Modification of electrical properties of TiO$_2$ by continuous-wave ytterbium fiber laser irradiation

Hiroyasu KIDO,† Masanari TAKAHASHI, Jun-ichi TANI, Masaya CHIGANE, Nobuyuki ABE* and Masahiro TSUKAMOTO

Osaka Municipal Technical Research Institute, 1–6–50 Morinomiya, Joto-ku, Osaka 536–8553, Japan
*Joining and Welding Research Institute, Osaka University, 11–1 Mihogaoka, Ibaraki, Osaka 567–0047, Japan

Polycrystalline plate-like TiO$_2$ specimens were irradiated with a continuous-wave Yb-fiber laser, and the electrical properties of the modified layers were investigated. The irradiated part was modified in color and electrical properties when the laser power was set above a certain threshold. The color changed from white to black, and the electrical resistivity drastically decreased from an initial value of 3.3 x 10$^7$ cm to 1.9 x 10$^2$ cm at 2.0 W. The Hall measurement showed that the modified layer was an n-type semiconductor, and the carrier concentration was 3.6 x 10$^{17}$ cm$^{-3}$ at 2.0 W.

Key-words: TiO$_2$, Yb-fiber laser, Laser modification, Morphology, Electrical properties

1. Introduction

The laser modification of the morphology and the physical properties of ceramics have attracted a great interest because of their potential application to microelectronic devices, and sensors.$^{1,2}$ The electrical properties of ceramics can be modified as writing patterns on the surface by using a laser beam. The irradiated part is melted and recrystallized in a very brief time, which saves energy. The cooling rate of a laser process is on the order of 10$^3$ K/s. This rapid process results in oxygen vacancies after irradiation in oxide ceramics. A drastic decrease in the electrical resistivity by excimer laser irradiation was observed for polycrystalline BaTiO$_3$, single-crystal SrTiO$_3$ and single-crystal TiO$_2$.$^3$ The decrease in resistivity was attributed to the generation of oxygen vacancies. Darkening of TiO$_2$ film surfaces and a decrease of their electrical resistance resulted from irradiation with an 800-nm femtosecond laser.$^6$

In recent years, an infrared Yb-fiber laser ($\lambda = 1070$ nm) has been developed to the level of industrial use. It has a high energy conversion efficiency ($>30\%$), high power, low heat evolution, and high beam quality ($M^2 = 1.1$). The application of the fiber laser to modify the properties of ceramics was reported in recent years. The fabrication of ion conductive lines on a glass surface,$^{7-9}$ preparation of MgB$_2$ superconductive phase lines,$^{10}$ and crystal growth in glasses$^{11,12}$ were conducted using a fiber laser. A Yb-fiber laser was also applied to the surface densification of porous ZrC$^{13}$ and the synthesis of TiO$_2$ nanoparticles.$^{14}$

We reported the modification of the electrical properties of ZnO irradiated by a Yb-fiber laser.$^{15,16}$ The electrical resistivity of ZnO was reduced by the laser irradiation from an initial value of $1.1 \times 10^4$ to $2.0 \times 10^{-1}$ $\Omega$ cm at 126 W. The Hall measurement showed that the modified layer was an n-type semiconductor, and the carrier concentration was $1.9 \times 10^{19}$ cm$^{-3}$ at 126 W.

The laser modification of electrical properties of oxide ceramics using a continuous-wave (cw) Yb-fiber laser has not been investigated. In this study, the electrical properties of sintered TiO$_2$ plates were modified by cw Yb-fiber laser irradiation. The morphology of the modified layer, electrical resistivity, carrier concentration, and conduction mechanism were examined.

2. Experimental procedure

Commercial-grade polycrystalline TiO$_2$ plates (Kojundo Chemicals Laboratory Co., Ltd., purity: 99.9%, relative density 93%, diameter: 106 mm, thickness: 5 mm) were cut into pieces (10 x 10 x 5 mm), which were used in the present study. The laser irradiation experiments were carried out with a cw Yb-fiber laser (IPG YLR-300-SM, emission wavelength $\lambda = 1070$ nm, beam diameter $r_g = 3.8$ mm, beam quality $M^2 = 1.1$) in air. The schematic diagrams of the laser modification and irradiation pattern are shown in Fig. 1. The emission beam was focused to a spot size of 12 $\mu$m through an object lens (Sigma Koki NYDL-30-60 PY1, focal length $f = 60$ mm). The TiO$_2$ plates were set on a stage (Laserack Corp.) and scanned at a constant speed of

\[ \text{Fig. 1. Schematic diagram of laser modification experiment. (a) Setup of laser irradiation experiment, (b) laser irradiation pattern. The pattern 1 is followed by 2 as showing a lattice pattern.} \]
5 mm/s in a lattice pattern [see Fig. 1(b), line separation is 100 μm]. The laser power, P, was monitored by a power meter (Ophir FL400A-BB-50). The crystal structure of a modified layer was identified by X-ray diffraction (XRD, Rigaku RINT2500) with monochromatic Cu Kα radiation. The microstructure was observed by scanning electron microscopy (SEM, JSM6700F and JSM6460LV). The X-ray photoelectron spectroscopy (XPS) spectra were obtained using a PHI ESCA 5700 instrument with a monochromatic Al Kα X-ray source (1486.6 eV, 150 W). The pressure in the analysis chamber was <10⁻⁶ Pa. The binding energies were corrected by referencing the C 1s peak to 284.8 eV.

The absorption of Yb-fiber laser may be conducted by a multi-photon process⁶ and an inverse-bremsstrahlung process which is caused by surface plasma.¹⁷ The detailed mechanism of absorption is under consideration. A power threshold for polycrystalline TiO₂ plates modification was found. The modification was observed above 2.0 W under the conditions described in the experimental chapter. In a very short interval, the melting and subsequent recrystallization took place, and modified layers were formed on the surface. The SEM images of TiO₂ specimens irradiated at laser powers of 2.0, 2.5, 5, and 10 W are shown in Fig. 2. The letter s indicates the distance between laser scanning zones. Many small cracks grew like the branches of a tree on the laser treated surfaces [inset Fig. 2(a)], which were due to the thermal shock. These small cracks became larger in size with increasing laser power. The cracks formed when the melt pools rapidly cooled to room temperature. The thermal stress was strongest at the central part of the melt pool. Therefore, large cracks formed along the laser scanning lines.

As shown from the cross-sectional SEM images (Fig. 2), the modified layers were clearly discriminated from the original sintered texture. The cross-sectional shape of a modified layer was flat and thin, which is typical of this type of thermocative laser processing.¹⁷ This type of modified layer was observed in the low laser power density range. The laser processing changes to the keyhole type with an increase in power density,¹⁷,¹⁸ where the melt pool surface becomes deep hollow. The keyhole type modification was reported for the laser modification of ZnO.¹⁷

A schematic diagram illustrating a relationship between the laser power and the surface appearance shapes in Fig. 2 is shown in Fig. 3. The dashed line represents the laser scanning line. The gray blocks illustrate the modified TiO₂ zones. The modified zones expanded in size with power. In the lower laser power region, w was less than s [Fig. 2(a)]. By increasing the laser power, the magnitude of w increased and reached s. The laser powers of 2.5 and 5 W were located in the region where s < w < 2s [Fig. 2(b)]. In this region w was given by the equation of w = 2(s-t). The power of 2.5 W corresponded to the laser power a little larger than where w = s and much smaller than where w = 2s. The power of 5 W was a little smaller than the power corresponding to the condition of w = 2s. Further increasing the laser power caused widening of a modified zone, and the upper border of a modified zone exceeded the upper scanning line [Fig. 2(c)].

The width (closed diamonds) and thickness (circles) of laser modified layers are shown in Fig. 4. The width was 60 μm at 2 W, 120 μm at 2.5 W, and 170 μm at 5 W. The thickness was 22 μm at 2 W, 29 μm at 2.5 W, 53 μm at 5 W, and 129 μm at 10 W. The modified width was larger than the modified thickness for all powers of 2.0, 2.5, 5, and 10 W.
laser powers. This is characteristic of thermo-conductive type laser processing. The thickness of the modified layer increased in proportion to the laser power. The width of modified layer showed a tendency toward saturation behavior as the laser power was increased, which was related to the initial change of laser processing type from the thermo-conductive type to the keyhole type.

XRD patterns of TiO₂ specimens are shown in Fig. 5. The letters (a) and (b) designate irradiated at 2.5 W and non-irradiated, respectively. All diffraction peaks were indexed on the basis of the Rutile-type structure. No peaks due to other phase were found in the XRD patterns. This result showed that the modified TiO₂ layer had the same crystal structure as the original one.

The XPS spectra of Ti 2p and O 1s for Yb-fiber laser irradiated at 2 W and non-irradiated TiO₂ are shown in Fig. 6. The binding energies of Ti 2p₁/₂ and Ti 2p₃/₂ for irradiated specimens were 458.4 and 464.0 eV, respectively. Those for non-irradiated specimens were 458.3 and 464.0 eV, respectively. Although the color and electrical resistivity changed after the laser irradiation, any change in the XPS spectra of Ti 2p was not observed. Similar XPS results were reported for excimer laser irradiated SrTiO₃.4) The O 1s spectra in Fig. 6 show one large peak near 530 eV and another small shoulder on the higher energy side. The main peaks were attributed to lattice oxygen, and the shoulder peaks were assigned to adsorbed oxygen.5) The binding energies of the O 1s main peak were 529.5 and 529.6 eV for irradiated and non-irradiated specimens, respectively. Those for the O 1s shoulder peak were 531.1 and 531.0 eV for irradiated and non-irradiated specimens, respectively. These peak values were in good agreement with the reported values.5) The shoulder peaks became smaller by the Yb-fiber laser irradiation which was the result of the removal of adsorbed oxygen. However, it was reported that the adsorbed oxygen peaks grew by excimer laser irradiation of SrTiO₃,4) and this effect was enhanced by increased laser fluence. This difference between the Yb-fiber laser treatment and excimer laser treatment may be due to a difference in the modification mechanism. The modification of electrical properties was caused by the photothermal process in the Yb-fiber laser. Meanwhile it is caused by the photochemical process as well as the photothermal process in the excimer laser.

The electrical resistivity, ρ, of original TiO₂ specimens and laser modified specimens is shown in Fig. 7. The ρ of the initial TiO₂ specimen was 3.3 × 10⁶Ω cm. It sharply decreased to 1.9Ω cm at 2.0 W, 4.6Ω cm at 2.5 W, and 5.4Ω cm at 5.0 W. We could not measure ρ of specimens irradiated at 10 W because of peel-off of modified layers. The power dependence of the electrical resistivity changed after the laser irradiation, any change in the XPS spectra of Ti 2p was not observed. Similar XPS results were reported for excimer laser irradiated SrTiO₃.4) The O 1s spectra in Fig. 6 show one large peak near 530 eV and another small shoulder on the higher energy side. The main peaks were attributed to lattice oxygen, and the shoulder peaks were assigned to adsorbed oxygen.5) The binding energies of the O 1s main peak were 529.5 and 529.6 eV for irradiated and non-irradiated specimens, respectively. Those for the O 1s shoulder peak were 531.1 and 531.0 eV for irradiated and non-irradiated specimens, respectively. These peak values were in good agreement with the reported values.5) The shoulder peaks became smaller by the Yb-fiber laser irradiation which was the result of the removal of adsorbed oxygen. However, it was reported that the adsorbed oxygen peaks grew by excimer laser irradiation of SrTiO₃,4) and this effect was enhanced by increased laser fluence. This difference between the Yb-fiber laser treatment and excimer laser treatment may be due to a difference in the modification mechanism. The modification of electrical properties was caused by the photothermal process in the Yb-fiber laser. Meanwhile it is caused by the photochemical process as well as the photothermal process in the excimer laser.

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ferromagnetism in TiO$_2$ films$^{21}$

The laser modified specimens at 2 W were heated at 573, 673, 773, and 973 K for 1 h in air to examine the stability of the defects. The $\rho$ of modified TiO$_2$ layers after the heat treatments is shown in Fig. 8. The $\rho$ was constant in the temperature range from 300 to 773 K, but sharply increased at 773 K. The black color gradually decayed. These phenomena were ascribed to the quenching of oxygen defects by heating in air, which is accompanied with the release of electrons from defects created by the laser irradiation. The electrical properties of the modified layer were stable below 773 K, which was higher than the corresponding temperature in the Yb-laser modified ZnO.$^{14}$

4. Conclusions

The electrical properties of polycrystalline TiO$_2$ were modified by Yb-fiber laser irradiation ($A = 1070\, \text{nm}$) above a threshold laser power of about 2 W. The electrical resistivity of modified TiO$_2$ layers was sharply decreased by the irradiation, which was caused by the formation of oxygen defects through a photo-thermal modification process. The modified layers were n-type semiconductor with a carrier concentration of $3.6 \times 10^{17} \, \text{cm}^{-3}$ at 2.0 W.

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