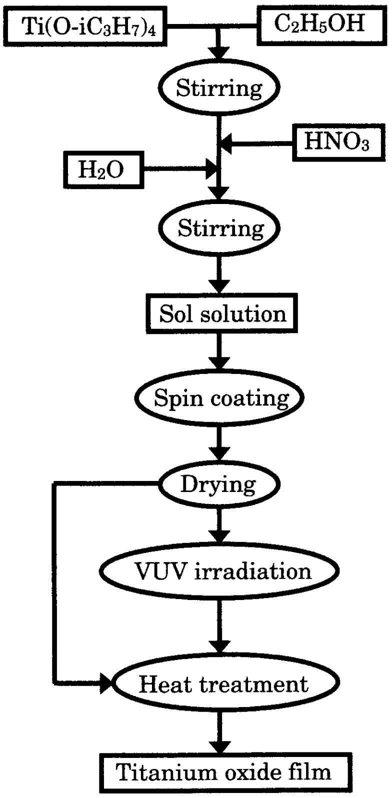

Fig. 1. Schematic diagram for preparation of titanium oxide thin films.

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 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.

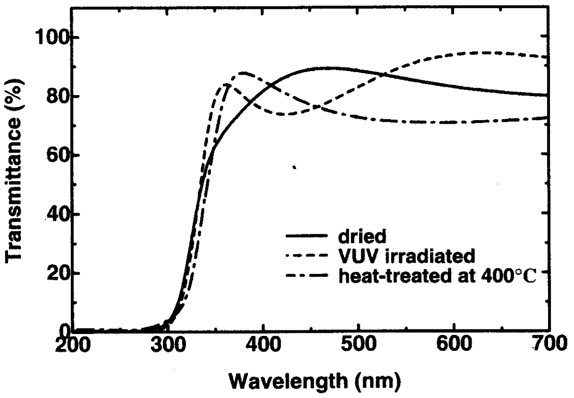

Fig. 2. Optical transmittance spectra of spin-coated titanium oxide films dried, VUV-irradiated and heat-treated at 400°C.

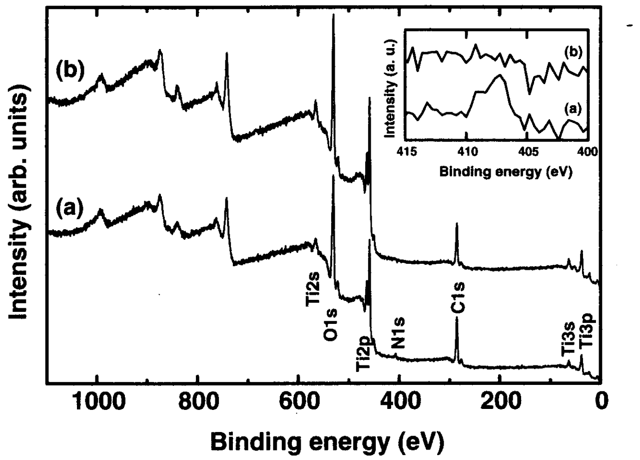

Fig. 3. XPS spectra of spin-coated titanium oxide films (a) before and (b) after VUV irradiation. The inset shows the N1s XPS spectra.

The composition and chemical states of titanium oxide films were investigated by XPS. Since Ar$^+$ ion sputtering causes a reduction of the TiO$_2$ surface,[23,24] the XPS measurements were performed without Ar$^+$ ion sputtering for removing surface contamination. Figure 3 shows wide-scan 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)]

$$I = I_0 \exp(-\varepsilon c d), \qquad (1)$$

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