Formation of Periodic Nanostructures on Titanium Dioxide Film by Femtosecond Laser Irradiation†

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Abstract

Periodic nanostructures formation on Titanium dioxide (TiO_2) film by scanning of femtosecond laser beam spot is reported. Periodic nanostructures, lying perpendicular to the laser electric field polarization vector, were formed on TiO_2 film by femtosecond laser irradiation for 1mm/sec at laser fluence from 0.35 J/cm^2 to 0.65J/cm^2. For 0.5mm/sec, they were formed at laser fluence from 0.35 to 0.55 J/cm^2. Periodic nanostructures were also formed on large areas of the film. The period of Periodic nanostructures was 200 nm.

KEY WORDS: (Femtosecond Laser), (Titanium dioxide), (Aerosol beam), (Periodic nanostructures)

1. Introduction

Metals are most widely used in medical devices. Titanium (Ti) is one of the most used biomaterials in metals, because of its excellent anti-corrosion and mechanical properties. However, Ti is an artificial material and has no biofunction. Thus, it is necessary to improve the bioactivity of Ti. It is well known that microstructures formation on Ti surface is one of the useful methods to improve its biocompatibility[1)]. Recently, coating of the titanium dioxides (TiO_2) film on Ti plate has been also proposed to improve biocompatibility of Ti[2)]. We have developed a coating method of TiO_2 film on Ti plate with an aerosol beam[3-4)]. Then, we proposed periodic microstructures formation on TiO_2 film. Biocompatibility of the TiO_2 film could be more improved than a bare TiO_2 film.

The femtosecond laser is one of the useful tools for creating microstructures on metals[5-7)] and semiconductors[8-9)]. In our previous study, periodic nanostructures, lying perpendicular to the laser electric field polarization vector, were formed on Ti plate by femtosecond laser irradiation[5-6)]. Femtosecond laser induced periodic nanostructure is self-formed in the laser spot. Period of periodic nanostructures is about 600 nm. This is shorter than the wavelength of the femtosecond laser. Periodic nanostructures were also formed on TiO_2 single crystal with femtosecond laser by another group[8)]. Then, the period of periodic nanostructures was about 200 nm. Hence, Periodic nanostructures could be formed on TiO_2 film by femtosecond laser irradiation. It is necessary for biomaterials to form periodic nanostructures on large areas of the TiO_2 film. Periodic nanostructures formation on Ti and TiO_2 film by scanning of a femtosecond laser focusing spot has not been elucidated yet.

In this study, we try to create periodic nanostructures on large areas of TiO_2 film by scanning of the femtosecond laser spot. The influence of the laser fluence and scanning speed for producing the periodic nanostructures was investigated. Period of periodic nanostructures of TiO_2 film was also examined. After femtosecond laser irradiation, TiO_2 film surface was observed by scanning electron microscope (SEM).

2. Experimental

TiO_2 film was produced on Ti plate by aerosol beam irradiation. 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. Pure Ti plate was used for

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substrate in this experiment.

Schematic diagrams of femtosecond laser irradiation are shown in **Figs. 1 (a)**. A commercial femtosecond Ti : sapphire laser system was employed in our experiments, which was based on the chirped pulse amplification technique. The wavelength, pulse duration, repetition rate, and beam diameter of the femtosecond laser were 775 nm, 150 fs, 1 kHz, and approximately 5 mm, respectively. The laser beam was focused on the TiO_2 surface by using a lens with 100 mm focal length. The Gaussian laser beam had a diameter of 60 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 as shown in **Fig. 1 (b)**. Scanning speed was changed from 0.5 to 1 mm/s. Laser fluence was changed form 0.25 J/cm^2 to 0.85 J/cm^2 by controlling the energy attenuator. To form periodic nanostructures on large areas of the film, laser beam was also scanned on the TiO_2 film surface by using the XY stage as shown in **Fig. 1 (c)**. Scanning speed, laser fluence and hatching distance was 1.0 mm/s, 0.35 J/cm2 and 20 µm, respectively. After the femtosecond laser irradiation, the film surface was observed with an SEM.

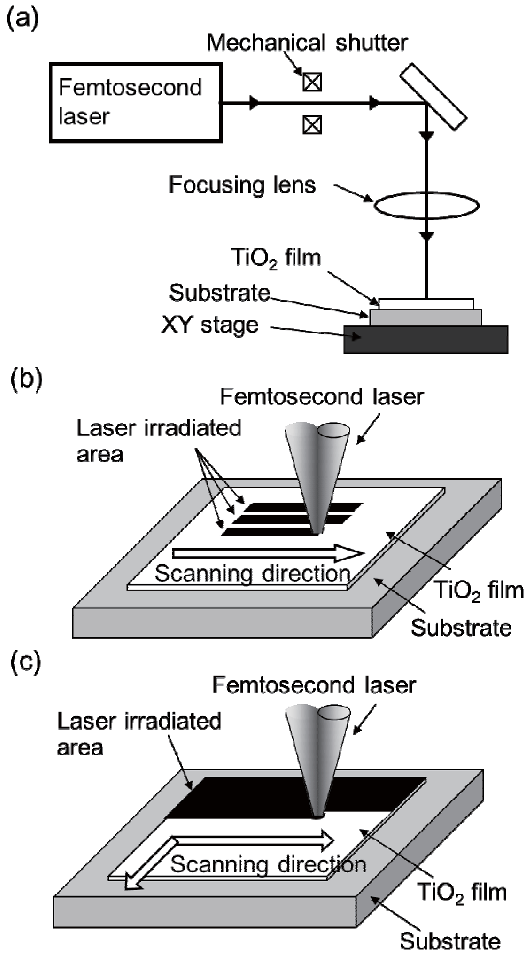

Fig. 1 (a) Schematic diagram of experimental setup for femtosecond laser irradiation. (b) Scanning of the laser focusing spot. (c) Scanning of the laser focusing spot to create periodic nanostructures on large areas of the film.

3. Results and Discussion

SEM images of bare TiO_2 film (no laser irradiated area) surface and femtosecond laser irradiated areas for 1 mm/sec at laser fluences of 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85 J/cm^2 are shown in **Figs. 2 (a), (b), (c), (d), (e), (f), (g) and (h)**, respectively. Periodic nanostructures were not formed on bare TiO_2 film surface as shown in Fig.2 (a). As Fig. 2 (b) shows, the topography of laser irradiated area was changed at 0.25 J/cm^2. However, periodic nanostructures formation was not clearly observed. As Figs. 2 (c), (d), (e) and (f) show, periodic nanostructures, lying perpendicular to the laser electric field polarization vector *E*, were formed on the film surface at 0.35, 0.45, 0.55 and 0.65 Jcm^2, respectively. The period of periodic nanostructures formed on the film 0.35 J/cm^2 was about 200 nm. It was not changed from 0.35 to 0.65 J/cm^2. Over 0.75 J/cm^2, the film was broken. But, periodic nanostructures were formed on Ti plate as shown in Figs. 2 (g) and (h). The period of periodic nanostructures formed on Ti was about 600 nm. These results show periodic nanostructures were

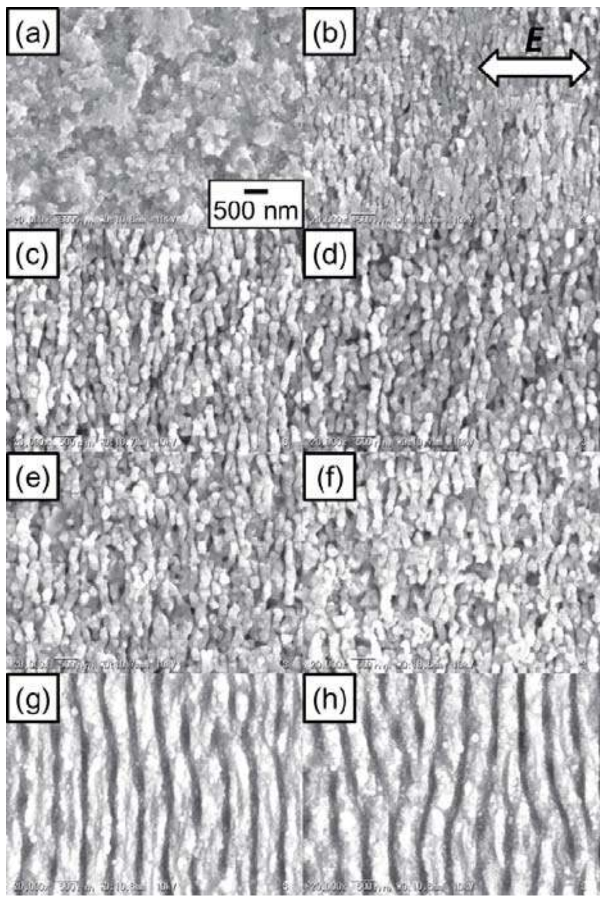

Fig. 2 SEM images of (a) bare TiO_2 film surface and TiO_2 film surface after femtosecond laser irradiation for 1 mm/sec at the laser fluence of (b) 0.25, (c) 0.35, (d) 0.45, (e) 0.55, (f) 0.65, (g) 0.75 and (d) 0.85 J/cm^2, respectively.

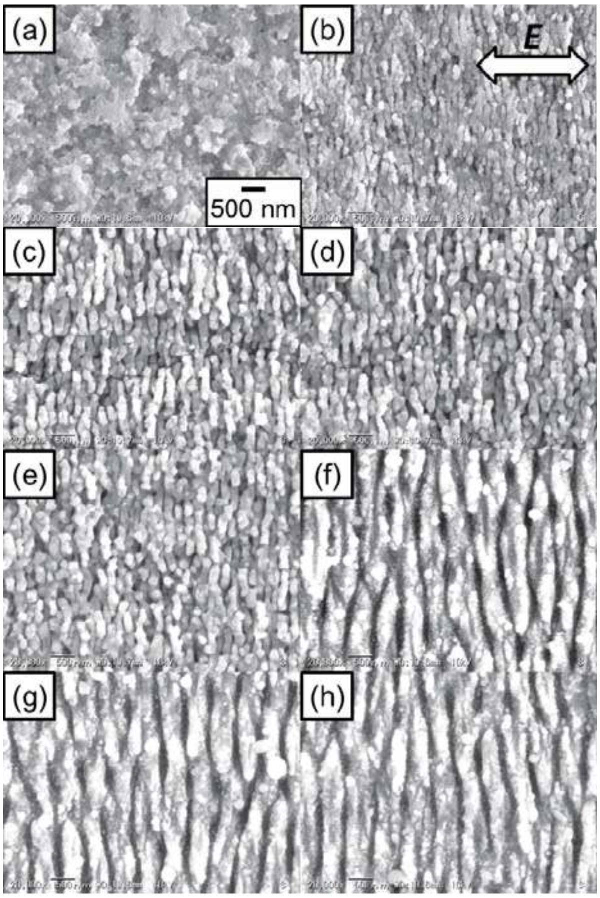

Fig. 3 SEM images of (a) bare TiO_2 film surface and TiO_2 film surface after femtosecond laser irradiation for 0.5 mm/sec at the laser fluence of (b) 0.25, (c) 0.35, (d) 0.45, (e) 0.55, (f) 0.65, (g) 0.75 and (h) 0.85 J/cm^2, respectively.

formed on the film by scanning of femtosecond laser spot for 1 mm/sec at laser fluence from 0.35 to 0.65 J/cm^2.

For 0.5 mm/sec, SEM images of bare TiO_2 film surface and femtosecond laser irradiated areas at laser fluences of 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85 J/cm^2 are shown in **Figs. 3 (a), (b), (c), (d), (e), (f), (g) and (h)** respectively. As Fig. 3 (b) shows, topography of laser irradiated area was changed at 0.25 J/cm^2. However, periodic nanostructures were not clearly formed on the film. As Figs. 3 (c), (d) and (e) show, periodic nanostructures, lying perpendicular to the laser electric field polarization vector *E*, were formed on the film surface at 0.35, 0.45 and 0.55 Jcm^2, respectively. The period of periodic nanostructures formed on the film at 0.35 J/cm^2 was about 200 nm. It was not changed from 0.35 to 0.55 J/cm^2. Over 0.65 J/cm^2, the film was broken. But, periodic nanostructures were formed on Ti plate as shown in Figs. 3 (f), (g) and (h), respectively. The period of periodic nanostructures formed on Ti was about 600 nm. These results show periodic nanostructures were formed on the film by scanning of femtosecond laser spot for 0.5 mm/sec at laser fluence from 0.35 to 0.55 J/cm^2.

To create periodic nanostructures on large areas of the film, we tried to form periodic nanostructures on

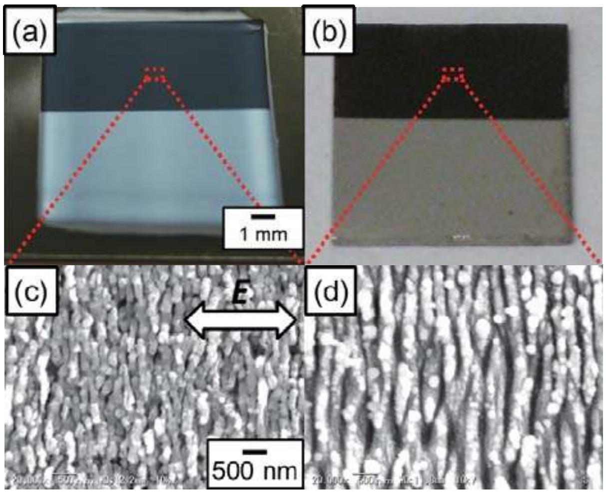

Fig. 4 Optical and SEM images of periodic nanostructures formation on large areas: (a) and (c) on TiO_2 film, (b) and (d) on Ti plate.

the TiO_2 film surface in 10 mm × 5 mm by scanning of the femtosecond laser spot as shown in Fig. 1 (c). Optical and SEM image of TiO_2 film surface after scanning of femtosecond laser beam spot for 1mm/sec at 0.35 J/cm^2 was shown in **Figs. 4 (a) and (c)**. As Figs. 4 (a) and (c) show, periodic nanostructures were clearly formed on film surface in 10 mm × 5 mm. The period of periodic nanostructures formed on TiO_2 film was about 200 nm. We also created periodic nanostructures on Ti plate with the same condition. Optical and SEM images of the Ti surface after scanning of a femtosecond laser beam spot for 1mm/sec at 0.35 J/cm^2 are shown in **Figs. 4 (b) and (d)**. As Figs. 4 (b) and (d) show periodic nanostructures were produced on Ti plate in 10 mm × 5 mm. The period of periodic nanostructures formed on Ti was about 600 nm. The period of periodic structures formed on TiO_2 film and Ti plate was very different by scanning of femtosecond laser spot. It was suggested that mechanism of periodic nanostructures formation is very different from TiO_2 film and Ti plate.

4. Summary

We tried to create periodic nanostructures on large areas of TiO_2 film. Periodic nanostructures were formed for 1 mm/sec at laser fluence from 0.35 to 0.65 J/cm^2. For 0.5mm/sec, they were formed at laser fluence from 0.35 to 0.55 J/cm^2. Periodic nanostructures were also formed on large areas of the film. The period of Periodic nanostructures was about 200 nm. It was very different form TiO_2 film and Ti plate.

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