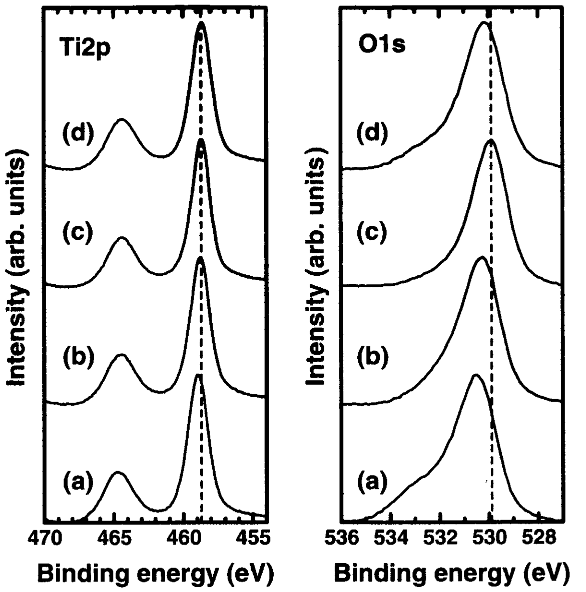

Fig. 4. Ti2p and O1s XPS spectra from spin-coated titanium oxide films (a) dried, heat-treated at (b) 200°C, (c) 600°C and (d) VUV-irradiated.

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 Ti^{4+} valence state of TiO_2.[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 Ti^{3+} and Ti^{2+}.[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 OH[29] 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 cm^{-1} are assigned to the vibrations of the O–H stretching and H–O–H bending, respectively, while the bands at 1350–1420 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 H_2O 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 sol–gel 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 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]

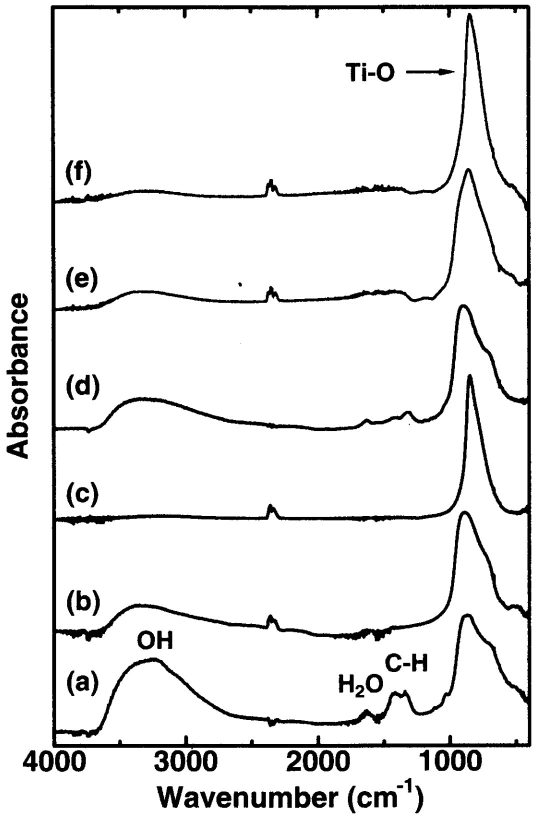

Fig. 5. FT-IR spectra of spin-coated titanium oxide films (a) dried, heat-treated at (b) 200°C, (c) 400°C, (d) VUV-irradiated, and heat-treated at 300°C (e) before and (f) after VUV irradiation.

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 TiO_2 has Raman bands at approximately 145, 396, 517 and 637 cm^{-1}.[30] When the film was heat-treated at 300°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