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Short communication

Preparation of TiO_2 thin film on SiO_2 glass by a spin coating–pyrolysis process

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Abstract

Highly transparent titanium oxide thin films were prepared on silica glass from a titanium naphthenate precursor. Films prefired at 500 °C for 30 min were heat-treated at 600 °C for 30 min in air. High resolution X-ray diffraction analysis was used for characterizing the crystallinity of the TiO_2 film. A sharp absorption edge of the TiO_2 film was observed. The estimated energy band gap for the film is larger than that of single crystal.

Keywords: A. Films; C. Optical properties; D. TiO_2

1. Introduction

Recently, titanium oxide (TiO_2) thin films have been emerged as one of the most promising oxide materials owing to their optical, electrical and photoelectrochemical properties. Many studies on TiO_2 thin films formed by conventional and advanced sol–gel processes have been reported [1–3]. As far as we know, however, previous studies indicate that the properties of TiO_2 films appear to strongly depend on the process conditions and starting materials used in the processes, because titanium alkoxide, which is commonly used in sol–gel method, is very unstable in air and demands a complicated procedure for the preparation of the coating sol. Furthermore, it should be noted that vaporization of the additives, such as alcohol, water and catalyst, etc., during prefiring and annealing might cause unwanted cracks and pores in the coating. On the other hand, in our work using a metal naphthenate precursor [4], prefiring involved the pyrolytic conversion of titanium naphthenate into TiO_2, while the final annealing produced the solid-state reaction. By using titanium naphthenate, it was observed [4] that annealed films were smooth and possible crack- and pore-free, while defects were easily observed at the surface of metal alkoxide derived films. However, during annealing at 600 °C, surface roughness was increased by abnormal grain growth probably due to sodium or calcium diffusion near the interface between film and soda-lime-silica glass (SLSG) substrate, resulting in higher root mean square (RMS) roughness [4].

In this work, we prepared TiO_2 film on alkali-free silica glass (SG) from titanium naphthenate to eliminate the effects of substrate on the film's properties.

2. Experimental procedure

The preparation for the TiO_2 thin films from titanium naphthenate is described in detail in our previous work [4]. Briefly, a precursor sol was prepared by mixing titanium

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naphthenate (Soekawa Chemical Co., Ltd., Japan) and toluene (concentration: 3 wt.% Ti/100 ml sol). SG substrates were cleaned in distilled water, immersed in H_2O_2 and finally rinsed in toluene. The precursor sol was spin coated onto the cleaned SG at 1500 rpm for 10 s. The as-deposited film was prefired at 500 °C for 10 min in air. The coating process was repeated three times. The final annealing was performed at 600 °C for 30 min in air by directly inserting the samples into a preheated tube-type furnace, followed by fast cooling.

The crystallinity of the annealed film was examined by high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands). Transmittance in the visible wavelength range was observed by using a UV–visible–NIR spectrophotometer (Cary 500 Scan, Varian Co., Australia). The surface roughness and topology of the film were studied with a scanning probe microscope (SPM, XE-200, PSIA, Korea). All the SPM measurements were performed in air using the tapping mode.

3. Results and discussion

Fig. 1 shows the XRD (Radiation used: Cu Kα) curve of TiO_2 thin films deposited on SG substrate. The XRD pattern consists of only anatase peaks such as (1 0 1) and (0 0 4) reflections. The films after prefiring exhibit amorphous character, not shown here.

Fig. 2 shows the visible spectra in the wavelength range 300–900 nm and SPM image of the TiO_2 film. Relative high transmittance at visible range and a clear absorption edge of the TiO_2 were observed. The high transmittance of the TiO_2 film is attributed to the small particle size, which eliminates light scattering [4,5]. The smoothness of the surface of the TiO_2 thin film from SPM analysis is relatively high. It is difficult to find three-dimensional abnormal grain growth for the TiO_2/SG structure, while, at 600 °C, the TiO_2 film coated on soda-lime-silica glass substrate contained needle-shaped abnormal grains owing to nonstoichiometry of the TiO_2 film [4]. We assumed that formation of the second phases was probably conducted by Na or Ca diffusion near the interface between TiO_2 and SLSG substrate [4]. We may reasonably conclude that, at the annealing temperature of 600 °C, SG substrate is more favorable than SLSG substrate to obtain highly transparent TiO_2 thin film in visible spectra range and smooth surfaces when using the spin coating—pyrolysis process with a titanium naphthenate precursor.

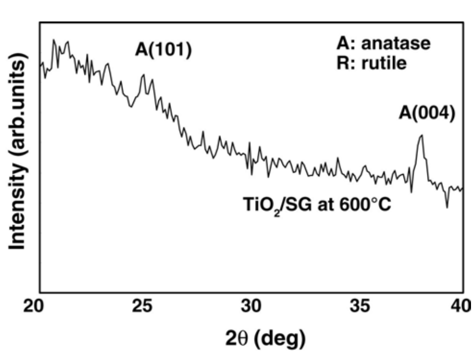

Fig. 1. XRD patterns of TiO_2 film on SG substrate annealed at 600 °C.

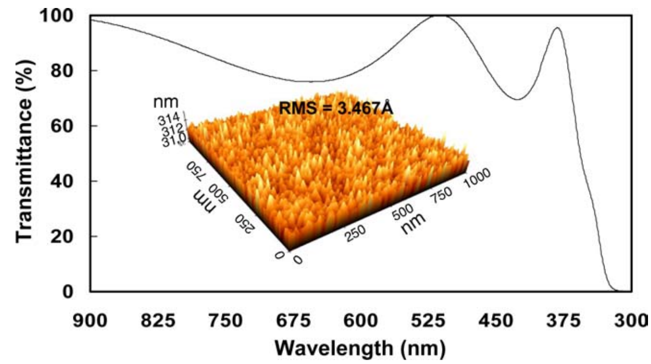

Fig. 2. Transmittance at visible range and SPM image of the TiO_2 thin film after annealing at 600 °C.

The optical absorption coefficient, α, is defined as,

$$I = I_0\,e^{-\alpha t} \tag{1}$$

where I is the intensity of transmitted light; I_0, intensity of incident light; and t, thickness of TiO_2 film. As the transmittance is defined as I/I_0, we obtain α from Eq. (1). In the direct transition semiconductor, α and optical energy band gap (E_g) are related by [6],

$$\alpha = (h\nu - E_g)^{1/2} \tag{2}$$

where h is Plank's constant, and ν is the frequency of the incident photon. Fig. 3 shows the plot of α^2 versus $h\nu$. The dependence of α^2 to $h\nu$ indicates that TiO_2 film on SG is a direct transition-type semiconductor. The photon energy at the point where α^2 is zero is E_g. Then E_g is determined by the extrapolation method [7]. Optical band gap, E_g, is 3.75 eV, as shown in Fig. 3. The estimated value of the band gap for the film is larger than for TiO_2 bulk (3.3 eV). The films consisting of fine crystallites show 'blue shift' [8]. We assume that the increase in the band gap is due to the

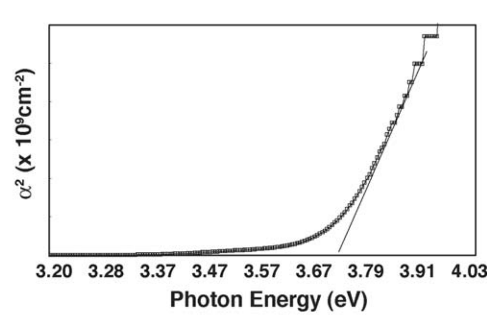

Fig. 3. Square of the absorption coefficient as a function of photon energy for the TiO_2 film after annealing at 600 °C.

quantum size effect (QSE), which occurs for semiconductor particles below 100 nm.

4. Conclusions

TiO_2 film was prepared on SG substrate at 600 °C from a titanium naphthenate precursor. Amorphous TiO_2 was crystallized to anatase TiO_2 film at the annealing temperature of 600 °C. The surface of the TiO_2, showing a high transmittance at the visible range, reveals relatively high surface smoothness without abnormal grain growth. The estimated value of the band gap for the film is larger than the intrinsic band-gap of anatase-TiO_2 (3.3 eV).

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