approximately 23 ns, and the repetition rate was 10 Hz. The irradiation time was 20 min. For subsequent PLD, the modified silicone rubber was immersed in 1 wt.% HF water solution for 30

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min to etch the 15-μm-thick surface of the modified layer including a 0.5 mm-thick SiO_2 top layer, as show in Fig. 1, because the intense PL was actually emitted at a depth of 15 to 50 μm in the modified silicone rubber.

3. Results and Discussion

3.1 Thin film deposition

Figure 1 shows the single pulse laser fluence dependence of the thickness of the deposited films. The laser fluence on the target surface was varied from 5 to 7.5, 10 and 20 J/cm^2. The irradiation time was 20 min. The thickness of the deposited films was measured to be 0.2, 1.2, 3.8 and 3.8 μm, respectively. The deposited films was yellowish white in color and was adhered closely to silica glass substrate

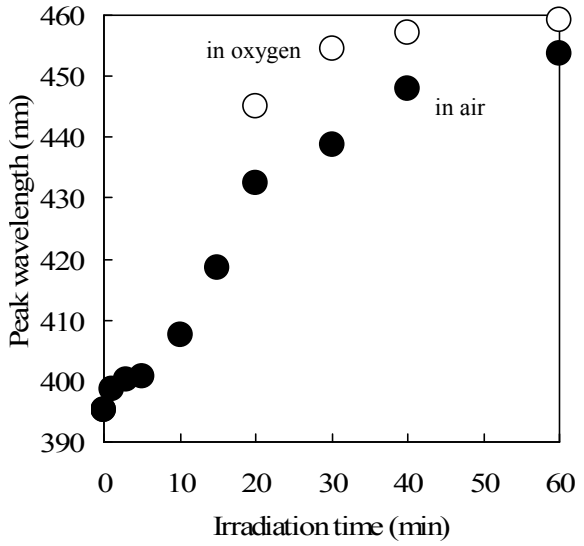

Fig. 1 Irradiation time dependence of the peak wavelength of PL spectra of the silicone rubber modified by the ArF excimer laser in oxygen gas and in air.

3.2 PL spectra

Table 1 shows the PL spectra of the deposited films at three different single pulse laser fluences. All the deposited films were kept at approximately 1 μm in thickness by adjusting the laser irradiation time and were confirmed to be photoluminescent, though the PL intensity was weak compared to the target due to the thin thickness of the deposited films. At the laser fluence of 7.5 J/cm^2, the PL spectrum was almost same to the target. With increasing the laser fluence, the PL spectrum was shifted toward red. Thus, the PL spectrum could be controllably changed by varying the single pulse laser fluence. By increasing the laser fluence, velocity of ejected species from the target becomes high; the ejected species can be easy to react with residual oxygen molecules in the chamber.

$$\oint_C H \cdot dl = I \tag{1}$$

Under the illumination of a 325 nm He-Cd laser, the change of the PL color was clearly observed. The multimode He-Cd laser irradiated the surface of the films deposited at the single pulse laser fluences of 7.5, 10 and 20 J/cm^2. The PL color could be controllably changed from bluish white to yellow by varying the single pulse laser fluence. The PL spectra of the deposited films were stable in air for a half year at least.

Table 1 Current as a function of voltage

Voltage [V]	1	2	3	4	5	6	7	8
Current [A]	2	4	6	8	10	12	14	16

4. Conclusions

The photoluminescent silicone rubber was ablated by the 193 nm ArF excimer laser to deposit the thin films of the photoluminescent silicone rubber on the silica glass substrates. The chemical bonding of the deposited thin films was almost identical to the photoluminescent silicone rubber target, under the compositional fidelity of the PLD. The deposited thin films emitted white light under the illumination of 325 nm He-Cd laser. The PL spectra of the deposited thin films could be controllably changed by varying the single pulse laser fluence. In addition, the thin films of the photoluminescent silicone rubber area-selectively deposited in micron size also gave emission under the illumination of 325 nm He-Cd laser. This result will open up the fabrication of the silicone rubber-based, light and flexible display, lighting or microchip for photonic application.

Acknowledgements

The authors are grateful to Ms. Minako Iyono, National Defense Academy, for assistance in experiments.

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