Effects of Vacuum Ultraviolet Light Illumination on the Residual Stress in Sol–Gel-derived Titanium Dioxide Films

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This study investigated effects of vacuum ultraviolet (VUV) illumination on the residual stress of sol–gel-derived titanium dioxide (TiO_2) films. After firing at 500 °C, VUV pre-illumination to TiO_2 precursor film decreases residual stress more than 30%. This effect is explained by the great shrinkage that occurs during VUV illumination.

Titanium dioxide (TiO_2) thin films attract great interest because of their intriguing photoinduced wettability conversion.[1] Their surfaces reach a highly hydrophilic state when UV is illuminated on the surface of polycrystalline TiO_2 coating. This property has been applied in antifogging and self-cleaning coatings for products such as automobile side view mirrors, window films, exterior tiles, and highway wall panels.[2] Recently, Shibata et al. investigated the stress effect on photoinduced hydrophilicity of polycrystalline anatase thin films using substrate materials with different thermal expansion coefficients.[3] They prepared polycrystalline anatase films using sputtering and demonstrated that external tension enhances photoinduced hydrophilicity, but compression inhibits it.

Crystallization is typically an important requirement for advanced functional thin films of inorganic materials because the coatings' crystal structure fosters various properties. Heat treatment is usually employed at high temperatures to allow sufficient crystallization. Because of the growing need for coatings on large substrates and plastic films, lowering processing temperatures is increasingly important. Crystallization can be enhanced through improving precursor film structures to those that facilitate crystallization. Photochemical processing using an excimer lamp as a vacuum ultraviolet light (VUV) source has been used for low-temperature crystallization of sol–gel-derived precursor films.[4–8] Various authors have reported beneficial effects of VUV illumination on crystallization and densification of sol–gel-based TiO_2 precursor films through heat treatment.[7,8] However, VUV illumination effects on residual stress in crystallized TiO_2 films have not been well investigated. For this study, we prepared TiO_2 films with and without VUV illumination on a Si(100) substrate and investigated VUV illumination effects on residual stress in crystallized sol–gel-derived TiO_2 films.

As substrates, we used 0.5-mm thick, 10-cm-diameter Si wafers (crystalline face ⟨100⟩; Aki Corp., Miyagi, Japan). Amorphous TiO_2 precursor films were prepared on Si substrates using a spin-coating method with a commercial titanium tetraisopropoxide solution (NDH-510C; Nippon Soda Co., Ltd.) at 4000 rpm for 15 s. After drying, the substrates were immersed for 1 h in an O_3 atmosphere at room temperature. Then, VUV light was illuminated for 1 h using a Xe excimer lamp (172-nm wavelength, UER-20; Ushio Inc., Tokyo, Japan) in dry N_2 at room temperature. The illumination photointensity was $20\,\mathrm{mW{\cdot}cm^{-2}}$. The substrates were subsequently heated at 500 °C for 1 h in air. For comparison, a TiO_2 film that received only heat treatment (no VUV pre-illumination before firing) was also prepared.

Surface roughness of these two films was evaluated using atomic force microscopy (AFM, MMAFM-2; Veeco Instruments, CA, U.S.A.). X-ray diffractometry (XRD, PW-3050; Philips Co., Amsterdam, The Netherlands) was used with a fixed X-ray incident angle of 1.0° to evaluate the crystalline phase. The full width at half-maximum (FWHM) value of the anatase (101) peak was measured. Film thickness and the refractive index were evaluated using ellipsometry (V-VASE; J. A. Woolam Co., Inc., Tokyo, Japan). The water contact angles on the thin film were measured using a black light under $10\,\mu\mathrm{W{\cdot}cm^{-2}}$ UV-light illumination. The thin films' hydrophilicity was evaluated by measuring the water contact angle (CA-X; Kyowa Interface Science Co., Ltd., Saitama, Japan). The experimental error of that measurement was 1°. The water droplets were $2.0\,\mu\mathrm{L}$.

The films' residual stress was evaluated using high-power XRD (D8 Discover; Bruker AXS GmbH, Tokyo, Japan) with a general area detector diffraction system and a 1/4 cradle stage. The shape of the Debye ring of anatase 101 reflection ($2\theta = 25°$) was obtained directly using this detector with an exposure period of 600 s/frame. The ring was obtained by measuring two ψ values by changing the ϕ value (0–180°; 20° steps). We measured the curvature of the resultant Debye ring and calculated the residual stress value using a Debye ring fitting system of the facility. The fundamental equation for stress characterization using the obtained two-dimensional X-ray diffraction data are given as,[9,10]

$$p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{13}\sigma_{13} + p_{22}\sigma_{22} + p_{23}\sigma_{23} + p_{33}\sigma_{33} = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right)$$

where

$$p_{ij} = \begin{cases} (1/E)[(1+\nu)f_{ij} - \nu] = (1/2)S_2 f_{ij} + S_1 & \text{if } i = j \\ (1/E)(1+\nu)f_{ij} = (1/2)S_2 f_{ij} & \text{if } i \neq j \end{cases}$$

and

$$f_{11} = h_1^2 \quad f_{12} = 2h_1h_2 \quad f_{22} = h_2^2$$
$$f_{13} = 2h_1h_3 \quad f_{23} = 2h_2h_3 \quad f_{33} = h_3^2.$$

Therein, f_{ij} are the strain coefficients expressed by the unit vector of the diffraction vector $\boldsymbol{H}_{hkl}$ in sample coordinates. The $\ln(\sin\theta_0/\sin\theta)$ component represents the diffraction cone distortion at a particular $(2\theta, \psi)$. For isotropic materials, only two independent elastic constants exist: Young's modulus E and Poisson's ratio ν and the macroscopic elastic constants $(1/2)S_2 = (1+\nu)/E$ and $S_1 = -\nu/E$. The stress tensor can be

Table 1. FWHM value of the anatase (101) peak, film thickness, and refractive index for prepared films

Treatment	FWHM /degree	Film thickness /nm	Refractive index
As-coated	—	703	1.55
after O_3 + VUV (in N_2)	—	116	1.98
after firing (without VUV)	0.37	91	2.08
after firing (with VUV)	0.33	77	2.28

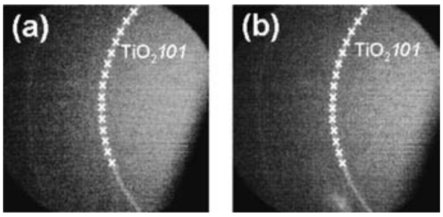

Figure 1. Debye rings of anatase 101 for the films: (a) without VUV pre-illumination, (b) with VUV pre-illumination.

determined by fitting the data points to the first equation using least-squares method.

No phase existed in the treated films except for anatase phase. Table 1 shows the FWHM value of the anatase (101) peak, film thickness, and refractive index for films with and without VUV pre-illumination. These results, which agree with those of precedent studies,[8] imply that VUV pre-illumination increases crystallinity and density of anatase polycrystalline films.

Figure 1 shows Debye rings of anatase 101 for films with and without VUV pre-illumination. Precise values of Young's modulus and Poisson's ratio on anatase were not reported. Therefore, we employed the values of rutile (Young's modulus: 287 GPa, Poisson's ratio: 0.268)[11] for residual stress calculation. The values obtained for the film without VUV pre-illumination (normal film) were 384 ± 81 MPa (σ_{11}) and 393 ± 73 MPa (σ_{22}); those for the film with VUV pre-illumination were 203 ± 89 MPa (σ_{11}) and 266 ± 81 MPa (σ_{22}). All stress was tension, as expected from the thermal expansion coefficients.[12] These results show that VUV pre-illumination decreases residual stress more than 30%, even when subsequent firing conditions are identical.

The TiO_2 precursor film is densified and shrunk remarkably by VUV pre-illumination at room temperature before firing (Table 1). During firing, film crystallization occurs around 300 °C[8] with additional slight shrinkage. The film volume is almost fixed and the stress state is nearly zero at that temperature. The film receives compressive stress from the substrate because of larger thermal expansion coefficients of anatase when the temperature is increased to 500 °C. Then, during cooling from the firing temperature, the stress is gradually released and reversed to tension. Finally, a slight tensile stress remains in the film at room temperature.

For the normal firing film, crystallization occurs at temperatures higher than 400 °C and great shrinkage occurs. The stress state is almost zero at this temperature. Therefore, the compressive stress at 500 °C is expected to be smaller than for the film with VUV pre-illumination. After cooling to room temperature, more tensile stress remains in the film (Figure 2).

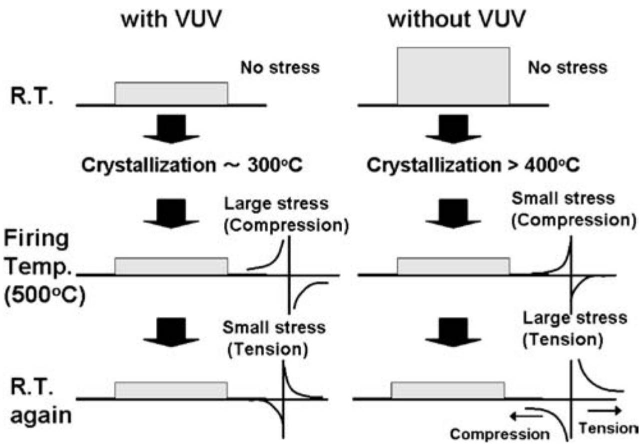

Figure 2. Shrinkage and stress states of films.

Surface roughness differences in these two films were negligible (a few nanometers), as confirmed using AFM. The photoinduced hydrophilicizing rate of the film with VUV pre-illumination was higher than that of the film without VUV pre-illumination.[13] Although VUV pre-illumination decreases residual stress, its difference is within a few-hundred-MPa order. The stress affecting photoinduced hydrophilicity of anatase polycrystalline thin films is reportedly of GPa order.[3] Therefore, the high photoinduced hydrophilicizing rate of the film with VUV pre-illumination is attributable to its high crystallinity[14] (Table 1).

We investigated the effect of VUV illumination on the residual stress in crystallized sol–gel-derived TiO_2 films. After firing at 500 °C, VUV pre-illumination to the TiO_2 precursor film decreases residual stress by more than 30% because of shrinkage that occurs during VUV illumination.

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