Apatite formation on rutile type TiO_2 films formed by laser irradiation

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Titanium oxide-coating films exhibit a wide variety of physical properties, allowing them to be useful in many applications such as photocatalysis [1], gas sensors [2], medical implants [3] and optical active coatings [4]. Among these applications, bioactive materials have received considerable attention due to their high biocompatibility in the living-body [5–7]. Anatase, one of the TiO_2 polymorphisms, is considered to be appropriate for bone-like apatite formation. Therefore, numerous studies have been carried out on the deposition of anatase films by physical vapor deposition, chemical vapor deposition [8–11] and sol-gel method [12]. On the other hand, little attention has been paid whether rutile crystals have the apatite-forming ability when soaked in SBF or implanted in the living-body.

Laser irradiation is a powerful tool to produce TiO_2 crystals on a substrate in a short irradiation period [13]. Gyorgy *et al*. prepared rutile and anatase crystals by irradiating a Nd:YAG laser to the titanium metal [14]. Robertson *et al*. reported the crystallization of rutile-type TiO_2 by the laser irradiation [15]. Thus, YAG laser irradiation seems to be preferable for rutile formation. In this work, we concentrated our attention on the formation of TiO_2-rutile film using Nd:YAG laser and its biomimetic apatite-forming ability to explore the bioactivity of the TiO_2 films.

Amorphous TiO_2 films were prepared using the sol-gel process through the hydrolysis of titanium (IV) n-butoxide with water at room temperature. The solution for TiO_2 coating was synthesized by mixing the titanium (IV) n-butoxide, diethanol amine as a chelating agent, ethanol and water, the molar ratio was kept to 1:1:26.5:1, respectively. TiO_2 films were deposited on a silica glass substrate by dip coating at withdrawing speed of 3 mm/s followed by annealing at 300 °C in air for 2 hr. The coating-heating process was repeated twice. No crystallization was found in the as-prepared films.

TiO_2 films were irradiated using a Nd:YAG laser at 355 nm wavelength, 600 mW power and a repetition rate of 10 Hz for 5 min. The laser-irradiated area was 8 mm diameter. The obtained films were observed using scanning electron microscopy (SEM) incorporating X-ray energy dispersive spectrometry (EDS), X-ray diffractometry and laser Raman spectroscopy.

Fig. 1 shows the SEM micrographs and EDS spectra of the TiO_2 films before and after the laser irradiation. The SEM micrograph in Fig. 1a shows that the as-prepared film has a smooth surface. The EDS spectrum (Fig. 1b) collected from its surface indicates a low intensity Ti ion with a strong intensity of the Si from the glass substrate. On the other hand, Fig. 1c shows the SEM micrograph of the sample surface after laser irradiation. Numerous fine particles of 0.5 to 1 μm were deposited on the substrate. The EDS spectrum collected from the particles indicates that the enhancement of Ti peak intensity due to crystallization as shown in Fig. 1d. These results suggesting that the amorphous TiO_2 films are melted by the high power of the laser beam to form aggregates during cooling [16].

Fig. 2A shows the TF-XRD patterns of the TiO_2 films before and after the laser irradiation. The as-prepared films were amorphous as represented in Fig. 2A-a. Contrary to the amorphous phase of the as-prepared films, the films irradiated with laser exhibited XRD peaks at $2\theta \approx 27.9$ and 36.0 degrees, suggesting the crystallization of rutile-type TiO_2 as shown in Fig. 2A-b. The formation of rutile becomes more clear from the laser Raman spectroscopy shown in Fig. 2B. The signals peaking at 607, 440, 240 and 144 cm^{-1} are attributed to the rutile phase [17], no signal referring to anatase was observed. Therefore, it is apparent that our sample consisted of rutile phase. Perez et al. estimated that the temperature at their samples surface reaches 1200 K at 300–400 mW laser power [18], which is enough to form the rutile [19, 20].

Biomimetic apatite-forming ability test of the prepared films was carried out by soaking for various periods at 37 °C in 100 mL of an aqueous solution with ion concentrations 1.5 times those of the simulated body fluid (1.5 SBF). The SBF solution was prepared by dissolving the reagents of NaCl, Na_2SO_4, KCl, $MgCl_2.6H_2O$, $CaCl_2$, Na_2HPO_4 and $NaHCO_3$ in ion-exchanged water to give the concentration of Na^+; 213.0, K^+; 7.5, Mg^{2+}; 2.25, Ca^{2+}; 3.75, Cl^-; 222.45, HCO_3^-; 6.3, HPO_4^{2-}; 1.5 and

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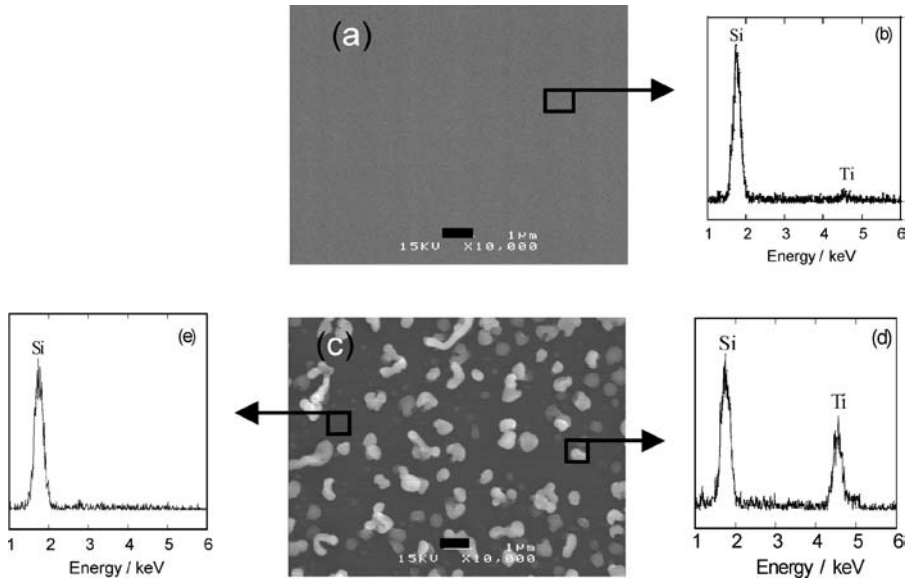


Figure 1 SEM micrographs and EDS spectra of TiO_2 films, (a) and (c) are the SEM micrographs of the as-prepared and the laser-irradiated films, respectively. (b), (d) and (e) are the EDS spectra collected from the marked areas.

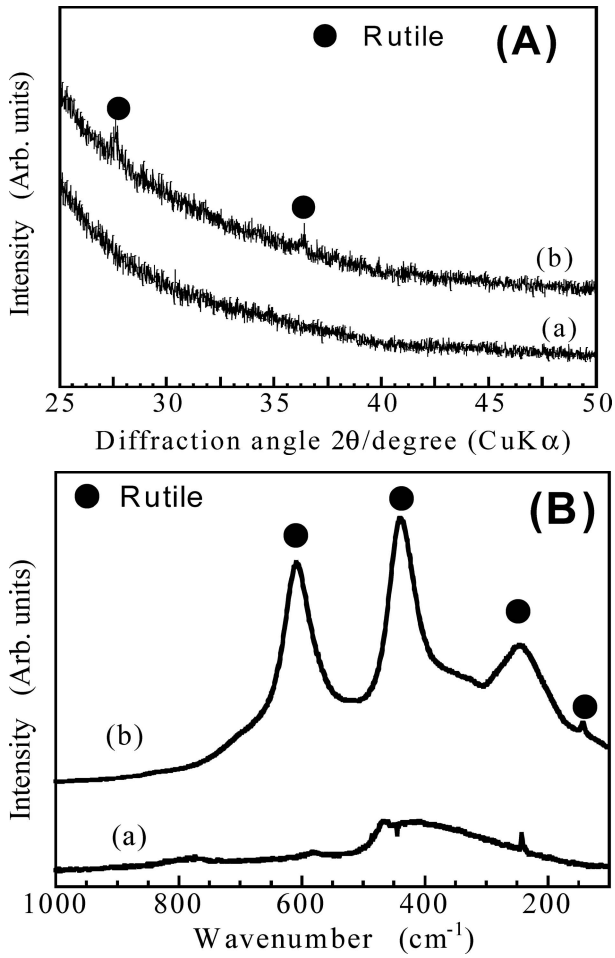


Figure 2 TF-XRD patterns (A) and laser Raman spectra (B) of TiO_2 thin films, (a) before and (b) after laser-irradiation. *Black circle indicates the rutile crystal.*

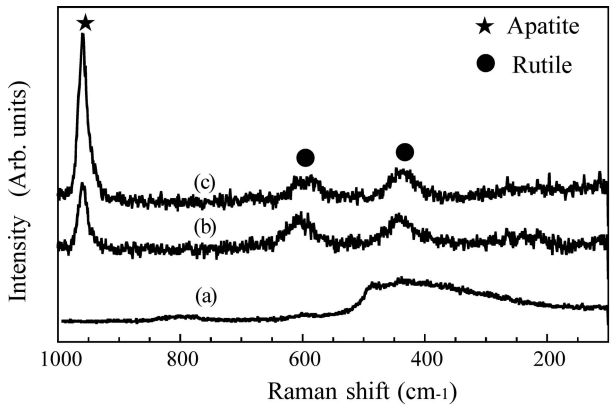
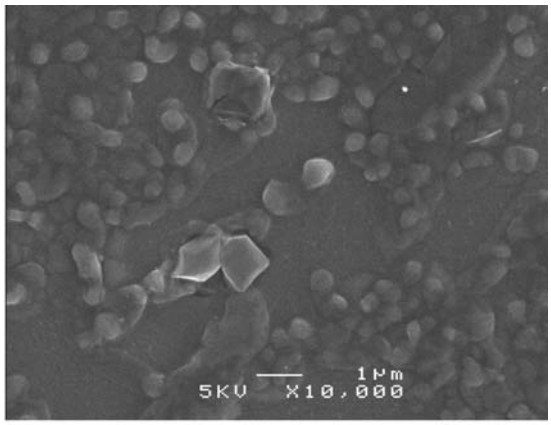


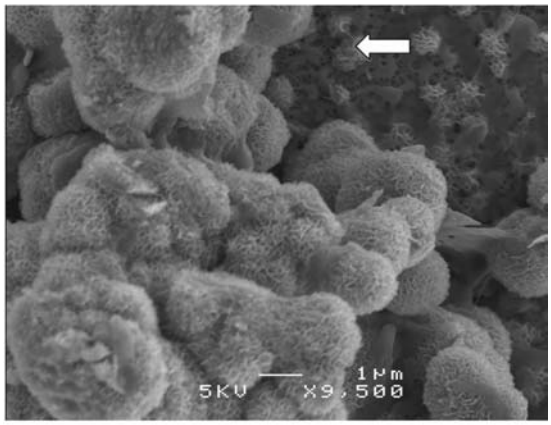
Figure 3 Laser Raman spectra of the TiO_2 films after soaked in 1.5 SBF; (a) for the as-prepared films soaked for 5 days in the SBF solution, (b), and (c) are the laser-irradiated films soaked for 5, and 14 days, respectively. *Black star indicates apatite crystal.*

SO_4^{2-}; 0.75, including $(CH_2OH)_3CNH_2$ 50 and HCl; 45.0 in mM.

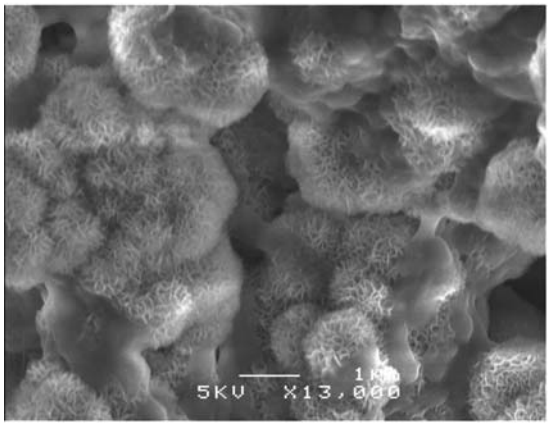
Fig. 3 shows the laser Raman spectra of the samples after soaking in the 1.5 SBF. The spectrum for the as-prepared TiO_2 films soaked in SBF solution for 5 days shows no apatite crystallization. On the other hand, the laser-irradiated films, exhibit a sharp signal at 964 cm^{-1} after soaking in the SBF solution for 5 days in addition to the signals of rutile as shown in Fig. 3b and c. This Raman signal is assigned to the existence of apatite (came from PO_4^{-3} groups) and the peak intensity rising as the soaking period increased. Fig. 4, shows the SEM micrographs of the samples soaked in SBF. Numerous depositions of leaf-like particles corresponding to the



(a)



(b)



(c)

Figure 4 SEM micrographs of the films after soaking in 1.5 SBF; (a) the as-prepared TiO_2 film soaked for 5 days, (b), and are the laser irradiated TiO_2 films soaked for 5, 14 days, respectively. *The arrow refers to the growth of apatite on the TiO_2 particles.*

apatite morphology were observed on the surface of the laser irradiated films [21]. Moreover, it was found that the apatite crystals grew with increasing the soaking time and completely covered the surface within 14 days. Neither occurred apatite formation on the as-prepared TiO_2 films nor the laser irradiated glass substrate. Some depositions were noted on the as prepared films, but not apatite.

It is well known that the TiO_2 gels-containing anatase and/or Ti–OH bonds act to induce apatite nucleation [22]. Kokubo *et al*. [23] reported that the sol-gel-derived silica glasses containing the Si–OH groups allow the formation of the apatite in SBF. Although our laser-irradiated films neither consist of anatase or Ti–OH bonds because of their exposure to high temperature of the laser beam. The apatite crystals are grown in the short soaking periods in SBF. Thus, our samples have the advantage for bio-applications.

In summary, using laser irradiation of Nd:YAG, the amorphous TiO_2 films were crystallized into rutile-type TiO_2. Further, it was found that, apatite crystals were deposited on the surface of the rutile particles by soaking in SBF solution and covered the whole surface of the films. It indicates that apatite formed on rutile and bioactivity can be produced at some desired positions on an implant using the laser-irradiation.

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