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Variation of Photoconductive Properties of Titanium Dioxide Film by Femtosecond Laser Irradiation[†]

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Abstract

Titanium dioxide (TiO₂) films were irradiated with a femtosecond laser to alter their photoconductive properties. The TiO₂ films irradiated with the femtosecond laser were darkened without changing the topography of the TiO₂ film surface. The electrical resistance of the films as a function of time were measured under visible light illumination. The transient electrical resistance decreased as time was increased after turning on the light, and then it increased as time was increased after turning off the light.

KEY WORDS: (Femtosecond Laser), (Aerosol beam), (Functional ceramics), (Titanium dioxide), (Photoconductive Property)

1. Introduction

Titanium dioxide (TiO₂) has been considered to be a photoconductive material, and is one of the n-type semiconductors¹⁾. TiO₂ thin films have attracted considerable attention because of their applications in photocatalysts, optical films, photosensors and solar cells²⁾. However, the use of TiO₂ films is restricted because their wide band gap (3.2 eV for anatase, corresponding to a photon with the wavelength of 388 nm) does not permit a response to visible light³⁾.

In our previous study, TiO₂ films were irradiated with a femtosecond laser⁴⁾. The TiO₂ film was darkened after the laser irradiation. The electrical resistance of TiO₂ films were decreased by the laser irradiation although laser ablation did not occur. In addition, an acetaldehyde test was carried out with the darkened TiO₂ films, which was one of the photocatalytic function tests⁵⁾. The acetaldehyde concentration decreased under visible light illumination. The result of the acetaldehyde test indicated that the darkened TiO₂ film had a photocatalytic function under visible light illumination. The results suggested that oxygen deficiencies in the TiO₂ lattice were the cause to promote the visible light activity. The darkened TiO₂ film might be changing photoconductive properties. However, the photoconductive property of TiO₂ films darkened by the femtosecond laser irradiation was not investigated. It is a promising method for application in a photoelectric device such as a photosensor if the photoconductive

property of the TiO₂ film is controlled by the laser irradiation.

In this study, we investigated variation of the photoconductive property of the darkened TiO₂ films. In the experiments, the laser fluence was changed within the region in which the topography of the TiO₂ film surface was not varied. The electrical resistances of the films were measured with and without visible light illumination. The transient electrical resistances of the films were measured as a function of time under visible light illumination.

2. Experimental

The TiO₂ films were fabricated with a coating system using an aerosol beam⁶⁻⁹⁾. The system primarily consists of an aerosol chamber and a processing chamber connected by a tube. Anatase TiO₂ particles with a size of about 200 nm were placed in the aerosol chamber. An aerosol was produced by mixing the TiO₂ particles with He gas using a vibration system. The processing chamber was pumped out using a mechanical booster pump and a rotary pump to produce a pressure difference between the two chambers. He gas flowed from the aerosol chamber to the processing chamber. The TiO₂ particles were accelerated by the flow of He and carried to the processing chamber through the tube and nozzle. The size of the nozzle orifice was 0.3 mm × 10 mm. The TiO₂ particles ejected from the nozzle impact with the substrate and are deposited on its surface. The substrate

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was a glass plate. The plate's position was controlled using XY stages connected to a computer. An area of 10 mm × 10 mm on the surface of the glass was scanned across the aerosol beam. Films of 5-μm thickness were deposited. The crystal structure of the film was observed by X-ray diffraction (XRD). The XRD patterns from the film indicate that crystallinity of the TiO₂ particles was retained throughout the coating process. Prior to laser irradiation, the surface and cross section of the films were observed using a scanning electron microscope (SEM). Individual TiO₂ particle shapes were not observed, indicating that a dense film was formed on the glass plate.

A schematic diagram of the experimental setup for femtosecond laser irradiation is shown in **Fig. 1(a)**. A commercial femtosecond Ti:sapphire laser system was employed based on chirped-pulse amplification. The wavelength, pulse width, repetition rate, and beam diameter of the laser were 775 nm, 150 fs, 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 onto the film surface by a lens with a 100 mm focal length. The Gaussian laser beam had a diameter of 250 μm (at the 1/e² intensity) on the film. In the experiment, in which darkened lines were formed, the films were scanned using the XY stages, as shown in **Fig. 1(b)**. The laser fluence was varied in the range of 20 to 140 mJ/cm². The surface topography of the films after irradiation was observed with an optical microscope and the SEM.

For the electrical resistance measurements, coplanar gold electrodes were sputter-coated. The electrodes distance between them was 1 mm. A constant bias voltage of 10 V was applied to the samples. In order to measure the photoconductive property, the samples were illuminated with visible light. A SCHOTT 100 W

Halogen lamp was used as a visible light source. A Kenko L41 UV filter was installed in front of the lamp to cut off ultraviolet light with a wavelength below 410 nm. The transient electrical resistance was recorded using a Keyence NR-1000 data acquisition system.

3. Results and Discussion

Observation of the irradiated film surface using the optical microscope and the SEM indicates that the color of the film surface became black at laser fluences exceeding 20 mJ/cm². Furthermore, the topography of the film surface was altered for laser fluences above 100 mJ/cm².

Optical images of the laser scanned area on the film surface irradiated at laser fluences of 20, 40, 60, 80, 100, 120 and 140 mJ/cm² are shown in **Fig. 2(a), (c), (e), (g), (i), (k), (m)**, respectively. As the laser fluence increased, the colors of the irradiated areas were gradually changed from white to black.

SEM images of the central region of the irradiated areas are shown in **Fig. 2(b), (d), (f), (h), (j), (l), (n)**, respectively. No topographical changes were observed at

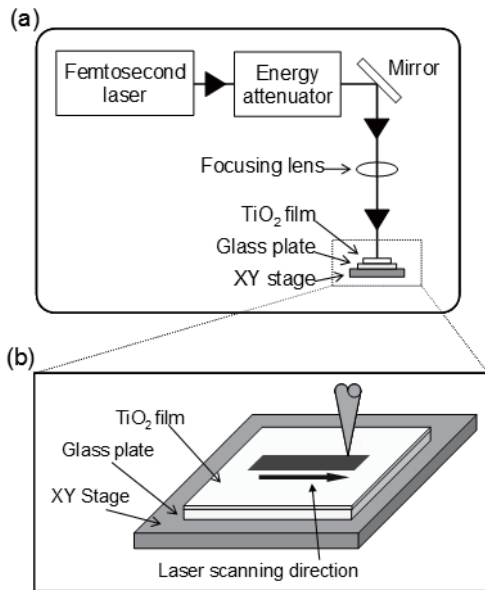


Fig. 1 Experimental setup for femtosecond laser irradiation.

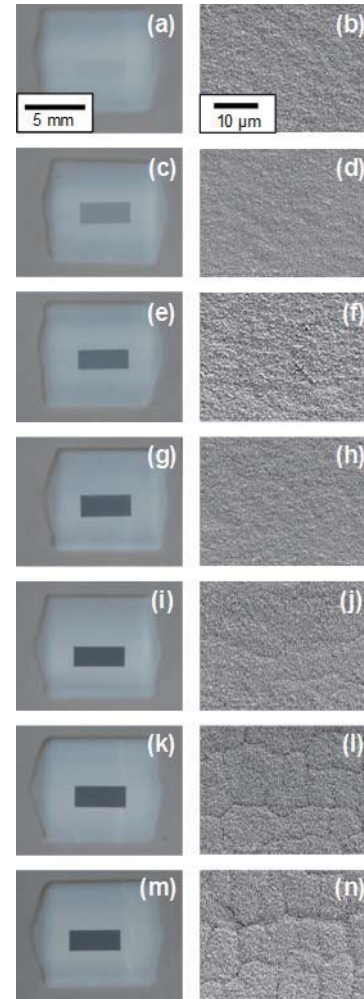


Fig. 2 Optical and SEM images of the film surface irradiated at laser fluences of a-b 20, c-d 40, e-f 60, g-h 80, i-j 100, k-l 120 and m-n 140 mJ/cm².

the four lowest fluences. But as **Fig. 2(j)** suggests, a laser fluence of 100 mJ/cm^2 is near the threshold of producing topographical changes since a small crack was generated in the irradiated area in this case.

Figure 3 shows the electrical resistances of the films in the irradiated areas for various laser fluences. Raw TiO_2 films had an electrical resistance too large to measure, as did the films after irradiation at merely 20 mJ/cm^2 . The raw TiO_2 is TiO_2 without the femtosecond laser irradiation. At 40, 60, 80, 100, 120 and 140 mJ/cm^2 , the electrical resistances of the films in the irradiated area were 4.0×10^7 , 1.5×10^5 , 1.8×10^4 , 1.2×10^4 , 1.1×10^5 and $9.0 \times 10^4 \Omega$, respectively. As the laser fluence increased, the electrical resistance was decreased up to 100 mJ/cm^2 . However, the electrical resistances at 120 and 140 mJ/cm^2 tended to become higher values. It was reported that laser-induced oxygen deficiencies in the TiO_2 lattice may be the reason for the darkening and changing the electrical resistance⁴⁾.

The transient electrical resistance of the films irradiated at a laser fluence of 80 mJ/cm^2 as a function of time was shown in **Fig. 4**. The electrical resistance of the film decreased from the time of turning on the light. The electrical resistance was decreased from 17670Ω to 17005Ω in the region between 100 s and 110 s. The electrical resistance was decreased from 16660Ω to 16617Ω in the region between 150 s and 160 s. These results indicate that there were two mechanisms of the reduction due to visible light illumination. The electrical resistance of the films irradiated at various laser fluences ($40 \text{ mJ/cm}^2 - 140 \text{ mJ/cm}^2$) decreased during visible light illumination. These results also suggest that there were two mechanisms of reduction due to visible light illumination.

As described above, the electrical resistance of the raw TiO_2 films was not changed by visible light illumination. When the electrical resistance is decreased, the conduction current is increased. Excited electrons in the conduction band contribute to the increase of a conduction current. Electrons in the valence band of the raw TiO_2 films are not excited to the conduction band by

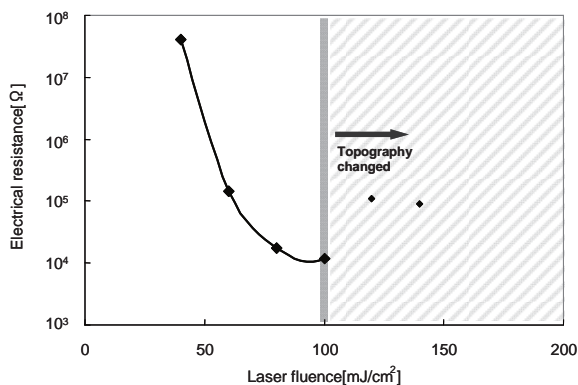


Fig. 3 Electrical resistance of the films irradiated with the femtosecond laser as a function of the laser fluence.

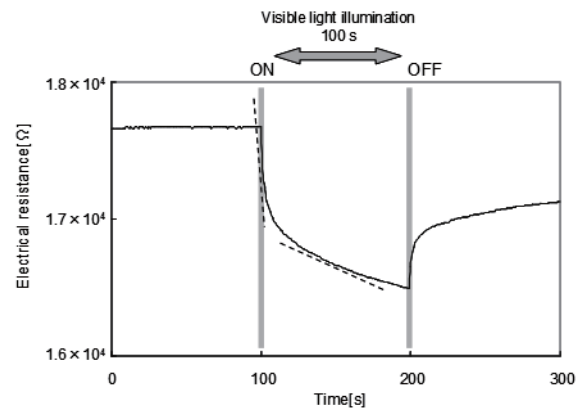


Fig. 4 Transient electrical resistance of the film irradiated with the femtosecond laser as a function of time under visible light illumination.

visible light illumination. However, the electrical resistance of the TiO_2 films irradiated with the femtosecond laser decreased during visible light illumination as shown in **Fig. 4**. These results suggested that any energy levels between the valence and conduction bands for raising the excited electrons to the conduction band were formed after the femtosecond laser irradiation.

4. Summary

We investigated the variation of the photoconductive property of TiO_2 films after femtosecond laser irradiation. The TiO_2 films irradiated with femtosecond laser were darkened without changing topography of the TiO_2 film surface. During visible light illumination, the electrical resistance of the darkened TiO_2 film was decreased.

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