Control of Electrical Resistance of TiO_2 Films by Femtosecond Laser Irradiation†

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1. Introduction

Titanium dioxide (TiO_2) is widely used in environmental cleaning because of its photocatalytic properties when irradiated by ultraviolet light. This photocatalytic property enables decomposition of organic matter such as bacteria, mold and odors[1, 2]. A coating technology has been developed to form functional ceramics films with an aerosol beam[3-6]. In this method, when submicron-size particles are accelerated by gas flow to velocities of several hundred m/s and collide with the substrate, a film is formed on substrate.

Recently, studies of surface modification for TiO_2 have been performed to expand its applications. It was reported that TiO_2 was darkened after nanosecond laser irradiation with wavelengths of 248 nm and 355 nm[7] and the bandgap energy of TiO_2 was decreased by plasma treatment[8]. It was believed that these phenomena were based on the oxygen deficiencies formed in the TiO_2 lattice[7, 8]. The surface modification with a laser can be used for precision materials processing and fine patterning since the laser can be focused in small area on the material. The conventional method using continuous-wave (CW) lasers, long pulsed lasers and nanosecond lasers gives a heat-affected zone and morphological change in the material workpiece around the laser irradiation spot[9, 10]. This limits the precision material processing capability for the surface modification. The femtosecond laser has an advantage for precision materials processing in comparison with nanosecond lasers[9, 10]. For femtosecond laser irradiation, a heat-affected zone and morphological change around a laser spot are suppressed since the advantages are based on very rapid creation of vapour and plasma phase, negligible heat conduction, and the absence of liquid phase.

In this study, we investigated the surface modification of TiO_2 films by the femtosecond laser irradiation. The films were formed with an aerosol beam. The experiments were performed to investigate the laser fluence dependence on the electrical resistance and surface morphology of the films. The objective of this study is to decrease the electrical resistance of the films in the irradiated area by femtosecond laser irradiation without the surface morphological changes.

2. Experimental

The system for film fabrication was primarily composed of an aerosol chamber and a processing chamber connected by a tube. The TiO_2 particle size was about 200 nm. An aerosol was produced by mixing the TiO_2 particles with He gas using a vibration system. The processing chamber was pumped down with a mechanical booster pump and rotary pump to produce a pressure difference between the two chambers. He gas flowed from the aerosol chamber to the processing chamber. The TiO_2 particles were accelerated by the flow of He gas and carried to the processing chamber through the tube and nozzle. The TiO_2 particles ejected from the nozzle impacted with the substrate and were deposited on the substrate's surface. The substrates were glass plates. The glass plate's position was controlled with XY stages connected to a computer. An area of 8×10 mm^2 on the surface of the glass was scanned by the aerosol beam. The films with thicknesses of 5 μm were used in this experiment.

A commercial femtosecond Ti : sapphire laser system was employed in our experiments, which was based on the chirped pulse amplification technique. Wavelength, pulse length, repetition rate and beam diameter of the laser were 800 nm, 100 fsec, 1 kHz and approximately 4 mm, respectively. An attenuator to reduce the output energy of the laser was composed of polarizing filters. The laser beam was focused on the film surface by a lens with a focal length of 100 mm. The

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films were scanned by a laser beam to a velocity of 17 μm/s with XY stages connected to a computer. The Gaussian laser beam took the shape of a circle with diameter of 100 μm at $1/e^2$ intensity. The average laser fluence was varied in the range of 63 to 446 mJ/cm^2 with the attenuator.

Surface morphology of the films after the laser irradiation was observed with an optical microscope and a scanning electron microscope (SEM). The electrical resistances were measured by a two-terminal method using two probes, a constant-voltage source and an ammeter. Steel probes with tip size of about 30 μm in diameter were used in this measurement. Two probes were both located on the laser scanning line (area). The distance between the probes was 1 mm and a voltage of 10 V was applied between the two probes with a constant-voltage source. The electrical resistances were evaluated by measuring the electrical currents between the two probes.

3. Results and Discussion

Optical images of the film surface irradiated at the laser fluence of 63, 95, 127, 191, 318 and 446 mJ/cm^2 are shown in Figs. 1 (a), 1 (d), 1 (g), 1 (j), 1 (m) and 1 (p), respectively. Surface color in laser scanned area varied through to black (dark color) after the laser irradiation. Widths of the dark color area were increased as the laser fluence increased. The dark color area's widths were 40, 50, 85, 90 100 and 100 μm at the laser fluence of 63, 95, 127, 191, 318 and 446 mJ/cm^2, respectively. As Figs. 1(p) shows, the film was removed in the scanned area by the laser ablation at the laser fluence of 446 mJ/cm^2. It is generally believed that the laser-affected oxygen deficiencies in TiO_2 (formation of TiO or Ti) may be the reason for the darkening[7].

SEM images of the film surfaces irradiated at the laser fluence of 63, 95, 127, 191, 318 and 446 mJ/cm^2 are shown in Figs. 1 (b), 1 (e), 1 (h), 1 (k), 1 (n) and 1 (q), respectively. High magnification images of Figs. 1 (b), 1 (e), 1 (h), 1 (k), 1 (n) and 1 (q), the center region of the irradiation area, are shown in Figs. 1 (c), 1 (f), 1 (i), 1 (l), 1 (o) and 1 (r), respectively. As Figs. 1 (b), 1 (c), 1(e), 1 (f), 1 (h) and 1 (i) shows, no surface damage was observed in the irradiation area for 63, 95 and 127 mJ/cm^2. As Figs. 1 (l) suggests, the laser fluence of 191 mJ/cm^2 is near to the damage threshold for the films since a small crack was generated in the irradiation area for this laser fluence. As Figs. 1 (n), 1 (o), 1 (q) and 1 (r) shows, the film was damaged in the irradiation area at 318 and 446 mJ/cm^2.

Figure 2 shows the electrical resistance of the films in the laser irradiation area as a function of the laser fluence. For the raw TiO_2 films, electrical current was too small to evaluate the electrical resistance in the laser irradiation area. For 63 mJ/cm^2, electrical resistance also could not be evaluated since electrical current was small. For 95, 127, 191 and 318 mJ/cm^2, the electrical resistances of the films in the laser irradiation area were 1.0×10^7, 7.1×10^5, 7.0×10^4 and 9.6×10^4 Ω/mm, respectively. For 446 mJ/cm^2, the electrical resistance of the films in the irradiation area could not be measured since the film in the irradiation area was removed by the laser ablation. For 95, 127 and 191 mJ/cm^2, the electrical resistances of the films in the irradiation area were decreased as the laser fluence increased.

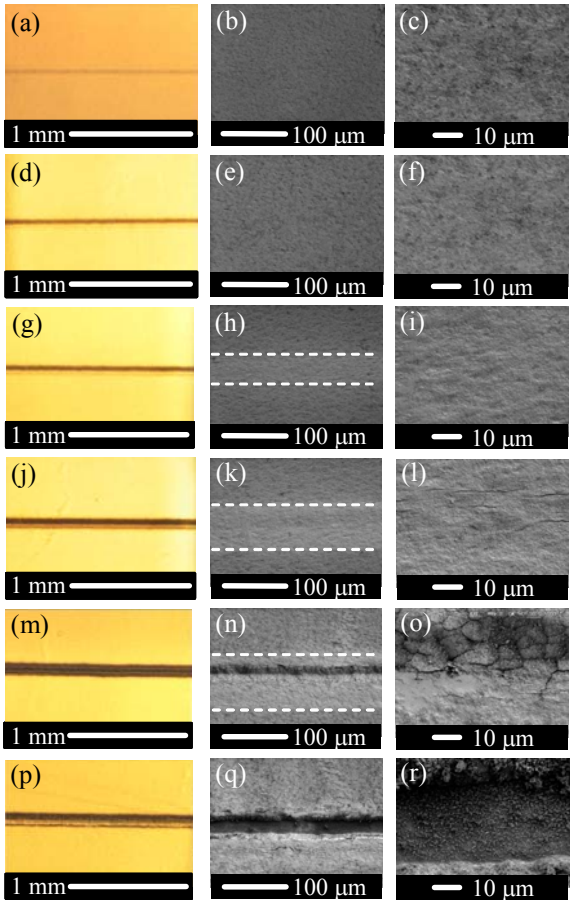

Fig. 1 Optical images of the film surface irradiated at the laser fluence of (a) 63, (d) 95, (g) 127, (j) 191, (m) 318 and (p) 446 mJ/cm^2. SEM images of the film surface irradiated at the laser fluence of (b) 63, (e) 95, (h) 127, (k) 191, (n) 318 and (q) 446 mJ/cm^2. High magnification images of (b), (e), (h), (k), (n) and (q) are shown in (c), (f), (i), (l), (o) and (r), respectively.

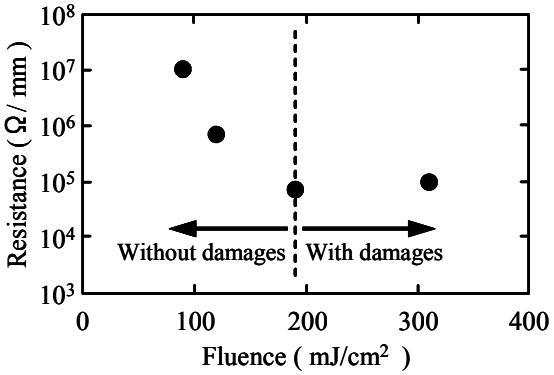

Fig. 2 Electrical resistance of the films in the irradiation area as a function of the laser fluence.

3. Summary

We investigated the laser fluence dependence on the electrical resistance and surface morphology of the films. Electrical resistance of the films at 191 mJ/cm^2 was minimum in the range between 95 and 318 mJ/cm^2 and no damage of the films was caused.

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