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Nickel-doped titanium oxide films prepared by chemical solution deposition

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15 mol% nickel-doped titanium oxide thin films were prepared from metal naphthenate precursors. Films prefired at 500 °C for 10 minutes were annealed at 600 °C for 30 minutes in air. The crystallinities of the annealed films were investigated by a high resolution X-ray diffraction system. A surface morphological study was made to characterize the surface structure of the films. A sharp absorption edge of the films was observed. The films containing nickel showed a shift towards the visible in the absorption threshold.

Key words: Nickel, TiO_2 film, crystallinity, absorption edge

Introduction

TiO_2 has been recognized as one of the better photocatalysts in heterogeneous photocatalytic applications as it combines two important complementary features for a photocatalyst: good UV absorption efficiency for the light harvesting process and good adsorption capacities, due particularly to the density of OH^- groups of amphoteric character. However, the band gap energy requires that near-UV light be used to photoactivate this very attractive photocatalyst [1-3]. Unfortunately, in solar energy applications only ~3% of the solar light is absorbed. It would be advantageous, therefore, if this metal oxide semiconductor (SC) could be photosensitized by visible light.

Doping TiO_2 with metal cations has been attempted for photo-catalytic applications by shifting the threshold for photonic excitation of the titanium oxide towards the visible [4-6]. However, as far as we know, there is little information on preparing Ni-doped TiO_2 thin films by chemical solution deposition (CSD).

In this study, we report on the preparation of transparent Ni-doped TiO_2 thin films on soda-lime-silica glass (SLSG) substrates by CSD using metal naphthenates as precursors.

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Experimental Procedure

The preparation for the films from metal naphthenates is described in detail in our previous paper [7]. Briefly, a precursor sol was prepared using Ti - and Ni - naphthenates (Nihon Kagaku Sangyo Co., Ltd., Japan) and by diluting the sol with toluene (concentration: 4 wt% metal / 100 ml sol). The nickel contents, as mol percentage, were 0 and 15, indicated as T100 and T85N15, respectively. The SLSG 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 SLSG substrates at 1500 rpm for 10 s. The as-deposited films were prefired at 500 °C for 10 minutes in air. The coating process was repeated five times. A final annealing was performed at 600 °C for 30 minutes in air.

The crystallinities of the films were investigated by high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands). Transmittance in the visible wavelength range was observed by using a ultra violet (UV) – visible – near infrared (NIR) spectrophotometer (Cary 500 Scan, Varian Co., Australia). The thickness of the annealed film was approximately 0.6-0.7 μm, as determined by observation of fracture cross-sections using a field emission – scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Japan). The surface structures of the films were studied with FE-SEM.

Results and Discussion

Figure 1 shows XRD patterns of the films after annealing. The XRD pattern of T100 contains only the

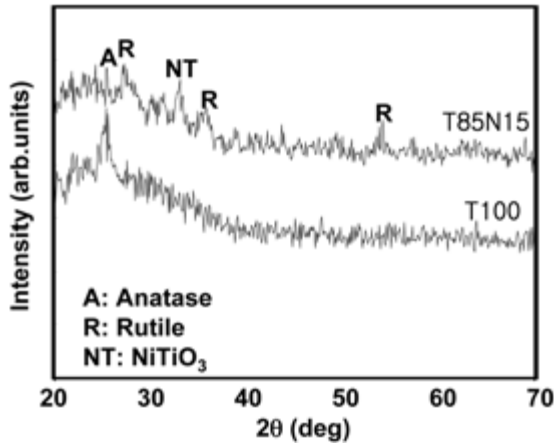

Fig. 1. XRD patterns of films after annealing.

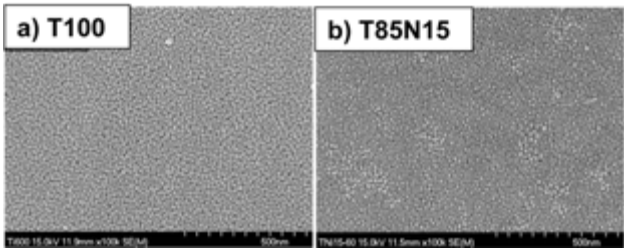

Fig. 2. FE-SEM photographs of the films on SLSG substrates after annealing at 600 °C.

anatase (110) reflection. The films after prefiring exhibited an amorphous character, not shown here. By contrast, rutile as well as $NiTiO_3$ reflections were obtained by Ni-doping at the same annealing temperature. There were no peaks for nickel oxide. Hence nickel oxide reacted with TiO_2 during annealing to form $NiTiO_3$. Ni would increase the number of oxygen vacancies in the TiO_2 crystal structure. These oxygen vacancies are responsible for the enhancement of the transformation from anatase to rutile [8].

Figure 2 shows FE-SEM photographs for the films annealed at 600 °C. A particulate structure is evident in all the films. It is noted that there is no evidence of aggregation of particles and nano-sized particles were obtained in all the films.

Figure 3 shows the visible spectra in the wavelength range 300-900 nm of the films on SLSG substrates annealed at 600 °C. A relatively high transmittance in the visible range and clear absorption edges of the films were observed. The high transmittances of the films are attributed to the small particle size which eliminates light scattering [7]. From these spectra, it is apparent that the films present relatively high optical quality, with an absorption in the visible region that is characterized by the typical interference pattern found when a transparent thin film is deposited onto a substrate of different refractive index. Furthermore, the film containing nickel showed a shift towards the visible in the absorption threshold.

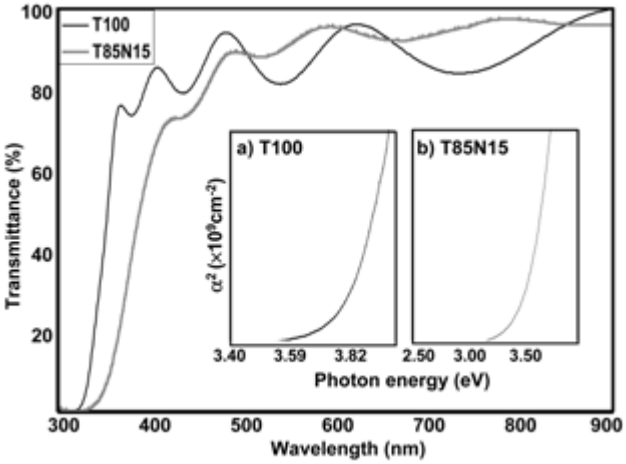

Fig. 3. Transmittance and α^2 as a function of photon energy of the films on SLSG substrates annealed at 600 °C.

The optical absorption coefficient, α, is defined as,

$$I = I_0 e^{-\alpha t} \quad (1)$$

where I is the intensity of transmitted light, I_0 is the intensity of incident light, and t is the thickness of the 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 [9],

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

where, h is Plank's constant, and ν is the frequency of the incident photon. As shown in inset Figs. 3(a) and (b), the linear dependence of α^2 on $h\nu$ indicates that films on SLSG substrates are direct transition-type semiconductors. The photon energy at the point where α^2 is zero is E_g. Then E_g is determined by the extrapolation method [10]. The optical band gaps, E_g, of T100 and T85N15 are 3.67 eV and 3.36 eV, respectively. The estimated value of the band gap for the T100 is much larger than that of TiO_2 bulk (3.3 eV). The film consisting of fine crystallites shows a 'blue shift' [11]. A comparison of optical energy gaps between pure TiO_2 and Ni-doped TiO_2 thin films shows an obvious red shift in Ni-doped TiO_2 films at the same annealing temperature.

Conclusions

Pure TiO_2 and Ni-doped TiO_2 thin films were prepared on SLSG substrates at 600 °C from metal naphthenates precursors. Transformation from anatase to rutile was enhanced by Ni-doping. The surface of the films showing a high transmittance in the visible wavelength range was of relatively high smoothness. A comparison of optical energy gaps between pure TiO_2 and Ni-doped TiO_2 thin films shows an obvious red shift.

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