Rewriting Process of Lower Electrical Resistance Lines on TiO_2 Film using Methods of Whitening with Electric Furnace and Darkening with Femtosecond Laser

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Rewriting process of lower electrical resistance lines on a titanium dioxide (TiO_2) film was developed. In this process, lower electrical resistance lines were written on a TiO_2 film without producing their surface topography changes by femtosecond laser irradiation. By heating with an electrical furnace under air, the electrical resistance of these lines was come back to the higher resistance with no topography changes. This result indicated that the lines could be erased by the heating method under air. When the erasing-treated area was irradiated with a femtosecond laser, the lower electrical resistance lines could be rewritten with no topography changes of the film surface.

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1. Introduction

Femtosecond laser is an attractive tool for creation of materials' new functions, such as three dimensional optical memories**[1-3]**, photonic crystals**[4]**, waveguide formation**[5,6]**, refractive-index modification**[7-11]**, periodic nanostructures formation **[12-15]** and lower electric resistance lines formation **[16]**. Electric resistance of the lines could be varied by controlling the laser fluence. By the laser focusing spot scanning on the TiO_2 film, patterning of the line was performed. Thus, electric circuit can be written on the film with the laser.

TiO_2 is widely used in environmental cleaning because of its photocatalytic properties. This photocatalytic property enables decomposition of organic matter such as bacteria, mold, and odors **[17, 18]**. In our prevsious study, darkening of TiO_2 film surfaces and reduction of their electrical resistance were induced by femtosecond laser irradiation **[16]**. Darkening could be generated without changing the topography of the film's surface. Thus, writing process of lower electrical resistance lines on the film could be performed using a method of darkening with a femtosecond laser. It is generally believed that laser-induced oxygen deficiencies in TiO_2, resulting in formation of TiO or Ti, may be the reason for the darkening **[16]**. Heating at the temperature under melting point is a useful method to repair the oxygen deficiencies. After heating process, the darkened area on the film can be whitened with increasing of its electrical resistance. The whitening of the darkened area indicates that erasing process of the lower electrical resistance lines or area on the film can be carried out by heating with an electric furnace. After the erasing process, the whitened lines or area on the film can be darkened again by femtosecond laser irradiation. Thus, rewriting process of lower electrical resistance lines or area on the film can be promoted using method of darkening with femtosecond laser.

In this study, we developed the rewriting processes of lower electrical resistance lines on the TiO_2 films. The films were formed by the method with an aerosol beam **[19, 20].** An aerosol beam used in the experiment was composed of TiO_2 particles and helium (He) gas. The darkened area was created on the films with a femtosecond laser. After writing process by the darkening, the film was heated with an electric furnace under air and vacuum to whiten the darkened area, which was an erasing process of lower electrical resistance area without changing of the film surface topography. Then, the film surfaces and its electric resistance were observed and measured. After the erasing process, the whitened area was irradiated with a femtosecond laser again to rewrite the darkened and lower electrical resistance lines on the films without producing surface topography changes.

2. Experimental procedure

Schematic diagrams of the experimental setup for femtosecond laser irradiation on the TiO_2 film surface and heating the TiO_2 film under air and vacuum are shown in

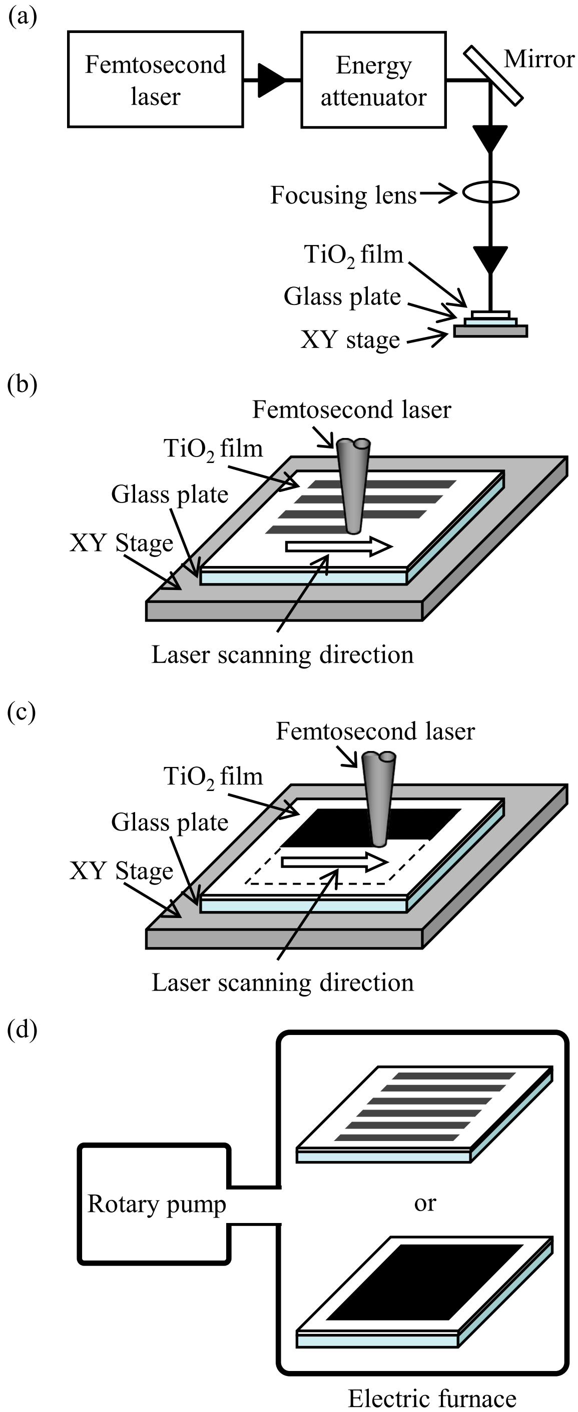

Fig.1 (a) Schematic diagram of experimental setup for writing and rewriting of lower electrical resistance lines and area on TiO_2 film with a femtosecond laser. Scanning direction of the laser focusing spot for writing and rewriting of the lines (b) and area (c). (d) Schematic diagram of an electrical furnace for heating the TiO_2 film under air and vacuum.

Figs. 1(a), (b), (c) and (d), respectively. The wavelength, pulse duration, repetition rate and beam diameter of the femtosecond 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 films were formed in area of 10 × 20 mm^2 on the surface of the glass plate with an aerosol beam **[19, 20]**. An aerosol beam consists of the anatase type TiO_2 particles

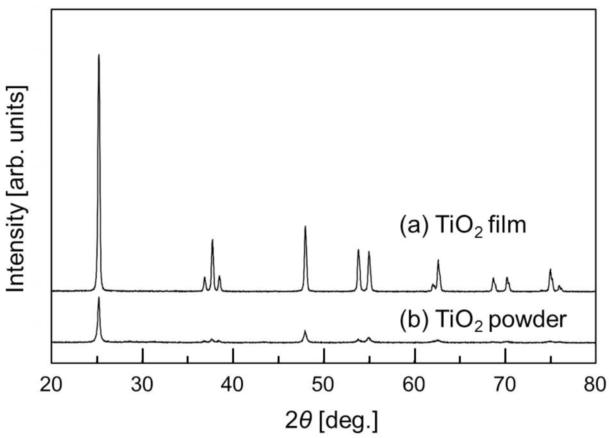

Fig.2 XRD patterns of (a) TiO_2 film and (b) TiO_2 powder.

with a size of about 200 nm and He gas. The thickness of the film was about 5 μm. XRD patterns of (a) TiO_2 film and (b) TiO_2 powder are shown in Fig. 2. As indicated in Fig. 2, anatase type crystalline structures were retained throughout the film formation. In the experiments for production of darkened area, the laser beam was focused onto the film surface by a lens with a 100-mm focal length and the film's position was controlled using XY stages connected to a computer. To produce the darkened lines on the film, X stage was moved at the scanning velocity of 1 mm/s during the laser irradiation as shown in Fig. 1 (b). The Gaussian laser beam had a diameter of 250μm (at the $1/e^2$ intensity points) on the film. The laser fluence was varied in the range of 20 to 220 mJ/cm^2 with the period of 10 mJ/cm^2. The electrical resistances were measured by a two-terminal method using two probes (two-probe method), a constant-voltage source, and an ammeter. Steel probes with a tip diameter of about 30μm were used. The two probes were both located along a laser-scanned line. The distance between the probes was 1 mm and a voltage of 10 V was applied between the two tips. The electrical resistances were determined by measuring the electrical current between the two probes. The raw TiO_2 films (not irradiated with the femtosecond laser) had an electrical resistance too large to measure by our two-probe method. To produce darkened area in 8 × 15 mm^2 on the film, X stage was moved at the scanning velocity of 2 mm/s during the laser irradiation as shown in Fig. 1 (c). Then, the Gaussian laser beam had a diameter of 300 μm (at the $1/e^2$ intensity points) on the film. The laser fluence was 100 mJ/cm^2. The films after the femtosecond laser irradiation shown in Figs 1(b) and (c) were heated in the electric furnace, as shown in Fig. 1(d), to whiten the darkened area. The heating was performed under vacuum or air at the temperature of 573, 673 and 773 K, respectively. The area whitened by the heating was irradiated with the femtosecond laser at the laser fluence of 20 ～ 260 mJ/cm^2 with the period of 20 mJ/cm^2, and 290mJ/cm^2 and 310 mJ/cm^2 to write the lower electrical resistance lines as shown in Fig. 1 (b). The surface morphology of the films after the femtosecond laser irradiation and the heating was observed with an optical microscope, a scanning electron microscope (SEM) and atomic force microscope (AFM). Roughness of the film surface was measured with surface profiler.

3. Results and Discussion

Optical images of the film surface irradiated with the femtosecond laser at the laser fluence of 100 mJ/cm^2 were shown in Figs. 3 (a), (c) and (e). Figures 3 (b), (d) and (f) indicate the surfaces of the film after heating in electric furnace at the temperatures of 573, 673 and 773 K, respectively. In Fig. 3 (b), the darkened area is still observed after heating at 573 K. The darkened areas were whitened after the heating at 673 and 773 K as shown in Figs. 3 (d) and (f), respectively. SEM images of the films' surface in Figs. 3 (e) and (f) are shown in Figs. 4 (a) and (b), respectively. As indicated in Figs. 4 (a) and (b), topography of the films' surfaces was not changed through the heating in the electric furnace at 773 K. Result of AFM analysis also indicates that there was no topography change. Ra was approximately 0.06 μm before the heating. This Ra was not changed after the heating. These results indicated that whitening of the darkened film was not due to removal of the darkened portion by heating with an electric furnace. Thus, the darkened area was erased by heating with an electrical furnace. Optical images of the darkened area on the film's surface before and after the heating with electric furnace at 773 K under vacuum are shown in Figs. 5 (a) and (b), respectively. As indicated in Figs. 5 (a) and (b), the darkened area was not whitened through the heating process under vacuum

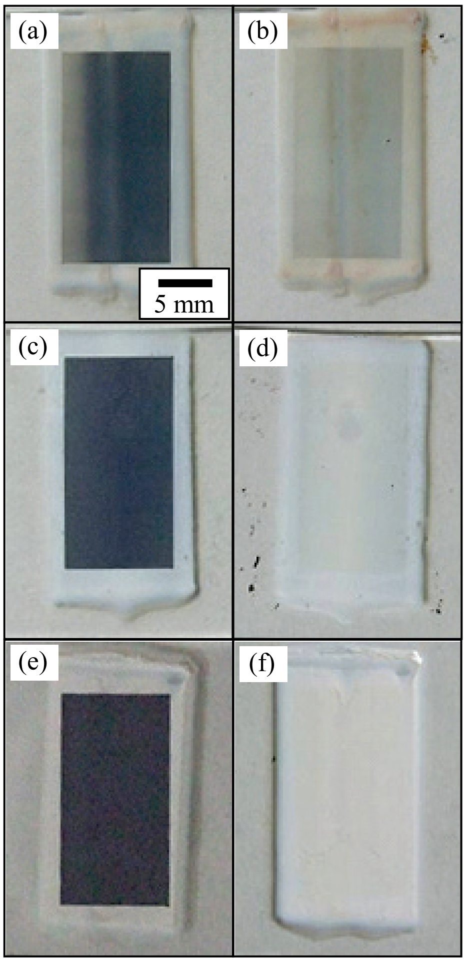

Fig.3 Optical images of the film surface irradiated with the femtosecond laser at the laser fluence of 100 mJ/cm^2 ((a), (c) and (e)) and after heating in the electric furnace ((b), (d) and (f)) at the temperatures of (b)573, (d)673 and (f)773 K, respectively.

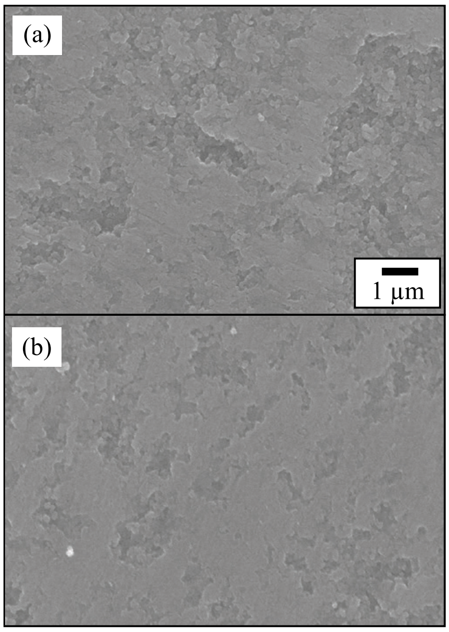

Fig.4 SEM images of TiO_2 film surfaces shown in Figs. 2 (e) and (f) were shown in (a) and (b), respectively.

although the darkened area was whitened by the heating at 773 K under air as shown in Fig. 3 (f). These results suggested that the cause of the darkened area formation was due to oxygen deficiencies since the whitening of the darkened area was not caused under vacuum. Lines on the film's surface shown at a1-a21 in Fig. 6 (a) were written using the darkening method with the femtosecond laser at the laser fluence of 20 to 220 mJ/cm^2 with the period of 10 mJ/cm^2. Observation of the lines of a15-a21 in Fig. 6 (a) with SEM indicates that topography changes were caused at 140 to 220 mJ/cm^2. Electrical resistance of these lines was decreased after the laser irradiation. These lines in Fig. 6 (a) were whitened by heating with an electric furnace at 773 K. This was the same as the result shown in Fig. 3 (f). Their electrical resistances were not indicated since they were too large to measure by our two-probe method. This indicated that the lower electrical resistance lines in Fig. 6

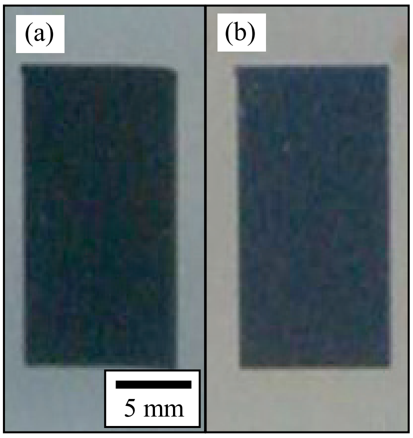

Fig.5 Lower electrical resistance area in an optical image (a) was formed on the film with a femtosecond laser at the laser fluence of 100 mJ/cm^2. The film with lower electrical resistance area was heated with an electrical furnace at 773 K under vacuum. After the heating, as an optical image (b) shows, lower electrical resistance area was retained on the film.

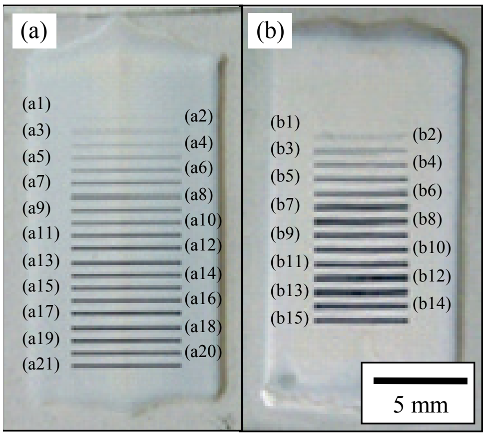

Fig.6 Lower electrical resistance lines in optical image (a) were written on the film with a femtosecond laser at the laser fluence of 20～220 mJ/cm^2 with the period of 10 mJ/cm^2. Lower electrical resistance lines in optical (b) were rewritten on the erasing-treated film with the laser at the laser fluence of 20～260 mJ/cm^2 with the period of 20 mJ/cm^2 , and 290 mJ/cm^2 and 310 mJ/cm^2.

(a) were increased after the erasing. Optical images of the darkened lines produced by femtosecond laser irradiation on the whitened area are shown in Fig. 6 (b). Figure 6 (b) shows that, by the femtosecond irradiation, the darkened lines could be written on the whitened area. Observation of the lines of b15-b20 in Fig. 6 (b) with SEM indicates that topography changes were caused at 140 to 220 mJ/cm^2. Squares and circles in Fig. 7 show the electrical resistances of the darkened lines shown in Figs. 6 (a) and (b) at various femtosecond laser fluences, respectively. As shown with squares in Fig. 7, the electrical resistances of the darkened lines were decreased as the laser fluence was increased. This result was the same as that obtained in Ref. [16]. The electrical resistances of the darkened lines formed on the whitened area by the femtosecond laser irradiation again was also decreased as the laser fluence was increased as shown with circles in Fig. 7. Results shown in Figs. 6 and 7 indicate that rewriting of lower electrical resistance lines on

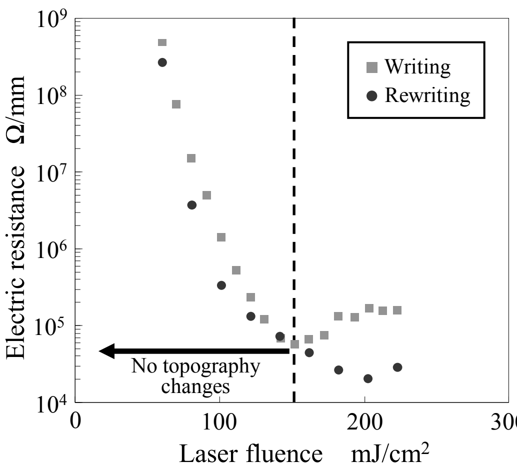

Fig.7 Electrical resistance along a 1 mm length of lines formed on the film as a function of the laser fluence. Square and circle indicate electrical resistances of written lines on the film and rewritten lines on the erasing-treated film with femtosecond laser, respectively.

the film could be promoted by the femtosecond laser irradiation.

4. Conclusion

Rewriting technology of lower electric resistance lines on the TiO_2 film could be developed using the method of whitening, erasing, by the heating with an electric furnace and darkening, writing, by the femtosecond laser irradiation. The darkened and the lower electric resistance lines on the film could be erased by the heating with an electric furnace under air. They could be rewritten on the erasing-treated film by the laser irradiation.

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