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Short Communication

Annealing Temperature Effects on Structural and Hydrophilic Properties of Magnesium-Doped TiO_2 Thin Films

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Abstract

Magnesium-doped TiO_2 thin films were deposited with the sol-gel spin coating technique. The effects of annealing on the structural and hydrophilic properties were studied. The films deposited on a Corning glass substrate were characterized by means of X-ray diffraction (XRD), UV-visible spectroscopy and Fourier transform infrared spectroscopy. The water contact angle was measured in order to investigate the hydrophilic property of the doped TiO_2 films. It was observed that the crystallite structure of the doped TiO_2 films improved significantly with increasing temperature. The formation of anatase and rutile phase was observed at 400 °C. The photo-induced hydrophilicity was found to improve for Mg-doped TiO_2 film annealed at 500 °C.

Keywords: TiO_2 thin films, Mg-doping, annealing, surface modification, hydrophilicity.

I. Introduction

Metal oxide thin films have found promising applications in various fields of science and technology. Titanium dioxide (TiO_2) is one of the most attractive wide band gap semiconductor oxides as it exhibits excellent chemical, electrical, optical and gas sensing properties [1]. TiO_2 has been found to be an excellent material for self-cleaning applications under ultraviolet (UV) irradiation [2, 3]. The chemical and mechanical properties of TiO_2 thin films make the material useful for wide-ranging applications including antireflection coatings, photo-oxidation of water and optical waveguides [4]. In the last few years, gas sensors based on TiO_2 thin films have been used to detect harmful gases (e.g. NO_x, NH_3 and CO) present in the environment [5–6].

The surface of TiO_2 has been tailored by doping with a number of transition, non-transition and noble metals [7–9]. Surface modification of TiO_2 films with different dopants improves the photo-response by slowing down the recombination rate of electron-hole pairs [10]. The dopants also introduce new electronic states into the surface of the TiO_2 lattice, which leads to a surface reaction of sensing films with many oxidizing or reducing gases. The effect of the concentration of magnesium into TiO_2 thin films for measuring the CO gas sensing response has been studied recently [11]. The photoactivity effect on the TiO_2 surface with doping of alkaline-earth metals ions such as Be^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}have been studied in the relevant literature [12]. But few studies have focused on the effect of the annealing temperature on the microstructure and hydrophilic properties of TiO_2 films doped with Mg^{2+} (alkaline-earth metal ion).

The most common techniques used for the preparation of Mg-doped TiO_2 films include chemical vapor deposition, magnetron sputtering, laser pyrolysis and sol-gel methods [13–15]. Owing to the complexity and high processing costs of other deposition techniques, we focused on the sol-gel method for preparation of the doped TiO_2 films [16]. XRD, UV-visible spectroscopy, FTIR and SEM were used to study the microstructural, optical and surface morphology properties of Mg-doped TiO_2 thin films at different annealing temperatures. The water contact angle was measured at different annealing temperatures (300 – 600 °C) to investigate the photo-induced hydrophilic property of Mg-doped TiO_2 films.

II. Experimental

(1) Film preparation of Mg-doped TiO_2

The simple and cost-effective sol-gel method was adopted for preparation of TiO_2 solution doped with 3 % (wt/v) $MgCl_2$. Titanium isopropoxide (TIP) from Sigma-Aldrich (purity 97 %) was used as a TiO_2 precursor and $MgCl_2.6H_2O$ (purity 97 %) from Rankem as the Mg^{2+} dopant, absolute ethanol (purity 97 %) from Aldrich as a solvent and acetic acid (purity 97 %) from Sigma-Aldrich as a catalyst. The chemicals were used as received from the manufacturers, without any further purification. Firstly, the TiO_2 sol was prepared at room temperature by mixing titanium isopropoxide, ethanol and acetic acid in the molar ratio of 1:9:0.1. The above mixture was stirred for 1 h using a magnetic stirrer with a hot plate at a temperature of 85 °C. Second, the 3 % wt/v (0.03 g) magnesium was added using the $MgCl_2$ solution in absolute ethanol

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(10 ml). Finally, the $MgCl_2$ solution was mixed with the TiO_2 solution and stirred continuously for 3 min.

The Corning glass substrates in the size 22 mm × 22 mm were cleaned in trichloroethylene, acetone, ethanol and DI water. The cleaned substrate was placed on the chuck of a spin coater and a few drops of prepared solution were placed on the surface of the substrate. The spin coater loaded with the substrate was allowed to spin for 60 s at a spin rate of 2000 rpm. The deposited films were then baked for 5 – 7 min at a temperature of 75 °C in ambient air. The Mg-doped titania films were sintered in a temperature-controlled furnace in dynamic air at elevated temperatures (300 °C to 600 °C) for 30 min.

(2) Characterization

The crystal phases of Mg-doped titania films were determined by means of X-ray diffraction measurement with an XPERT-PRO diffractometer. 40 kV voltage was applied to the X-ray tube maintaining a current of 30 mA, equipped with Cu Kα radiation of the wavelength $\lambda = 1.54\ \text{Å}$. The optical absorbance spectra of doped films were observed with a UV-VIS spectrometer lambda-650 from Perkin-Elmer in the wavelength range of 200 – 900 nm with a time interval of 2 ms. Fourier transform infrared (FTIR) transmission spectra of the deposited films were measured at room temperature on a Perkin Elmer-Spectrum RX-IFTIR model. It has a resolution of 1 cm^{-1} and scan range of 4000 cm^{-1} to 250 cm^{-1}. The FTIR spectrum was obtained using the potassium bromide (KBr) disk method. The morphology of the Mg-doped TiO_2 films was determined by means of scanning electron microscopy (SEM) using JEM-1200 EX (JEOL) model with full automatic and manual adjustable electron gun power with accelerating voltage fixed at 20 kV. A back-scattered electron detector was used in the SEM characterization. The water contact angle (WCA) was measured using a homemade contact angle measurement system with UV light illumination. An Hg lamp having a wavelength in range of 325 – 390 nm was used as an illumination source. The contact angle measurements were carried out immediately after annealing as well as four weeks after annealing. The volume of the water droplets used for the measurement was 3 μL.

III. Results and Discussion

Fig. 1 shows the XRD patterns of 3 % (wt/v) Mg-doped TiO_2 thin films deposited on Corning glass substrate. All the films were annealed at different temperatures ranging from 300 – 600 °C for 30 min. Both the rutile and anatase phases were observed in X-ray diffraction patterns of the doped TiO_2 thin films. On account of the almost similar ionic radii of Mg^{2+}(0.57Å) ion and Ti^{4+}(0.68Å), the ions of magnesium are easily inserted into the crystal lattice of the titania. Individual peaks of magnesium were not observed in the XRD pattern. The highest peak (101) observed at 2Θ value of 25.8° corresponds to anatase phase. The other peaks (110), (200) were recorded at 2Θ values of 27.85°, 38.41° and indicated the rutile phase. Both the rutile and anatase phases exhibit a hydrophilic property, but it is observed slightly more in the case of the anatase phase [17–18]. The peaks observed at the angles 37.57°, 54.45° and 55.86° were assigned to (004), (105) and (211) planes for anatase phase. The intensity of the peaks of diffraction pattern of films annealed in the temperature range from 300 °C to 600 °C shows an improvement of the crystalline structure of TiO_2 film. The anatase phase is observed to be dominant phase of Mg-doped TiO_2 films annealed at temperatures above 500 °C. Further, the phase transformation of Mg-doped TiO_2 films occurred at high annealing temperature [19].

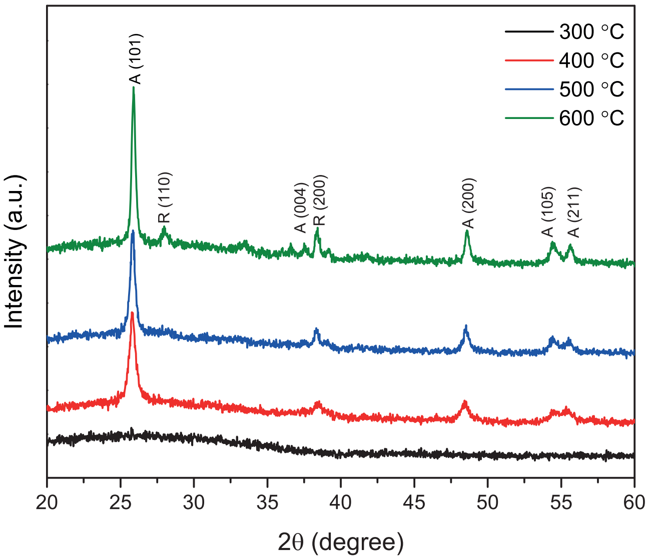

Fig. 1: XRD patterns of Mg-doped TiO_2 thin films annealed at different temperatures.

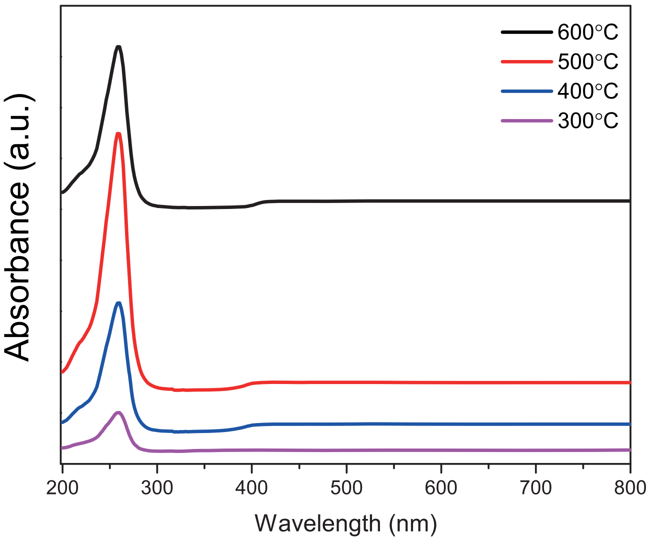

Fig. 2: UV-vis absorption spectra of Mg-doped TiO_2 films annealed at different temperatures.

Fig. 2 shows the UV-visible absorption spectra for 3 % (wt/v) Mg-doped TiO_2 films deposited on Corning glass substrate annealed at different temperatures. The increase of the annealing temperature above 300 °C causes the increase of intensity of the absorption edge towards longer wavelengths (370 – 800 nm). The intensity of the absorption edge reached a maximum at the annealing temperature of 500 °C. Further, the intensity of the UV-visible spectra of the doped TiO_2 films is slightly reduced at annealing temperatures above 500 °C. The extinction coefficient (*k*) of Mg-doped TiO_2 film is determined using relation (1),

$$k = \frac{\lambda\alpha}{4\pi} \qquad (1)$$

where
λ = wavelength,
α = absorbance coefficient of material.

Fig. 3 shows the curve plotted between the extinction coefficient and wavelength. The curve suggests that the extinction coefficient increased with the increase in annealing temperature from 300 °C to 500 °C. But as the annealing temperature increased to 600 °C, the extinction coefficient was found to decrease, which may be due to the modifications in the crystalline structure of the Mg-doped TiO_2 films.

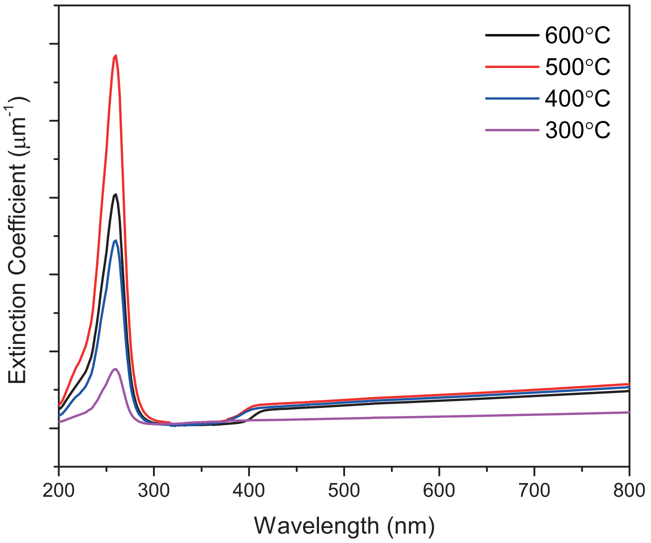

Fig. 3: Extinction coefficient of Mg-doped TiO_2 films annealed at different temperatures.

The scanning electron microscopy images of the Mg-doped TiO_2 films annealed at 600 °C temperature are shown in Fig. 4. The rough and microporous structure was observed from the morphology images of the doped TiO_2 films. The formation of the extremely porous structure extends the surface roughness, which appeared to be different approach to obtain a super-hydrophilic surface[20]. Fig. 5 shows the FTIR spectrum of various functional groups present in Mg-doped TiO_2 films at different annealing temperatures. The relationship between the hydroxyl and hydrophilicity conversion process can be examined with the Fourier transform infrared spectroscopy technique[21]. The stretching vibration of Ti-O/Mg-O band appears at about 500 cm^{-1}. The stretching band was observed in the range of 875 – 1680 cm^{-1} in the temperature range of 300 °C – 500 °C. The OH^- bending vibration and stretching vibration bands were observed at 1613 – 1750 cm^{-1} and at 2270 – 2630 cm^{-1} respectively, which indicates the insertion of Mg ions into TiO_2. Further, the intensity of peak is increased at 600 °C with the stretching and bending band. At a temperature of 600 °C, a large portion of adsorbed H_2O molecule is removed from TiO_2. The formation of the hydroxyl group was observed with the increase of the annealing temperature above 400 °C. The film with surface hydroxyl can easily make contact with H_2O molecules to form a hydrogen bond that results in hydrophilic conversion process. The stretching vibration of Ti-O-Ti band is appeared at 2820 – 2850 cm^{-1}. Further, the number of Ti-O-Ti and O-Ti-O bands of TiO_2 crystallization is increased at 3415 – 3550 cm^{-1} with the increase in annealing temperature. The variations of the peak position as observed in the FTIR spectrum are due to the change in particle size as the temperature changed to a higher level.

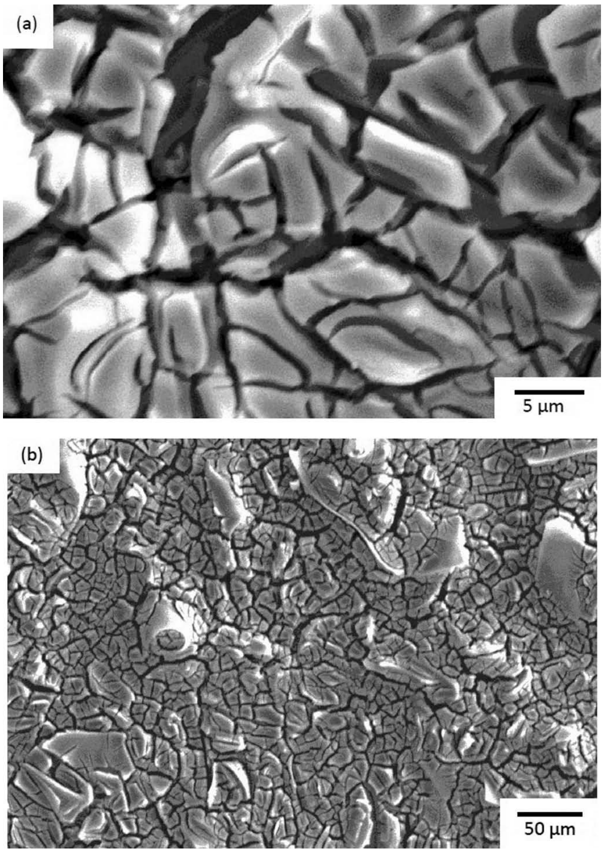

Fig 4: SEM images of Mg-doped TiO_2 films annealed at 600 °C temperature (a) 5 μm (b) 50 μm magnification.

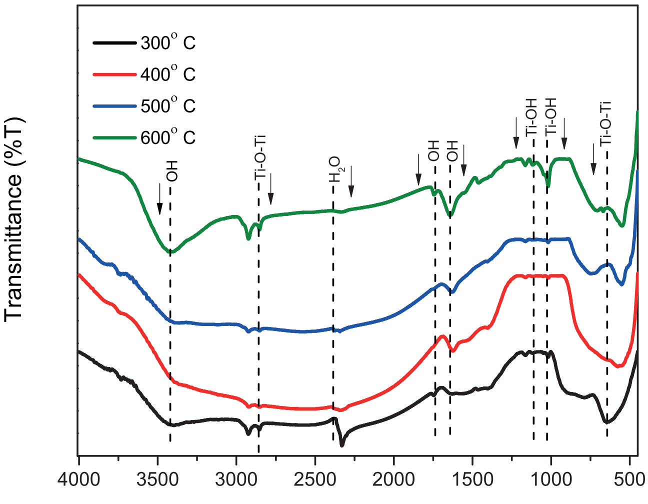

Fig. 5: FTIR spectra of Mg-doped TiO_2 films at different annealing temperatures.

The hydrophilic property of Mg-doped films annealed at different temperatures ranges (300 °C – 600 °C) was observed by measuring the water contact angle (WCA) with UV light illumination. Fig. 6 shows the measured values of the WCA for different annealing temperatures. Initially, the value of the contact angle was observed to be 87° at the annealed temperature of 300 °C. The contact angle was observed at 53 °C and 23 °C at the annealed temperatures 400 °C and 500 °C respectively. It was observed that the WCA decreases as the annealing temperature changes from 300 °C to 500 °C. At a maximum annealing temperature of 600 °C, the contact angle was observed to increase. The hydrophilic property of doped titania film was excellent at the annealed temperature of 500 °C under UV light irradiation.

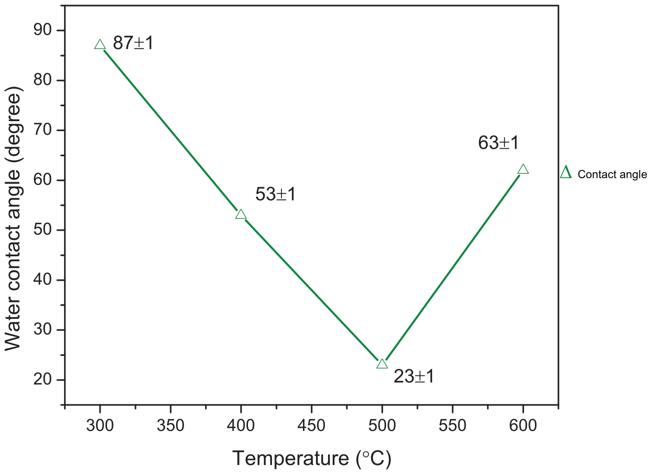

Fig. 6: Contact angle as a function of the annealing temperature.

The enhancement in the hydrophilic property with the high annealing temperature is related to a number of factors. As the doped TiO_2 thin films were annealed, contaminants were removed from the surface and followed by the transformation of Ti^{3+} into Ti^{4+}. In addition to this, the formation of anatase/rutile phase or combination of these phases also contributes to the enhanced hydrophilicity. Surface roughness is one more parameter that contributes towards hydrophilicity. Since the rough surface has a large surface area, so contributing towards the hydrophilic behavior of Mg-doped TiO_2 films at elevated temperature for the photo-induced mechanism.

IV. Conclusions

Mg-doped TiO_2 thin films were successfully deposited on the surface of Corning glass substrate by means of the sol-gel spin coating technique. The phase transformation from rutile to anatase of Mg-doped TiO_2 films was observed at annealing temperatures above 500 °C. The films annealed at 500 °C show much improved hydrophilicity in comparison with films annealed at lower temperatures. The absorption edges shifted to the visible light region with increasing annealing temperature. The FTIR spectra confirm that the removal of H_2O molecules with the formation of the hydroxyl group results in a reduction of the water contact angle, which makes Mg-doped TiO_2 film a potential material for self-cleaning applications.

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