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Raman Spectroscopy as a Useful Probe of Mechanisms of Deterioration of Metal Oxide Materials due to Laser Irradiation

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Raman spectroscopy provides a very useful means to study mechanisms of deterioration of metal oxide materials due to laser irradiation. Excimer laser irradiation (308 nm) induced transition of anatase of TiO_2 to rutile, while it did not cause substantial changes for rutile or HfO_2. The deterioration mechanism is essentially a thermal one, as supported by the morphological changes monitored by SEM measurements.

In view of the extensive use of a variety of metal oxides for optical thin films in science and technology, it is very important to establish a practical and reliable method of in-situ nondestructive monitoring of deterioration mechanisms of these metal oxides after exposure to intense light such as that of UV pulsed lasers. To date several methods, viz. crystallographic,[1,2] microstructural,[2] optical,[1—3] or photothermal deflection,[4] have been used for this purpose. Raman spectroscopy was used by Exarhos et al.[5,6] to monitor the change of amorphous TiO_2 prepared by sol–gel method into anatase on heating above 300 °C and after focused pulsed or continuous-wave laser irradiation.

Several studies of phase changes of metal oxides by Raman spectroscopy have been reported. Ikeya and Senna[7] used Raman spectroscopy to study structural changes of Ta_2O_5 under mechanical stressing; a monoclinic to rhombic phase change on mechanical vibro-milling was followed by Raman spectroscopy. Asahi and Ishigame[8] studied polymorphism in ZrO_2 at high pressure by Raman spectroscopy. Voron'ko et al.[9] investigated high-temperature phase transitions of pure ZrO_2 and of ZrO_2 and HfO_2 containing Yb_2O_3 or Gd_2O_3 by Raman methods. For ZrO_2, the spectrum at 300 K consisted of 14 narrow lines attributable to a monoclinic phase with the C_{2h}^5 symmetry, while that of 1500 K gave six lines due to a tetragonal phase with the D_{4h}^{15} symmetry. Monoclinic-tetragonal change was observed for HfO_2 containing Yb_2O_3 or Gd_2O_3. Pressure and temperature dependences of Raman spectra of ZrO_2 and HfO_2 were studied by Kourouklis and Liarokap:[10] a monoclinic to tetragonal phase transition occurred at 3.5 GPa at 300K, while only monoclinic phase was observed for HfO_2 for pressure$\lesssim$10 GPa and temperature below 800 K. Lagarec and Desgreniers[11] used Raman spectroscopy to probe the effect of applied pressure up to 70 GPa on single crystal anatase.

In the present paper, Raman spectroscopy has been used to probe phase changes of a few metal oxides relevant to optical thin films, i.e. titanium dioxide (anatase and rutile) and hafnium dioxide.

Experimental

Samples (ca. 0.3 g each) of polycrystalline bulk metal oxides (anatase and rutile of TiO_2, Ti_3O_5, and HfO_2) were compressed at 40 MPa into a pellet (11 mm$\phi \times$2 mm thick). (This compression procedure did not result in any essential change in the Raman spectra.) These pellets were irradiated at room temperature in ambient atmosphere by an excimer laser (Lambda Physik LPX-105, operated at 308 nm (XeCl line)). The laser light was softly focused using a $f = 400$ mm quartz lens, and shot at 45 ° to the sample surface. Irradiated area was typically 1 cm^2. The pulse width was ca. 20 ns, and the repetition rate was 5 Hz. Fluence on the sample surface was controlled by variation of focusing condition with a quartz lens.

Raman spectra of bulk metal oxides before and after excimer laser irradiation were measured by a JASCO CT-80D double monochromator equipped with a Hamamatsu R649/C1050 photomultiplier/photon counting unit. Excitation for Raman measurements was made by the 514.5 nm light from a Spectra Physics 165 Ar ion laser. SEM images were obtained using a Hitachi S-2300 scanning electron microscope.

Polycrystalline TiO_2 (anatase and rutile) and Ti_3O_5 samples were provided by Ise Vacuum Optics, Co. The HfO_2 sample was a generous gift from Professor K. Kamiya of this department. Crystal structure of the Ti_3O_5 sample used was probed with a Shimadzu X-ray diffractometer XD-610 using the Cu $K\alpha$ line monochromatized by a Ni filter. The data were in accordance with those of β-Ti_3O_5 crystals.[12,13]

Results

Titanium Dioxide (Anatase and Rutile). Anatase and rutile are the low- and high-temperature phase of TiO_2, respectively. Absorption edges of anatase and rutile are located at 3.2 and 3.0 eV,[14] corresponding to 387 and 413 nm, respectively. Both of these absorb light at 308 nm. The Raman spectrum of anatase irradiated by an XeCl excimer laser (308 nm) at 80 mJ cm^{-2} $pulse^{-1}$ for 1 h is shown in

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Fig. 1(a), together with those of anatase (c) and rutile (d) before irradiation.[15] The spectrum (a) indicates a partial change into rutile. However, a closer look at the spectrum reveals the presence of a broad feature in the lower wavenumber region, in addition to the bands of anatase and rutile. In order to know the origin of this broad feature, the Raman spectrum of the β-Ti_3O_5 sample was measured and is shown in Fig. 1(e). (We did not find the Raman spectrum of β-Ti_3O_5 in the literature, so we believe that this is a new spectrum.) When the synthesized spectrum (b) (curves of anatase (c) +rutile (d) +Ti_3O_5 (e) in the 1 : 1 : 1 ratio) is compared with the measured spectrum (a), a reasonable fit was obtained. It indicates that the 308-nm irradiation caused a partial change of anatase to rutile, accompanied by the formation of Ti_3O_5 with a loss of oxygen atoms.

The result of excimer laser (308 nm) irradiation on a rutile sample is given in Fig. 2. Little change was observed.

SEM pictures of an anatase sample before and after 308-nm irradiation are shown in Fig. 3(a) and (b), and the corresponding ones for rutile in Fig. 4(a) and (b). These pictures clearly indicate that the starting materials were once melted and had resolidified. The melting point of rutile is 1855 °C. Anatase is known to change into rutile at much lower temperatures. These results show the temperature rise of the sample surface above 1855 °C in the experimental conditions. Close similarity in the SEM images in Fig. 3(b) and Fig. 4(b) indicates that the anatase sample was transformed into rutile and then melted.

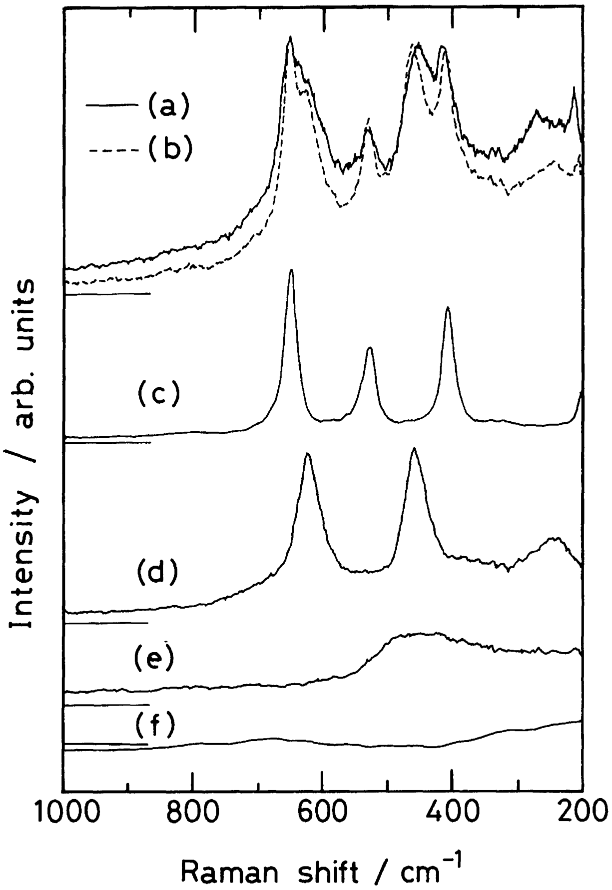

Fig. 1. Raman spectra of (a) anatase irradiated by a XeCl excimer laser (308 nm) at 80 mJ cm^{-2} pulse^{-1} for 1 h, (c) anatase, (d) rutile, (e) Ti_3O_5 without irradiation, (b): synthesized one of (c)+(d)+(e) in the 1 : 1 : 1 ratio. (f): residual difference.

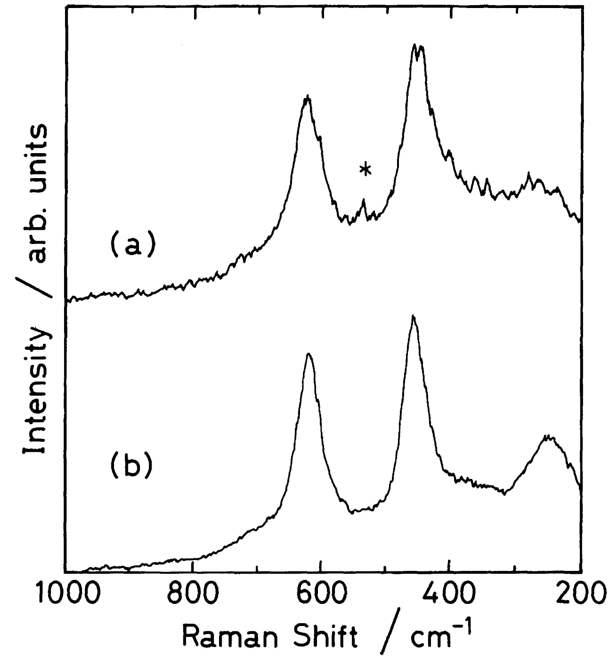

Fig. 2. Raman spectra of (a) rutile irradiated at 308 nm (76 mJ cm^{-2} pulse^{-1}, 0.5 h), in comparison with (b) that of rutile without irradiation. * spurious line due to laser plasma emission which is observed because of the poorer S/N ratio.

Hafnium Dioxide. Hafnium dioxide is transparent at 308 nm. Irradiation with 308 nm laser light (40 mJ cm^{-2} pulse^{-1}) of HfO_2 did not cause any appreciable change in its Raman spectrum, which has the character of monoclinic crystals.[16] Monoclinic (low temperature) to tetragonal (high temperature) transition occurs at ca. 1800 °C at 1 atm. The result shows that HfO_2 does not absorb light at this wavelength and hence does not undergo this phase transition even under focused laser irradiation.

Discussion

Results of the action of laser light on materials are twofold: the energy of laser light can be used directly to break chemical bonds photolytically, or it is converted to thermal energy before the occurrence of any photolytic scission events. While both modes of laser action have been manifested in organic polymer materials,[17,18] the photolytic mode is less plausible for inorganic materials with strong chemical bonds. Experimental results of laser irradiation reported in the present paper lead to an essentially thermal mechanism, i.e., the energy of laser light is converted into thermal energy and this is used to heat the samples. Focused laser irradiation can yield a large amount of thermal energy. It is known that it can instantaneously heat the sample surface to 1000—2000 °C.[19] However, the thermal energy is lost by heat conduction

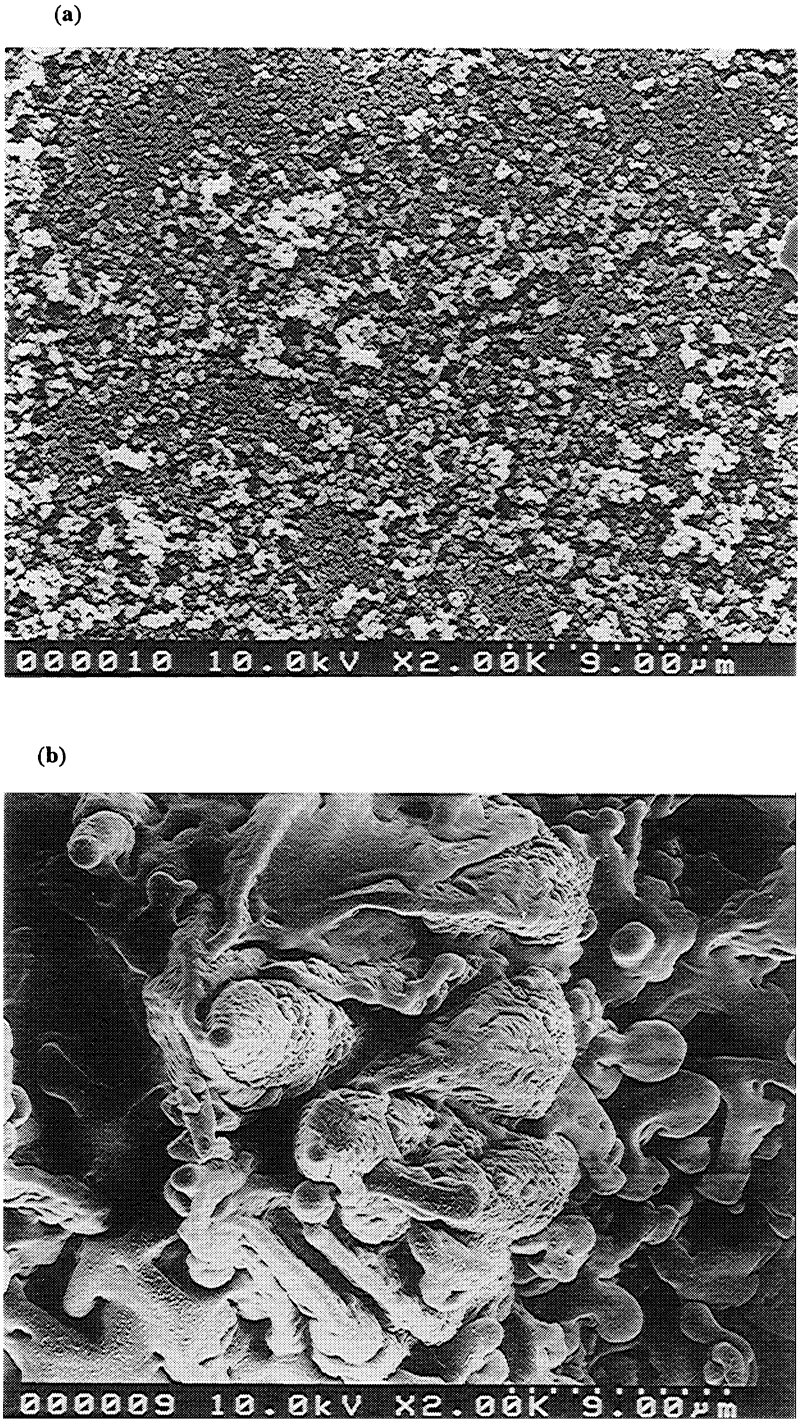

Fig. 3. SEM images of anatase (a) before and (b) after irradiation at 308 nm. The condition of irradiation is 70 mJ cm^{-2} pulse^{-1} for 0.5 h.

to the environment before the next laser pulse arrives.

Expressions for the surface temperature on pulsed-laser irradiation have been given by Lin and George[20)] and Brand and George.[21)] According to them, the time evolution of the surface temperature for a heat source at the surface of a semi-infinite solid is given as

$$T(t) = \frac{1-R}{(\pi K \rho c)^{1/2}} \int_0^t \frac{I(t-t')}{(t')^{1/2}} \mathrm{d}t' + T_0, \qquad (1)$$

where R is the reflectivity, K is the thermal conductivity, c is the heat capacity, ρ is the density, T_0 is the initial surface temperature, and $I(t-t')$ is the temporal distribution of the incident laser intensity. The maximum surface temperature rise for a rectangular pulse with constant intensity I_0 and

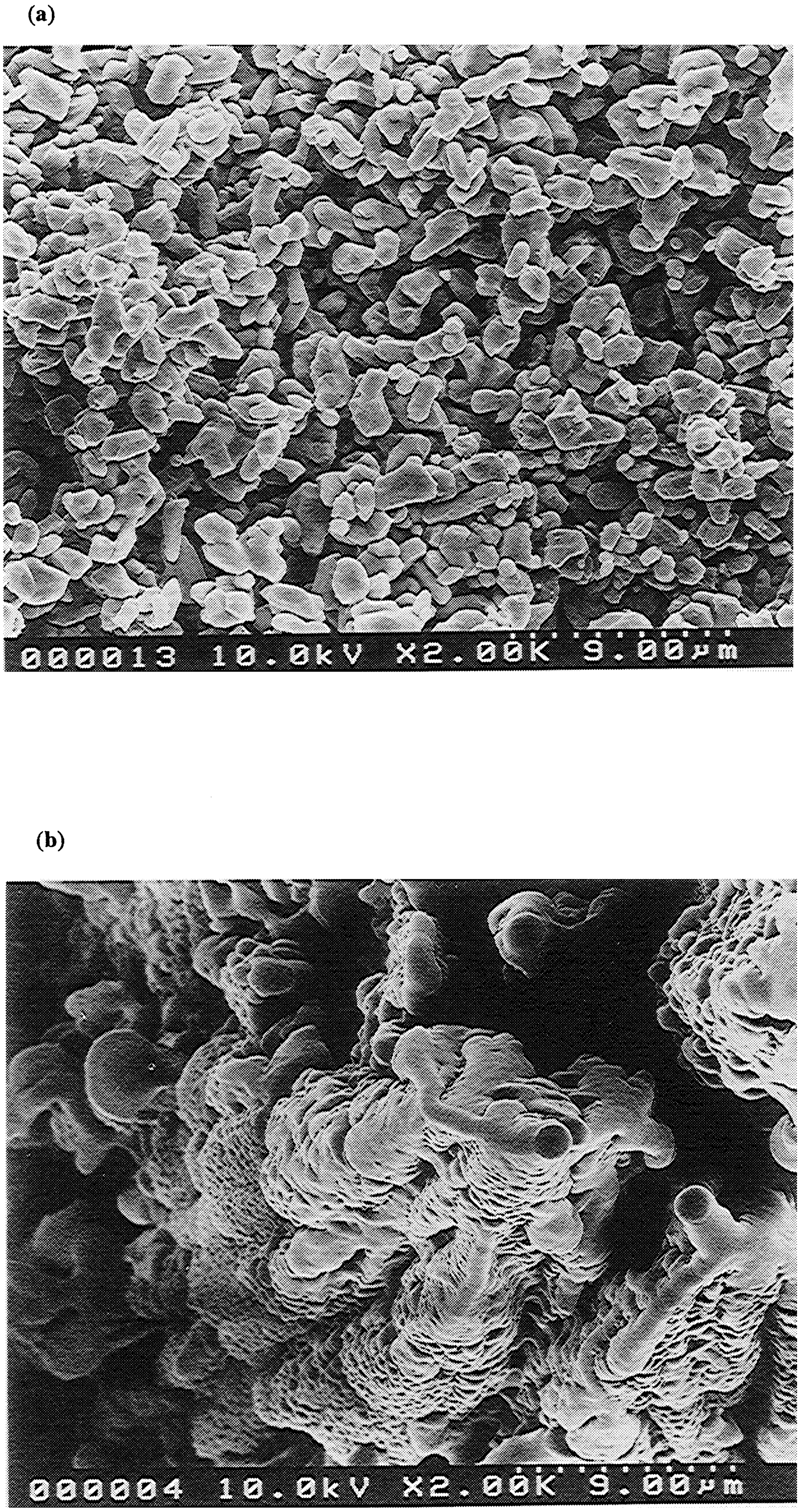

Fig. 4. The same as Fig. 3, for rutile (a) before and (b) after irradiation at 308 nm. The condition of irradiation is 85 mJ cm^{-2} pulse^{-1} for 0.5 h.

duration t_p is

$$\Delta T_s^{\mathrm{rect}} = 2I_0(1-R)t_p^{1/2}/(\pi K\rho c)^{1/2}. \qquad (2)$$

They gave the corresponding expression for a triangular pulse as

$$\Delta T_R^{\mathrm{tri}} = (4I_0/3)(1-R)t_b^{1/2}/(\pi K\rho c)^{1/2}, \qquad (3)$$

where t_b is the bottom time length, for an "increasing" triangular pulse with $I=0$ at $t=0$ and $I=I_0$ at $t=t_b$. Figure 2 in Ref. 20 gives the result for a "decreasing" triangular pulse which better approximates the real pulse as

$$\Delta T_s^{\mathrm{tri}} \approx 0.7\Delta T_R^{\mathrm{tri}}. \qquad (4)$$

The time course of surface temperature calculated by these authors for typical 20—100 ns pulses shows that the surface temperature returns to the initial value in 50—100 pulse-lengths, i.e. 1—10 μs.

We can make a very rough estimate of the maximum surface temperature on the assumption that light absorption occurs in the very thin layer close to the surface, using Eq. 4 with relevant values for TiO_2 in the case of excitation at 308 nm, $R=0.40$, $K=8\times10^{-2}$ W cm^{-1} K^{-1}, $\rho=4.25$ g cm^{-3}, $c=0.7$ J g^{-1} K^{-1}.[22] Taking the peak fluence (I_0) of the excimer laser to be 40 MW cm^{-2} and $t_b=20$ ns, we obtain a temperature rise of 2400—2500 K. Although such treatment remains a very rough initial estimate because we neglect the temperature dependence of these properties, it can give a rough picture of the temperature rise that the substrate surface experiences.

Recall the pulse duration is ca. 20 ns and the repetition rate is 5 Hz in our experimental conditions. Then the heated surface experiences rapid cooling. The sample is quickly cooled after instantaneous heating to 1900—2000 °C. The result of thermal phase transition is retained, and oxide samples remain in the high-temperature phase.

The present study demonstrates a high potentiality of Raman spectroscopy in elucidating deterioration mechanisms of metal oxide materials. Hsu et al.[23] reported Raman measurements of submicron titania coatings. The Raman method must be valuable for a similar study on optical thin films made of metal oxide materials like those reported in the present study.

Conclusions

Effects of excimer laser irradiation (308 nm) on some metal oxides relevant to optical thin films (anatase and rutile of TiO_2, and HfO_2) are studied by Raman spectroscopy. Absorbed laser light caused partial changes of anatase into rutile, a higher temperature modification of TiO_2. The laser light must have caused rapid heating of the sample, leading to thermal phase changes, the results of which are retained on rapid cooling after laser irradiation. The thermal nature of the changes is supported by SEM measurement in the anatase case. The present study demonstrates high potentiality of Raman spectroscopy in elucidating deterioration mechanisms of these oxide materials. Such a technique must be valuable for optical thin films made of these materials.

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