Aerosol Beam and CW Fiber Laser Irradiation for Creation of TiO_2 Film with Lower Electric Resistance†

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Abstract

The heating process is a useful method to change TiO_2 film property. When using a continuous wave (CW) fiber laser, local heating can be performed. In our experiments, the film was formed by aerosol beam irradiation. The films were irradiated with a CW fiber laser in vacuum and in air. The film was darkened after the CW fiber laser irradiation in vacuum. The electric resistance of the darkened area on the films was decreased as the energy per unit area was increased. However, the film was not changed after the CW fiber laser irradiation in air. In our previous study, the films were darkened by femtosecond laser irradiation in air. Then, electrical resistance of the darkened area on the films also decreased. Electric resistance of the darkened area after CW fiber laser irradiation in vacuum was much smaller than that after femtosecond laser irradiation.

KEY WORDS: (CW fiber Laser), (Aerosol beam), (Functional ceramics), (Titanium dioxide), (Electric resistance)

1. Introduction

Titanium dioxide (TiO_2) has photoconductivity and photocatalytic properties. To change the property of TiO_2 film, formation of donor level might be one of the useful methods [1-2]. When the band gap between conduction band and valance band is narrowed by formation of donor levels, electric resistance of TiO_2 film can be decreased. If the electric resistance of a local area in the TiO_2 film is decreased, local electric circuit can be written on the local area of the film. A coating method by aerosol bean irradiation has been developed to form functional ceramics film [3-4]. This coating method is performed at low temperature. So, TiO_2 films can be formed on the local area of plastic plate or glass plate at room temperature.

In our previous study, TiO_2 film coated with an aerosol beam was irradiated with a femtosecond laser [5]. After femtosecond laser irradiation, the laser irradiated area in the film was darkened without variation of topography of the film [5]. It is known that the oxygen deficiencies in TiO_2 (formation of TiO or Ti) might be the cause for the darkening [1, 6-7]. Thus, donor levels could be formed in the laser irradiated area. Electric resistance of the laser irradiated area was measured by our two-terminal method. It was decreased to 1×10^5 Ω/mm as laser intensity was increased without variation of topography of the film. But, reduction of electric resistance was saturated when topography of the film was changed. It might be caused by laser ablation. It is considered that further reduction of electric resistance is very important to form local electric circuits in the film.
Oxygen deficiencies of single crystal TiO_2 were also generated by heating in the electric furnace under vacuum or reduction atmospheres [6-7]. Electric resistance of the single crystal TiO_2 after heating in the electric furnace was not measured in Ref. [6, 7]. But, electric resistance might be reduced because donor levels are formed in the TiO_2. Then, oxygen deficiencies could not be generated in the local area of TiO_2 film by heating with the electric furnace because whole area of TiO_2 film was heated. Local heating can be performed by CW fiber laser irradiation. In our post experiment, we found that temperature of the laser irradiated area on the TiO_2 film was increased by CW fiber laser irradiation. Thus, oxygen deficiencies might be formed in the local area on the TiO_2 film by CW fiber laser irradiation under the vacuum. Laser fluence after CW fiber laser irradiation is much higher than that after femtosecond laser irradiation. Therefore, the number of oxygen deficiencies after CW laser irradiation might be much larger than that after

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femtosecond laser irradiation. So, electric resistance after CW fiber laser irradiation could be much lower than that after femtosecond laser irradiation.

In this study, we tried to decrease the electric resistance of the local area in the TiO_2 film by local heating with a CW fiber laser. Atmosphere is important for creation of oxygen deficiency by heating process with the CW fiber laser [6-7]. In the experiment, TiO_2 film was formed on the stainless steel plate by aerosol beam irradiation. The film was irradiated with a CW fiber laser in vacuum and air. The laser irradiated area was observed with optical microscope and scanning electron microscope (SEM). Electric resistance of the laser irradiated area was measured by the two-terminal method.

2. Experimental

The film coating system using an aerosol beam primarily consisting of an aerosol chamber and a processing chamber connected by a tube. Anatase TiO_2 particles with a size of about 200 nm are in the aerosol chamber. An aerosol beam is produced by mixing the TiO_2 particles and Helium (He) gas. The TiO_2 particles are accelerated by the flow of He gas and carried to the processing chamber through the tube and nozzle. After TiO_2 particles impact with the substrate, TiO_2 films are deposited on the substrate. Stainless steel plate (SUS-304) was used for substrate in this experiment. Film deposition area was 10×10 mm^2.

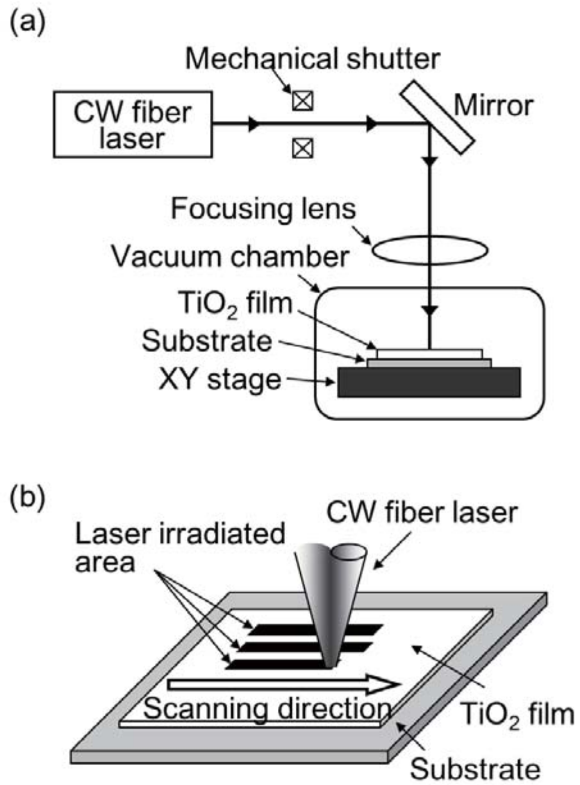

Fig. 1 (a) Schematic diagram of experimental setup for CW fiber laser irradiation. (b) Scanning direction of the laser focusing spot.

Schematic diagrams of CW fiber laser irradiation are shown in **Figs. 1 (a)** and **(b)**, respectively. A single mode Yb fiber laser was used in this experiment. The wavelength and maximum power of CW fiber laser was 1076 nm and 100 W, respectively. The laser beam was focused on the TiO_2 surface throughout the vacuum chamber by using a lens with 250 mm focal length. The Gaussian laser beam had a diameter of 280 μm (at the $1/e^2$ intensity points) on the film. The laser beam was scanned on the TiO_2 film surface by using the XY stage in the vacuum (2.1×10^{-2} Pa) or air (1.0×10^5 Pa) as shown in **Fig. 1 (b)**. Scanning speed and distance of scanning area was 1 mm/s and 1.5 mm, respectively. The power of the CW fiber laser on the TiO_2 film was changed from 1.62 W to 8.10 W. Then, laser fluence was changed from 5.79×10^2 to 2.60×10^3 J/cm^2. Laser fluence is calculated as follows:

$$L_f = E / S \quad (1)$$

Here, L_f (J/cm^2) is laser fluence. E (J) is Energy per beam spot. S (cm^2) is unit area after CW laser irradiation, as shown in **Fig. 2**. E and S are calculated as follows:

$$E = p\times t \quad (2)$$

$$S = 100a\times 100b \quad (3)$$

Here, p (W), t (s), a (m) *and* b (m) are power of CW fiber laser on the TiO_2 film, time throughout unit area, beam diameter, distance per unit area, respectively. t is calculated as $t = b$ (m) / v (m/s). Then, v is the scanning speed. From equals (1) – (3), laser fluence L_f (J/cm^2) is calculated as follows:

$$L_f = p / 10000av \quad (4)$$

After the CW fiber laser irradiation, the film surface was observed with an optical microscope and

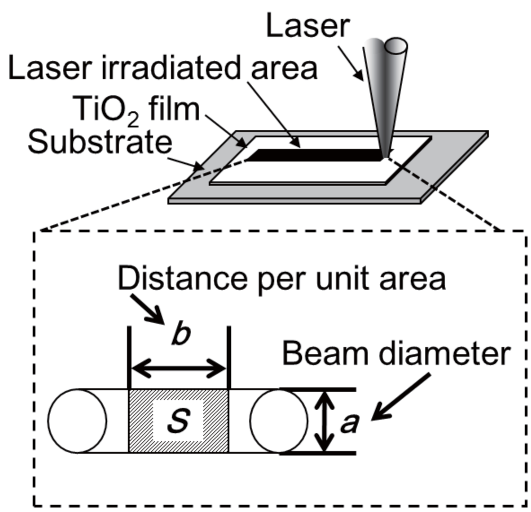

Fig. 2 Schematic diagram of laser irradiated area.

SEM. The electrical resistances of laser irradiated area were measured by a two-terminal method using two probes, a constant voltage source, and an ammeter. Two steel probes with a tip diameter of about 30 μm were used. The two probes were both located along a laser scanned line. A voltage of 10 V was applied between the two tips. The distance between the probes was 1 mm. The electrical resistances were determined by measuring the electrical current between the two probes. The bare TiO_2 films without laser irradiation had an electrical resistance too large to measure by our two-terminal method.

3. Results and Discussion

Optical images after CW fiber laser irradiation in the vacuum and air are shown in **Figs. 3 (a)** and **(b)**, respectively. (a-1), (a-2), (a-3), (a-4), (a-5), (a-6), (a-7), (a-8) and (a-9) in **Fig. 3 (a)** indicate that the laser irradiated area in the vacuum at laser fluence of 5.79×10^2, 8.68×10^2, 1.16×10^3, 1.45×10^3, 1.74×10^3, 2.03×10^3, 2.31×10^3, 2.60×10^3 and 2.89×10^3 J/cm^2, respectively. (b-1), (b-2), (b-3), (b-4), (b-5), (b-6), (b-7), (b-8) and (b-9) in **Fig. 3 (b)** indicate that the laser irradiated area in the air at same laser fluence in the vacuum. As **Fig. 3 (a)** shows, laser irradiated area was darkened at laser fluence over 1.16×10^3 J/cm^2. SEM images of laser irradiated area in the vacuum over 2.03×10^3 J/cm^2 show that the topography of the darkened area was changed. These results suggested that TiO_2 film or stainless steel plate might be damaged by thermal effect over 2.03×10^3 J/cm^2.

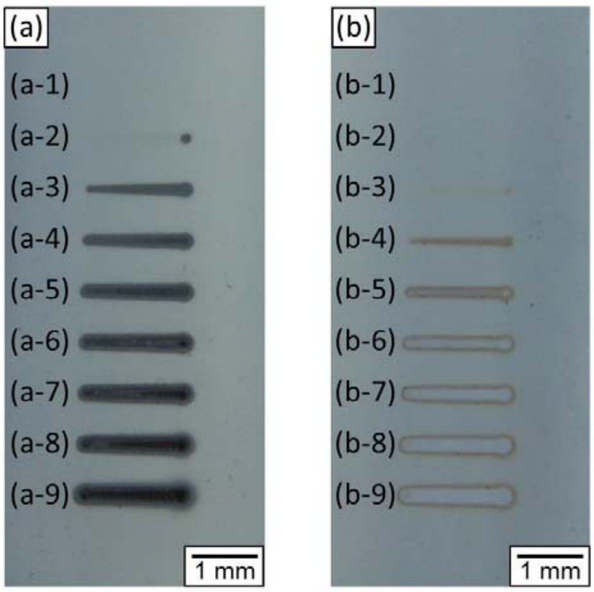

Fig. 3 Optical images of TiO_2 film after CW fiber laser irradiation in the vacuum (a) and air (b) : laser fluence was changed at 5.79×10^2 J/cm^2 (a-1) and (b-1), 8.68×10^2 J/cm^2 (a-2) and (b-2), 1.16×10^3 J/cm^2 (a-3) and (b-3), 1.45×10^3 J/cm^2 (a-4) and (b-4), 1.74×10^3 J/cm^2 (a-5) and (b-5), 2.03×10^3 J/cm^2 (a-6) and (b-6), 2.31×10^3 J/cm^2 (a-7) and (b-7), 2.60×10^3 J/cm^2, (a-8) and (b-8), and 2.89×10^3 J/cm^2 (a-9) and (b-9).

In the air, laser irradiated areas were not darkened at any laser fluence like laser irradiated area in the vacuum as shown in **Fig. 3 (b)**. But, the color of the laser irradiated areas was changed over 1.74×10^3 J/cm^2. SEM images of laser irradiated area in the air show the topography of laser irradiated areas were not changed at any laser fluence. These results suggested that temperature in the laser irradiated area during CW fiber laser irradiation in the air might be lower than that in the vacuum. Then, reduction of the electric resistance of the laser irradiated area in the air was not detected because electrical resistance too large to measure by our two-terminal method. These results suggested that oxygen deficiencies in the TiO_2 film might not be caused in the air.

Diamonds and circles in **Fig. 4** show the electrical resistances of the laser irradiated areas after CW fiber laser in the vacuum and femtosecond laser in the air at various laser fluence, respectively. Wavelength, repetition rate and pulse width of femtosecond laser were 775 nm, 1 kHz and 150 fs, respectively. The Gaussian femtosecond laser beam had a diameter of 250 μm (at the $1/e^2$ intensity points) on the film. Scanning speed and distance of scanning area were 1 mm/s and 1.5 mm, respectively. Laser fluence of femtosecond laser was changed from 6.54×10^0 J/cm^2 to 3.49×10^1 J/cm^2. As shown with circles in **Fig. 4**, the electrical resistances of the femtosecond laser irradiated area in the air decreased from 5.0×10^8 Ω/mm to 2.1×10^5 Ω/mm as the laser fluence was increased from 1.31×10^1 J/cm^2 to 2.62×10^1. This result was almost the same as that obtained in Ref. [5]. As shown with diamonds in **Fig. 4**, the electrical resistances of the CW fiber laser irradiated area in the vacuum decreased from 2.5×10^3 Ω/mm to 5.0×10^2 Ω/mm as the laser fluence was increased from 1.16×10^3 J/cm^2 to 2.03×10^3 J/cm^2. These results showed the electric resistance of laser irradiated area after CW fiber laser irradiation is much lower than that after

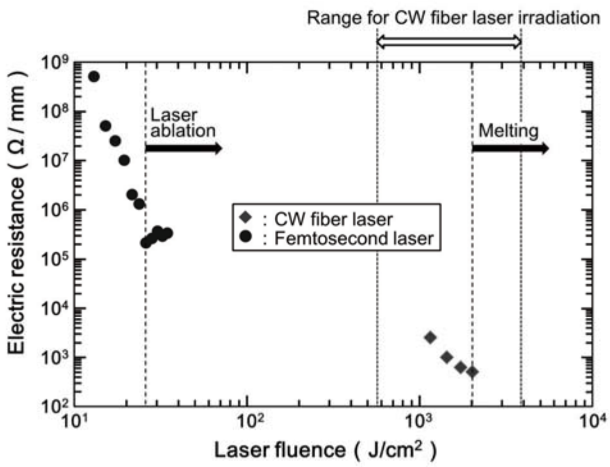

Fig. 4 Electric resistances of the TiO_2 film after CW fiber laser irradiation in the vacuum and femtosecond laser irradiation in the air as a function of laser fluence.

femtosecond laser irradiation. Electric resistance of laser irradiated area after CW fiber laser irradiation under the 8.68×10^2 J/cm^2 was not detected by our two-terminal method because electric resistance was too high. It was drastically changed in the range of 8.68×10^2 J/cm^2 to 1.16×10^3 J/cm^2. This result suggested that temperature in the laser irradiated area during the CW fiber laser irradiation under the 8.68×10^2 J/cm^2 might not allow for generation of oxygen deficiencies. And temperature in the laser irradiated area during the CW fiber laser irradiation might be drastically changed in the range of 8.68×10^2 J/cm^2 to 1.16×10^3 J/cm^2. Over 2.31×10^3 J/cm^2, electric resistance of the topography changed area was also not detected by our two-terminal method because two probes were shorted. This result suggested that stainless plate might be melted and deposited on the TiO_2 film over 2.31×10^3 J/cm^2. In our future plan, we will measure temperature in the laser irradiated area during the CW fiber irradiation at any laser fluence.

4. Summary

We try to decrease the electric resistance of local areas in the TiO_2 film by CW fiber laser irradiation to achieve control of the electric resistance. Electric resistance of the laser irradiated area after CW fiber laser irradiation in the vacuum decreased as laser fluence was increased. It was much lower than after femtosecond laser irradiation in the air.

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