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Fabrication of multicolor photochromic thin film

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Thin films of Ag-SiO_2-TiO_2 composite oxides with SiO_2/TiO_2 of 20/80 molar compositions were prepared by the sol-gel method, using tetraethylorthosilicate (TEOS) and titanium isopropoxide (TIP) as precursors. Ag-SiO_2-TiO_2 films coated on commercial glass substrates have successfully been synthesized using sol-gel method. The Ag-SiO_2-TiO_2 film with 0.5% Ag-added concentration and 20 mol% SiO_2-mixture gives optimal results on crystalline structure, optical property, surface area, and photochromic property. Absorption near the wavelength of the incident light decreased gradually. The reversibility of the two-photon writing process in Ag-SiO_2-TiO_2 film is clearly seen.

Key words: Films, Sol-Gel method, Ag-SiO_2-TiO_2, Photochromism, Coating.

Introduction

Photochromic materials reversibly change their color under illumination. They have been suggested for a wide range of applications. These films consist of Ag nanoparticles embedded in anatase TiO_2 and were prepared photocatalytically using the sol-gel technique [1, 2]. Here, the photochromic effect relies on reversible spectral hole burning in the particle-plasmon band of the particles. Particle plasmons are collective oscillations of conduction electrons and generally show themselves as pronounced resonances in optical spectra of metal nanoparticles. The photochromic effect adds an interesting new aspect to the rich optical behavior known from Ag nanoparticles and clusters, such as light scattering and absorption, nonlinear signal enhancement, electroluminescence, and photoactivated fluorescence [3-5].

The anatase phase of TiO_2 is a well-known photoactivated material; it is chemically stable and optically transparent. When TiO_2 is irradiated by sunlight with a wavelength of less than 387 nm (ultraviolet range), electrons are passed across the band gap into the conduction band, leaving holes in the valence band. These holes have high oxidation power, thus can easily react with adsorbed hydroxide ions to produce hydroxyl radicals, the main oxidizing species which are responsible for the photooxidation of organic compounds [6, 7]. Titania has a large band gap (3.20 eV for anatase TiO_2) and therefore, only a small fraction of solar light can be absorbed. The effective way to improve the TiO_2 photocatalytic activity is to introduce metal ions into TiO_2. Because it affects to a large surface area and prevents the electron-hole pairs recombine rapidly after excitation [8-10]. Preparation of transition metal doped TiO_2 nanoparticles by sol-gel method, characterization and investigation of their photocatalytic activity have been reported in recent literature [11, 12]. During the drying and calcining process Ag+ ions would gradually migrate from the volume of TiO_2 grains to the surface and further to the surface of the TiO_2 powder under the action of heat [13]. These Ag^+, Ag^0 and metal Ag play the role trapping photo induced electrons and holes. So recombination of photo induced electrons and holes were effectively inhibited. Otherwise, increment of adsorbed O^2 and OH^- on the surface of TiO_2 due to Ag depositing on the surface also improved photocatalytic activity of Ag/TiO_2. Besides, Ag ions effect to crystallite size and anatase to rutile phase transformation [14, 15].

SiO_2-TiO_2 materials were most widely investigated in the photocatalysis field because they exhibited higher photocatalytic activity than pure TiO_2. This could be explained by the addition of SiO_2 into TiO_2 retarding or inhibiting the crystallization of anatase phase [16]. It is noted that crystallization of TiO_2 in the composite films will lead the TiO_2 phase to segregate from the SiO_2 phase. Accordingly, the resultant inhomogeneous structure can cause considerable scattering of light [17, 18]. Sol-gel synthesis can easily modulate the composition of materials with excellent chemical uniformity and desirable optical properties. Sol-gel derived silica-titania gel films provide considerable interest since they enable fine control of refractive index and thickness for optical applications [19-21].

This work aims to investigate the effect of calcinations temperature on the photochromic properties of Ag-SiO_2-TiO_2 thin films coated on glass substrates which were prepared by the sol-gel and dip coating processes.

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Experimental

Titanium isopropoxide (TIP) and tetraethylorthosilicate (TEOS) were used as precursors for titania and silica, respectively. First, TEOS and TIP were dissolved in absolute ethanol separately to form two pre-solutions. TEOS was hydrolyzed in an aqueous HCl solution, and a TIP ethanol mixture (1 mol TIP per 20 mol ethanol) was slowly introduced dropwise. The molar concentration of Si/Ti in the solutions was chosen at an optimal value of 15 mol% [16]. The Si/Ti ratios in the SiO_2-TiO_2 films agree with the TEOS/TIP molar ratio in the sol-gel precursor. The two presolutions were mixed with TEOS/TIP molar ratios (20/80) and stirred for 1 hr. Films were deposited on the cleaned glass substrate by dip coating with pulling velocity 7 cm/min and dried at 150 °C for 20 minutes after each deposition.

The SiO_2-TiO_2 resulting films were immersed in 1 M $AgNO_3$ aqueous solution for 3 min and rinsed with pure water. We also performed another way to obtain the Ag-SiO_2–TiO_2 film, hydrolyzed TEOS and a TIP ethanol mixture prepared by an optimal value and then slowly dropping a certain amount $AgNO_3$ in ethanol solution together with 2 M nitric acid into the mixed precursors under vigorously stirring at room temperature for 60 min. The procedure from coating to drying was repeated three times. Afterward, the substrates were calcined at various temperatures for 2 hrs.

The phases in the calcined powder was identified by XRD (Rigaku Geigerflex X-ray diffractometer) using a Cu-Kα radiation at 30 kV and 20 mA, and was identified by comparing spectra with standard data in JCPDS file index.

Optical properties of the films SiO_2 ranging from 0.1 to 0.9% of concentration percent and from 20 to 80 mol%, respectively and calcined at different temperatures were performed.

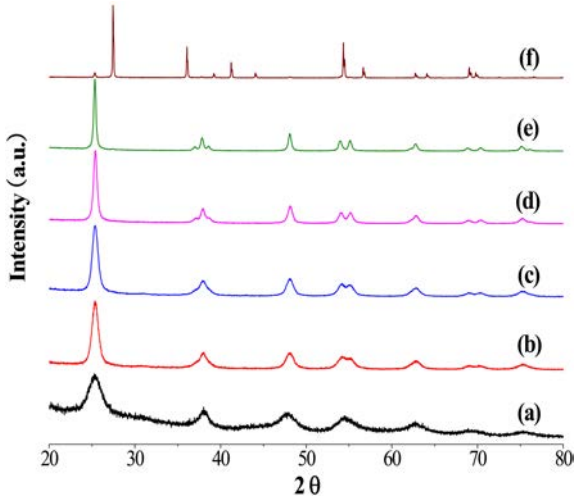

Fig. 1. XRD patterns of Ag-SiO_2-TiO_2 powder with different calcination temperature. (a) as-dried, and calcined at (b) 350 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C and (f) 800 °C.

Results and discussion

The powder XRD diagrams of samples with different calcined temperature are shown in Fig. 1. Samples of 350, 400 and 500 °C showed only the anatase phase with high intensity and other crystal phases (rutile or brookite) weren't detected. The XRD patterns of anatase have a main peak at $2\theta = 25.2°$ corresponding to the 101 plane (JCPDS No. 21-1272) while the main peaks of rutile and brookite phases are at $2\theta = 27.4°$ (110 plane) and $2\theta = 30.8°$ (121 plane), respectively. From XRD pattern, it can be seen that anatase single phase appears at the temperature at 350-500 °C. The rutile phase starts to appear at the temperature of 600 °C. In other report, the phase content of anatase seems to increase with an increase in Ag addition from 0-2% Ag and tends to decrease when Ag doped into TiO_2 more than 3% Ag [22].

It is noted that the films coated on glass are near transparent and colorless. The optical absorbance spectra of the Ag-SiO_2-TiO_2 thin films with different annealing temperature measured in the region of 350 - 1000 nm are shown in Fig. 2. The $0.2SiO_2$-$0.8TiO_2$ containing Ag loading content of 0.5% was prepared. The percentage of the Ag concentration indicated refers to the molar percentage to TiO_2. The data shown in Fig. 2 sad for the as-deposited film show no absorption characteristic of Ag particles and thus confirm the observation made above regarding the absence of such particles. The absorption edge below 400 nm is due to interband transitions in the TiO_2, which has a band-gap energy of 3.2 eV. For the film annealed at 300 °C, a broad absorption band centered at around 550 nm is visible. It is caused by the particle plasmon resonance of the Ag nanoparticles; this resonance is inhomogeneously broadened due to a broad distribution of particle sizes and shapes in the films, and due to possible inhomogeneities in the dielectric environment of the particles [2]. The absorption edge shifted towards longer wavelengths (i.e. red shift) with the increase of annealing temperature from 300 to 500 °C. It is well

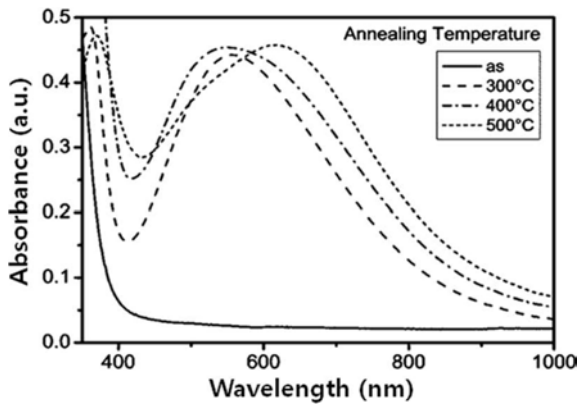

Fig. 2. Optical-absorption spectra for varying annealing temperatures.

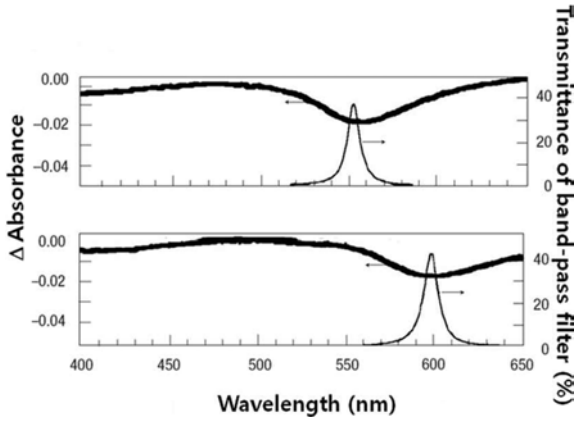

Fig. 3. Differential absorption spectra of the Ag-SiO_2-TiO_2 film after visible light irradiation using a xenon lamp with bandpass filters.

known that the particle plasmon resonance is a function of particle shape and size and increasing particle size generally leads to a redshift of the resonance position. A higher annealing temperature leads to a slight increase in absorbance, presumably due to a growth of particles at the cost of the Ag finely dispersed in the TiO_2 matrix [23-25].

The near colorless film was irradiated with visible light (> 400 nm, ~ 50 m Wcm^{-2}) in air using a xenon lamp with a filter to block ultraviolet light and an absorbance changes of the Ag-SiO_2-TiO_2 film were examined by irradiating with monochromatic visible light using a xenon lamp with a bandpass filter (533 or 600 nm; full-width at half-maximum, 10 nm). As a result, absorption near the wavelength of the incident light decreased gradually (Fig. 3). This behavior was also reversible, in each case the spectrum reverted to the initial one in response to ultraviolet irradiation. After irradiation by monochromatic visible light, the Ag-SiO_2-TiO_2 film showed colors corresponding to that light.

Optical density is a convenient tool to describe the transmission of light through a highly blocking optical filter (when the transmission is extremely small). Optical density is defined as the negative of the logarithm (base 10) of the transmission, where the transmission varies between 0 and 1. Optical density = $-\log_{10}(T)$. The reversibility of the two-photon writing process in Ag-SiO_2-TiO_2 film is clearly seen in Fig. 4, which shows the optical density dynamics under long-term writing radiation activity (segment 1) and after the radiation is shut off (segment 2). Relaxation (segment 2) occurs during probe radiation. The probe radiation intensity is selected such that relaxation efficiency is much lower than writing efficiency, and the probe radiation has almost no effect on the writing process.

Conclusions

Ag-SiO_2-TiO_2 thin films were prepared by a combination of the sol-gel and dipping coating technique.

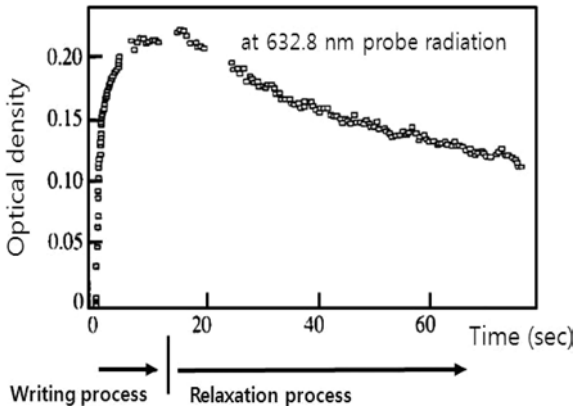

Fig. 4. Induced optical density D in a film versus time.

The Ag-SiO_2-TiO_2 film with 0.5% Ag-added concentration and 20 mol% SiO_2-mixture gives optimal results on crystalline structure, optical property, and photochromic property. Ag-SiO_2-TiO_2 films coated on commercial glass substrates have successfully been synthesized using sol-gel method. From XRD pattern, it can be seen that anatase single phase appears at the temperature at 350-500 °C. The rutile phase starts to appear at the temperature of 600 °C. For the film annealed at 300 °C, a broad absorption band centered at around 550 nm is visible. The absorption edge shifted towards longer wavelengths (i.e. red shift) with the increase of annealing temperature from 300 to 500 °C. It is well known that the particle plasmon resonance is a function of particle shape and size and increasing particle size generally leads to a redshift of the resonance position. We examined absorbance changes of the Ag-SiO_2-TiO_2 film by irradiating with monochromatic visible light using a xenon lamp with a bandpass filter. As a result, absorption near the wavelength of the incident light decreased gradually. The reversibility of the two-photon writing process in Ag-SiO_2-TiO_2 film is clearly seen.

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