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# 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.
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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 sputtering[7] 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 ($O(^1D)$) 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 oxide[15–18] and tantalum oxide[19–21] 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 $TiO_2$ were prepared by a spin-coating method. To prepare the coating solution, 5 m*l* of titanium isopropoxide ($Ti(O\text{–}iC_3H_7)_4$) was dissolved in 30 m*l* of dehydrated ethanol ($C_2H_5OH$). The solution was mixed with continuous stirring at room temperature. Then, 0.26 m*l* of 60% nitric acid and 0.31 m*l* 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 $Xe_2^*$ excimer lamp as that used during the cleaning of the substrate in $N_2$ 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 heat-treated 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$\alpha$ 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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