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A study on the optical and structural properties of transparent Tio_2 thin films prepared by sol-gel method

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ABSTRACT

In this research, the optical and structural properties of TiO_2 thin film were studied. The films were made by dip-coating technique of sol-gel method on quartz and glass substrates. Optical and structural properties of films were given by UV-Visible spectra and XRD pattern respectively. The results have shown that transmittance, porosity and band gap reduced by increasing the annealing temperature. Thickness and refractive index of films increased with increasing the annealing temperature. Furthermore, structure of films has anatase type at 400, 600 and 800 °C and transform into rutile phase at annealing temperature of 1000 °C.

INTRODUCTION

TiO_2, which is well known as a metal oxide semiconductor, has been employed in many industrial applications for its fine physical, chemical and optical properties. TiO_2 thin films have attracted considerable attention for use as photocatalysts[1, 2], photoelectrodes[3], electrochromic displays[4] and gas sensors[5]. A variety of techniques have been used for the preparation of TiO_2 films including chemical vapor deposition (CVD)[6, 7], sol-gel[8], sputtering[9], physical vapor deposition (PVD), molecular-beam epitaxy (MBE) and electron-beam epitaxy (EBE)[10, 11]. The properties of TiO_2 films strongly depend on their microstructure that should be strictly controlled in order to obtain a desired performance. The sol-gel coating method is one of the promising methods because the microstructure of film is easily controlled with changing the solution composition and deposition condition. In addition, it provides uniform porous TiO_2 films with large specific surface area, which is favorable in achieving good photoactivity. There are many different techniques in sol-gel method to make a thin film, like dip-coating, spin-coating, spray pyrolysis, electrophoresis and thermophoresis. Transparent TiO_2 thin films on glass could form the basis for self-cleaning indoor windows, lamps or automotive windshields. In the present study, TiO_2 transparent thin films have been coated on glass substrates by dip-coating techniques in sol-gel method. The optical properties of films were investigated by pointwise unconstraint minimization approach (PUMA) by analyzing the transmitted UV-Visible spectra of the films[12]. Moreover structural properties of films have been obtained by XRD pattern.

EXPERIMENTAL

Preparing the sols

The TiO_2 coating sol was prepared via a sol-gel method and synthesized as follows. To verify the effect

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of change in annealing temperature on the properties of TiO_2 thin films, 20 mL of alkoxide of tetrabutyl titanate $(Ti(OBu)_4)$ used as precursor and mixed drop by drop to 100 mL of isopropanol as solvent while stirring. Then 10 mL HCl acid added to sol drop by drop as catalyst to increase the rate of hydrolysis reaction. Stirring was going on for 1 hour.

Making the films

The films were made on quartz and glass substrates (75.4 mm× 25.2 mm). The substrates were washed by ethanol thoroughly and then were putted in ultrasonic cleaners to remove pollutions.

To study on the effect of change in annealing temperature on the properties of TiO2 thin films, four films were coated on quartz substrates as follows by means of sol number one. All of them were coated three times and 15 cm/min withdrawal rate. After that the films were annealed at 400, 600, 800 and 1000 °C respectively by rate of 5 °C /min in a furnace.

To investigate on the effect of change in HCl acid used in sol on the properties of TiO_2 thin films, 4 films were coated by sols number 2 to 5 respectively with three times coating and 15 cm/min withdrawal rate. In both steps to complete the condensation reaction the films was calcinate at a furnace at 400 °C temperature. UV-Visible spectra were obtained by VARIAN Cary 100-Scan spectrophotometer and XRD patterns were given by a Philips PW3710 diffractometer using CuK radiation at 35 kV and 25 mA.

RESULTS AND DISCUSSION

Analyzing the optical and structural constants

To determine the optical constant of films, like thickness (d), refractive index (n) and absorption coefficient, the pointwise unconstraint minimization approach (PUMA) method was employed as follows[12]:

The optical transmission of a thin film deposited on a transparent substrate is given by

$$T=\frac{A\chi}{B-C\chi+D\chi^2}$$

Where

$$A=16s(n^2+k^2),$$

$$B=16s\,[(n+1)^2+k^2][(n+1)(n+s^2)+k^2],$$

$$C=[(n^2-1+k^2)(n^2-s^2+k^2)-2k^2(s^2+1)2\cos\phi-k[2(n^2-s^2+k^2)+(s^2+1)(n^2-1+k^2)]2\sin\phi$$

$$D=[(n-1)^2+k^2][(n-1)(n-s^2)+k^2],$$

$$\phi=\frac{4\pi nd}{\lambda},\chi=e^{-ad},\ a=\frac{4\pi k}{\lambda},$$

Where λ is wavelength, s is refractive index of thick transparent substrate, is a slowly varying function of λ. n is the real part of the refractive index of the film. α is the absorption coefficient of the film and k is the extinction coefficient, d is the thickness of film that has to be uniform and homogeneous, otherwise interference effects are destroyed or severely affected.

Furthermore to calculate the porosity of films, below relation was used:

$$porosity=[1-\frac{n^2-1}{n^2_d-1}]\times\%100$$

Which n_d is the refractive index of a pore free structure of TiO2 in anatase phase that equals to 2.52[13].

Analyzing the XRD pattern and find the crystalline size of TiO2 thin films can be deduced from Scherrer equation:

$$L=\frac{k\lambda}{\beta\cos\theta}$$

Where L is the crystallite size of TiO2 thin films, K is a constant (=0.94), λ is the wavelength of X-ray (CuKα=15.406 nm) radiation, β is the true maximum half-peak width, and θ is the half diffraction angle of the centroid of peak in degree[14]. Any contributions to broadening due to non-uniform stress were ignored and the instrumental line width in the XRD apparatus was subtracted.

Variation of optical and structural properties of TiO_2 thin films versus annealing temperature

Figure 1 shows the transmitted spectra of films. As be seen, the transmittance of films reduces by increasing in annealing temperature. ' 1 shows the film thicknesses, refractive indices, porosities (at λ_{ref} = 550 nm) and band gap of films versus annealing temperature. As be seen the thickness and refractive index of films increases while porosity of films decreases with the annealing temperature increasing. By increasing in annealing temperature, the energy band gap decreases because of increasing in film absorption due to crystalline size. Figure 2 and TABLE 2 indicate XRD patterns of annealed TiO2 thin films prepared by sol 1 at four different annealing temperatures.

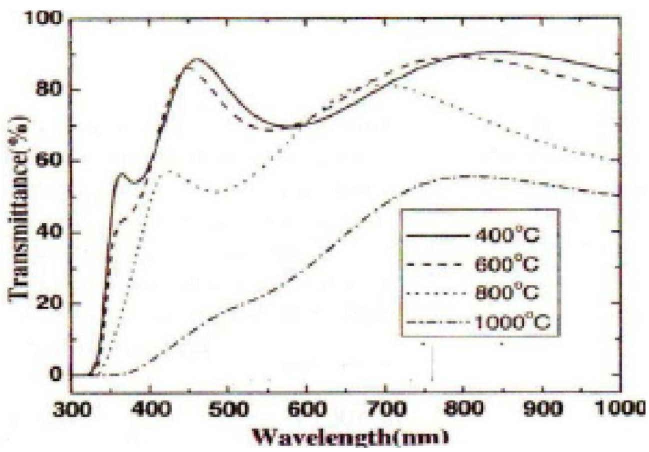

Figure 1 : Transmitted spectra of films by change in annealing temperature

It can be clearly seen from XRD patterns that the phase structure of TiO2 thin films at 400 and 600 °C is mainly of anatase phase. As the temperature increases from 400 to 600 °C, the intensities of the anatase peaks increase, indicating an improvement in crystallinity.

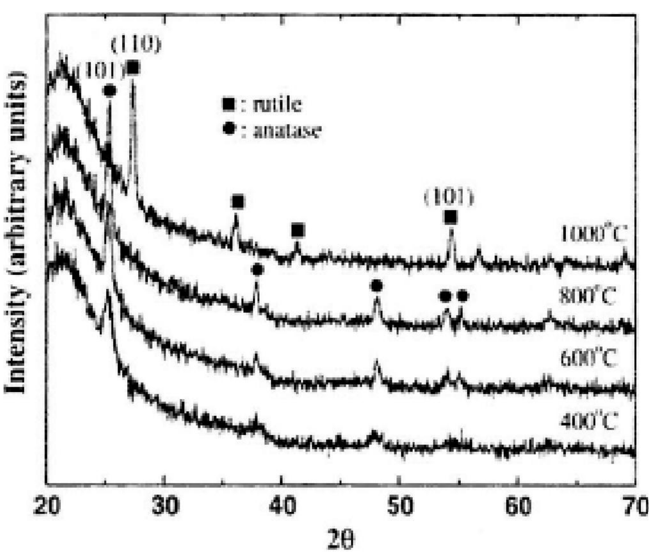

Figure 2 : XRD pattern of TiO2 thin films for 4 different annealing temperatures

At temperature of 800 °C, the anatase peaks gain maximum intensities and the crystallinity becomes more obvious. But at temperature of 1000 °C, the crystal phase change to pure rutile type. In real, between temperature of 800 and 1000 °C the crystal phase of films changes to rutile from anatase.

TABLE 1 : Film thickness, Refractive index, porosity, and band gap energy of TiO_2 thin films versus change in annealing temperature

Temperature	400 °C	600 °C	800 °C	1000 °C
Thickness (nm)	411	471	506	564
Refractive index	1.90	1.93	1.95	2.06
Porosity (%)	51.22	49.7	47.62	39.38
E_g (eV)	3.439	3.356	3.320	3.211

TABLE 2 : Crystallite size of the TiO_2 thin films made at various annealing temperature

Temperature		400 °C	600 °C	800 °C	1000 °C
Anatase	(101)	16.3	19.9	23.6	--
Rutile	(110)	--	--	--	24.4
Rutile	(101)	--	--	--	23.6

CONCLUSION

In this research, TiO_2 thin films were prepared by means of tetrabutyl titanate as precursor, and effect of annealing temperature was investigated on the optical and structural properties of films. Transmittance of thin films decrease with increasing the annealing temperature, but the thickness and refractive index of films increase with increase in annealing temperature while porosity and energy band gap of films decrease. Structure of TiO_2 thin films had anatase phase at 400, 600 and 800 °C and finally the structural phase transform into pure rutile at annealing temperature of 1000 °C. The crystallite size of the thin films is increased with increasing the annealing temperature. The optical properties of the films are found to be closely related to the crystal structure which strongly depends on the annealing temperature.

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