Preparation of Sol–Gel Derived Titanium Oxide Thin Films Using Vacuum Ultraviolet Irradiation with a Xenon Excimer Lamp

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Titanium oxide thin films are prepared by the sol-gel technique with 172 nm vacuum ultraviolet (VUV) irradiation using a Xe_2^* excimer lamp. The effect of VUV irradiation on spin-coated films was investigated by UV-visible absorption, X-ray photoelectron, Fourier transform infrared and Raman spectroscopies. The results showed that VUV irradiation causes the removal of hydroxyl and organic functional groups from the transparent coating film without causing the reduction of titanium, so that the film begins to transform into an oxide from a hydroxide. It was found that VUV irradiation onto a dried coating film is effective in accelerating the formation of Ti–O networks and crystallization. [DOI: 10.1143/JJAP.43.6315]

KEYWORDS: titanium oxide, thin film, sol-gel, vacuum ultraviolet, excimer lamp

1. Introduction

Titanium oxide (TiO_2) has been of interest for its excellent properties such as electrochemical behavior, high refractive index, and good chemical stability. Thus, TiO_2 thin films have recently attracted considerable attention due to their various applications, such as microelectronic devices, electrochromic displays, superhydrophilic films and antireflection coatings. A sol–gel process has been adopted for the formation of TiO_2 films^{1–5)} with various methods, such as electron beam evaporation,⁶⁾ ion sputtering⁷⁾ and anodic oxidation of titanium.⁸⁾

The sol-gel process is an industrially promising technique for the preparation of thin films, because it offers many advantages in terms of low energy cost, low material consumption rate, simplicity, and speedy deposition on substrates with good homogeneity as well as its nonrequirement of expensive vacuum equipment. However, to densify and remove the remaining hydroxyl and organic functional groups in the films, heat treatment at several hundred degrees is required after coating. The heat treatment at a high temperature will limit a substrate to a thermostable material, and also has the problem of thermal damage.

Recently, the photochemical reaction using an excimer lamp^{9,10)} as a vacuum ultraviolet (VUV) light source with easy handling has been used for the cleaning of liquid crystal panels, or the surface modification of polymeric materials.¹¹⁻¹³⁾ These applications utilize the cleavage of chemical bonds by photon energy, and the oxidation reaction due to active oxygen species $(O(^{1}D))$ and/or ozone (O_{3}) generated via the absorption of VUV light of oxygen molecules.¹⁴⁾ The process using photoirradiation is expected as a new technique without thermal damage for fabricating a sol-gel thin film on thermolabile substrates such as polymer sheets. If the processing temperature for sol-gel thin film formation decreased, it would be possible to extend an application sphere or to find a new usage. Moreover, what irradiation onto a specific region is also possible by a masking method using light and is considered an advantage. The photoirradiation solution-phase processing of such inorganic materials, such as silicon oxide¹⁵⁻¹⁸⁾ and tantalum oxide¹⁹⁻²¹⁾ has been reported. However, there is little information on the chemical states and crystal structures of the titanium oxide films prepared by the sol-gel process using excimer lamps because few reports are available.²²⁾

In this study, titanium oxide films were synthesized by combining the sol-gel process and photoirradiation using a Xe_2^* excimer lamp. The formation of the films was investigated by optical, chemical and structural measurements.

2. Experimental

Thin films of TiO₂ were prepared by a spin-coating method. To prepare the coating solution, 5 ml of titanium isopropoxide (Ti(O-iC₃H₇)₄) was dissolved in 30 ml of dehydrated ethanol (C₂H₅OH). The solution was mixed with continuous stirring at room temperature. Then, 0.26 ml of 60% nitric acid and 0.31 ml of distilled water were added and stirred for 3 h.

Quartz glass plates were used as substrates. They were photochemically cleaned by irradiating VUV light (wavelength 172 nm) of 100 W/m^2 for 2 min using a Xe^{*}₂ excimer lamp (Quark Systems Co., Ltd.) in air. The coating solution was spin-coated onto the substrate at 500 rpm for 10 s and at 2500 rpm for 40 s. After drying at 60°C for 10 min using a hot plate, the coatings were irradiated with VUV light using the same Xe₂^{*} excimer lamp as that used during the cleaning of the substrate in N₂ gas with an oxygen concentration of 10% with a flow rate of 1 l/min, followed by annealing in an electric furnace for 1 h at various temperatures between 200 and 500°C. The distance between the sample and the lamp window was set at 2 mm. In addition, the thin films heattreated at various temperatures between 200 and 600°C without irradiation were also produced. The thickness of the dried film was determined to be about 150 nm using a Sloan Dektak-3030ST stylus profilometer. A scheme for the preparation of coatings to obtain the titanium oxide films is shown in Fig. 1.

The optical transmittance spectra of the films were obtained with a Hitachi U-3000 spectrophotometer in the 200–700 nm wavelength range. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI–Perkin–Elmer model 5500 small-area spectrometer system, consisting of a concentric hemispherical analyzer (CHA) and a MgK α X-ray source (1253.6 eV) at 350 W. Photoelectron binding energies were calibrated at the C1s binding energy of the hydrocarbon at 285 eV. Fourier transform infrared (FT-IR)

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Fig. 4. Ti2p and O1s XPS spectra from spin-coated titanium oxide films (a) dried, heat-treated at (b) 200°C, (c) 600°C and (d) VUV-irradiated.

observed. The titanium peaks for irradiated films are located at 458.7 eV (Ti2p_{3/2}) and 464.4 eV (Ti2p_{1/2}), and are in agreement with the value of the Ti⁴⁺ valence state of TiO₂.²⁸⁾ This indicates that VUV irradiation under these irradiation conditions will not induce a significant change in Ti chemical states having different oxidation states, such as Ti³⁺ and Ti²⁺.^{23,24)} In the dried film, the O1s peak position is centered at 530.5 eV in Fig. 4(a) and this is mainly attributed to hydroxide. Another small component of high binding energy due to the presence of adsorbed water or OH²⁹⁾ was detected. The intensity in this component attenuates with heat treatment and VUV irradiation. Then the binding energy of the O1s peak shifted to low binding energies, indicating the formation of an oxide.²⁸⁾

Figure 5 shows the FT-IR spectra of the titanium oxide films prepared by drying, heat treatment and VUV irradiation. The absorption bands at approximately 3400 and $1610 \,\mathrm{cm}^{-1}$ are assigned to the vibrations of the O-H stretching and H-O-H bending, respectively, while the bands at $1350-1420 \text{ cm}^{-1}$ are assigned to the C-H bending vibrations in organic starting materials. With the increase in heat treatment temperature, the intensity of these absorption bands decreased, and they disappeared at 400°C. The disappearance of these absorption bands suggested the removal of hydroxyl groups and H₂O molecules, and the decomposition of the organic compounds from the film was achieved. On the other hand, the absorption band corresponding to the Ti-O bond at approximately 840 cm⁻¹ sharpens as temperature increases, suggesting the densification of the films. As shown in Fig. 5(d), the irradiation of the VUV light onto the films decreases the absorption due to C-H and O-H. To examine the impact of irradiation on solgel reactions such as a condensation reaction, we performed the VUV irradiation before the heat treatment. The FT-IR spectra of the films heat-treated at 300°C before and after the VUV irradiation are shown in Figs. 5(e) and 5(f), respectively. In the films heat-treated after the VUV irradiation, the band of O-H has almost disappeared and the band of Ti-O



Y. NAGANUMA et al.

6317



Fig. 5. FT-IR spectra of spin-coated titanium oxide films (a) dried, heattreated at (b) 200°C, (c) 400°C, (d) VUV-irradiated, and heat-treated at 300°C (e) before and (f) after VUV irradiation.

bond is sharp compared with that of the merely heat-treated one. The FT-IR spectrum of the film heat-treated at 300°C after the VUV irradiation is comparable to that of the film heat-treated at 400°C. This result suggests that many more Ti–O networks are formed owing to progress of the dehydration and dealcoholization when VUV irradiation is performed. This, in addition, is probably ascribed to the effect of the incorporation and oxidation of active oxygen species in the films by VUV irradiation.^{13,20,21}

To evaluate the crystallinity of the prepared films, the Raman spectra were measured. The changes in the Raman spectra of the films heat-treated at 300°C before and after VUV irradiation are shown in Fig. 6. The anatase phase of TiO₂ has Raman bands at approximately 145, 396, 517 and $637 \,\mathrm{cm}^{-1}$.³⁰⁾ When the film was heat-treated at $300^{\circ}\mathrm{C}$ without VUV irradiation, the intensity of the Raman bands originating from an anatase is small and the film is almost an amorphous structure. Nevertheless it should be noted that the VUV irradiation to the film prior to heat treatment increases the intensity of the Raman band at 145 cm^{-1} , indicating that the amorphous film transforms to its anatase. In irradiation from a light source, the influence of heat on the sample is negligible, because infrared radiation is not generated. Consequently, these observations suggest that VUV irradiation before the heat treatment of the films advances crystallization at low temperatures. This is so because the reaction in the subsequent heat treatment was assisted because only the VUV irradiation without the heat treatment already removes hydroxyl and organic functional groups, as shown in Fig. 5(d). Furthermore, it is likely that the



Fig. 1. Schematic diagram for preparation of titanium oxide thin films.

absorption spectra were recorded over a range of wave numbers from 4000 to 400 cm^{-1} on a Shimadzu FT-IR-8200PC spectrometer using the diffuse reflection method at a resolution of 4 cm^{-1} with a TGS (Triglycine Sulfate) detector. Raman spectra were recorded using a JASCO NR-1800 spectrometer. An argon ion laser with a wavelength of 488 nm was used as the light source. The acquisition time per scan was set at 200 s. Gold-deposited quartz glass plates were used as substrates for FT-IR and Raman measurements.

3. Results and Discussion

Figure 2 shows the change in the optical transmittance spectra of the dried films after VUV irradiation and heat treatment. These transmittances are more than 70% in the visible range. The spectrum of the irradiated film has a sharp



Fig. 2. Optical transmittance spectra of spin-coated titanium oxide films dried, VUV-irradiated and heat-treated at 400°C.



Fig. 3. XPS spectra of spin-coated titanium oxide films (a) before and (b) after VUV irradiation. The inset shows the N1s XPS spectra.

absorption edge similarly to that of the film heat-treated at 400°C and an interference fringe due to multiple reflections was observed. The transmittance of the VUV-irradiated film was higher than that of the dried one near the absorption edge. This suggests that the decomposition of the starting materials occurred by irradiation.

The composition and chemical states of titanium oxide films were investigated by XPS. Since Ar^+ ion sputtering causes a reduction of the TiO₂ surface,^{23,24)} the XPS measurements were performed without Ar^+ ion sputtering for removing surface contamination. Figure 3 shows widescan XPS spectra obtained from dried titanium oxide coatings before and after the VUV irradiation. For the nonirradiated film the peaks of carbon, oxygen, nitrogen and titanium were observed, whereas for the VUV-irradiated film the peak of nitrogen was absent in the observed spectra. This result can be explained as follows: The intensity of the VUV light irradiated from the lamp window under atmospheric pressure is given by^{25,26)}

$$I = I_0 \exp(-\varepsilon cd), \tag{1}$$

where I_0 is the intensity of incident light, ε is the absorption coefficient of an oxygen molecule in VUV light with a wavelength of 172 nm, c is the oxygen concentration and d is the distance between the sample and the lamp window. By calculating eq. (1) using the absorption coefficient reported by Inoue et al.,¹⁴⁾ we noted that about 74% of the photon in the incident light had reached the sample surface. The photon energy of the VUV light, i.e., 698 kJ/mol of the Xe^{*}₂ excimer lamp, is sufficiently high as compared with the binding energy of the chemical bonds, such as C-C (347.7 kJ/mol), C–O (351.5 kJ/mol) and C–N (291.6 kJ/ mol).²⁷⁾ Thus VUV irradiation can break chemical bonds. Furthermore, oxygen molecules generate active species by absorbing the VUV light, and the conversion to the volatile products of nitrogen due to the strong oxidation of the active species results in nitrogen elimination.

The Ti2p and O1s XPS spectra from titanium oxide films after drying, heat treatment and VUV irradiation are shown in Fig. 4. The XPS measurements showed no explicit change in Ti2p spectra due to the heat treatment and VUV irradiation although a slight shift of the peak position was



Fig. 6. Raman spectra of spin-coated titanium oxide films heat-treated at 300° C (a) before and (b) after VUV irradiation.

incorporation of the active oxygen species to the films brings about the decrease in the density of defects,^{20,21,31)} and accelerates crystallization during the heat treatment. The films prepared using the VUV irradiation are expected to have a lower defect density than the films which were only heat-treated. This may have brought about the increase in the hardness of the films, and the decrease in the leakage current density in I-V characteristics.

4. Conclusions

The preparation of titanium oxide thin films by the sol-gel technique using 172 nm VUV irradiation with an excimer lamp was investigated. VUV irradiation causes the removal of hydroxyl and organic functional groups from the transparent coating film without causing the reduction of titanium. Then the film begins to transform into an oxide from a hydroxide. It was found that the VUV irradiation before the heat treatment promotes the formation of the Ti-O networks and crystallization at comparatively lower temperatures in subsequent heat treatment as compared with that under the nonirradiation condition. These results suggest that the photoirradiation sol-gel process is promising for preparing titanium oxide films on the thermolabile substrates used in optical and electronic applications. It is conceivable that this technique is applicable to the preparation of other metal oxides.

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