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Short communication

Hydrophilic/hydrophobic conversion of Ni-doped TiO_2 thin films on glass substrates

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Abstract

Nickel-doped titanium oxide thin films were prepared on soda–lime–silica glass substrates by using a metal naphthenate. Films prefired at 500 °C for 10 min were finally annealed at 600 °C for 30 min in air. Contact angle measurement was used for analyzing hydrophilic/hydrophobic conversion. $NiTiO_3$, rutile and anatase peaks were obtained for the film after nickel doping. The film containing nickel showed a shift towards the visible in the absorption threshold.

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

1. Introduction

Titanium oxide (TiO_2) has been recognized as one of the better photocatalysts in heterogeneous photocatalysis applications. However, the band gap energy requires that near-UV light be used to photo activate this very attractive photocatalyst [1–3]. Unfortunately, in solar energy applications only ~3% of the solar light is absorbed. Therefore, it would be advantageous if this metal oxide 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 TiO_2 towards the visible. These systems are being prepared in the form of films due to the advantages of their use as electrodes, transparent coatings, etc. [4–6]. However, as far as we know, there is little information to prepare nickel (Ni)-doped TiO_2 films by chemical solution deposition (CSD).

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

2. Experimental procedure

The preparation for the films from metal naphthenate is described in detail in our previous work [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 Ni contents, as mole percentage, were 0 and 10. 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 at 1500 rpm for 10 s. The as-deposited films were prefired at 500 °C for 10 min in air. The coating was repeated five times. A final annealing was performed at 600 °C for 30 min in air.

Crystallinity was investigated by high-resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands). Transmittance in the visible region was observed by using a

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UV spectrophotometer (Cary 500 Scan, Varian Co., Australia). The thickness of the film was approximately 0.6–0.7 μm, as determined by the observation of fracture cross-section. The hydrophilic/hydrophobic conversion of the films was evaluated by examining the contact angle for water of the films. Irradiation in the UV was performed using an UV lamp (UVGL-58, 366 nm, UVP Co., USA) at 1.0 mW/cm^2. Contact angles were measured with a contact angle micrometer (CAM Plus-Micro ×12, Tantec Inc., USA). Water droplets were placed at five different positions for one sample and the averaged value was adopted as the contact angle.

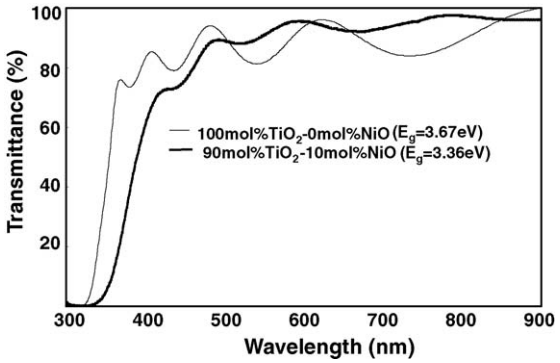

Fig. 2. Transmittance of the films on SLSG annealed at 600 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the films after annealing at 600 °C. The XRD pattern of pure TiO_2 consists of only anatase (1 1 0) reflection at $2\theta = 25–26^\circ$, whereas rutile as well as $NiTiO_3$ peaks were obtained by Ni-doping at the same temperature, 600 °C. There were no peaks for nickel oxide. Hence, nickel oxide reacted with TiO_2 during annealing to form $NiTiO_3$.

Interesting difference in the crystalline structure appear between pure TiO_2 and Ni-doped TiO_2 samples. Pure TiO_2 film was crystallized into anatase. This behavior has already been observed for other TiO_2 samples [8]. By contrast, the films containing Ni yielded a mixture of anatase, rutile, and $NiTiO_3$. Phase transition from anatase to rutile was accelerated at the same annealing temperature for the Ni-doped TiO_2.

Nickel oxide is known to promote the anatase–rutile transition in TiO_2 [9]. This enhancement effect has been explained on the basis of Ni^+ diffusion into the TiO_2 lattice, which generates the oxygen vacancies that are needed to maintain charge neutrality, favoring rutile nucleation. These oxygen vacancies are responsible for the enhancement of anatase to rutile transformation [9].

Fig. 2 shows the visible spectra in the wavelength range 300–900 nm of the films annealed at 600 °C. Relative high transmittance at visible range (>80%) and a clear absorption edge of the films were observed. 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 Ni showed a shift towards the visible in the absorption threshold. Optical band gap, E_g, is 3.67 and 3.36 eV, for pure TiO_2 and Ni-doped TiO_2, respectively. The estimated value of the band gap for the pure TiO_2 is larger than for TiO_2 bulk (3.3 eV). It can be clearly observed that the band gap energy decreases with Ni-doping.

Contact angle measurement was conducted to examine the surface wettability of the thin films. Fig. 3 shows the time dependence of the water contact angle of the film upon UV illumination. When UV light was shone on the surface to film for above 45 min, the surface gradually converted to a hydrophilic state. Stored in the dark for 300 min, the surface gradually reconverts to the hydrophobic state. The hydrophobic to hydrophilic conversion

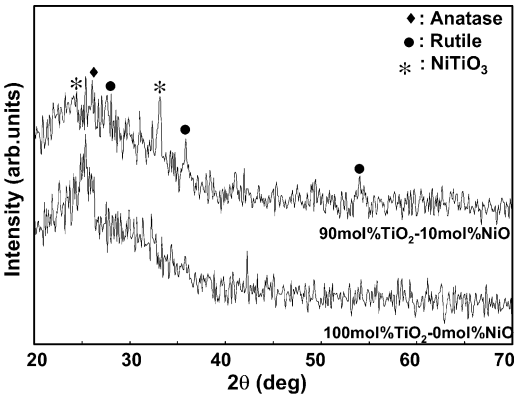

Fig. 1. XRD patterns of the films on SLSG substrates after annealing at 600 °C.

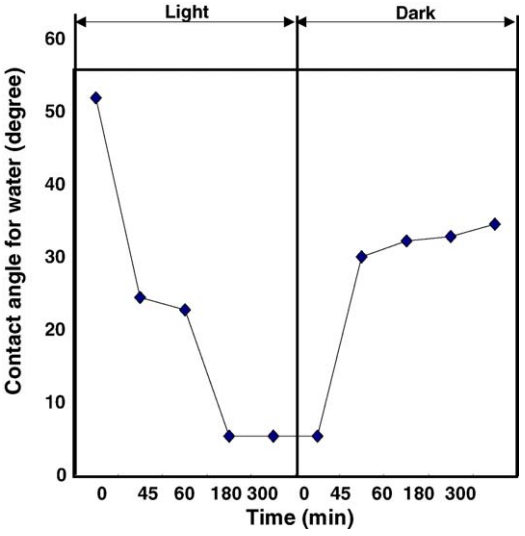

Fig. 3. Hydrophilic–hydrophobic conversion upon UV illumination and storage in dark for the Ni-doped film.

is explained by assuming that surface Ti^{4+} sites are photoinduced to the Ti^{3+} state [10], and oxygen vacancies are created at the surface. The produced oxygen vacancies are presumably favorable for water adsorption [11]. Usually water molecules are dissociatively adsorbed on defect sites to form singly coordinated or doubly coordinated surface hydroxyls [11], and as a result, a highly hydrophilic surface is formed.

4. Conclusions

Pure TiO_2 and Ni-doped TiO_2 thin films were prepared on SLSG substrate at 600 °C from metal naphthenates precursor. The transmittance at the visible region is high. A comparison of optical energy band gaps shows an obvious red shift in Ni-doped TiO_2 at the same temperature. The film containing Ni showed hydrophilic to hydrophobic conversion after UV illumination or dark storage.

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