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TITANIUM DIOXIDE THIN FILMS: PREPARATION AND OPTICAL PROPERTIES

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ABSTRACT

In the recent years TiO_2 films are extensively studied because of their interesting chemical, optical and electrical properties. TiO_2 thin films have received great attention, because of having excellent photocatalytic and antibacterial properties when exposed to UVA light (320 – 400 nm) and find a wide range of applications in various fields like photocatalysis, gas sensing, antibacterial and protective coatings, antireflecting coatings, dielectric films, etc.

This work presents some results on the deposition and investigation of the optical properties of TiO_2 thin films. Ti films were deposited by conventional thermal evaporation and cathodic arc plasma deposition and after that were annealed to TiO_2. Transmittance spectra were measured and refractive indexes and band gaps of TiO_2 films were evaluated.

Keywords: TiO_2, thermal evaporation, cathodic arc deposition, transmittance spectra.

INTRODUCTION

In the recent years TiO_2 films are extensively studied because of their interesting photocatalytic properties. TiO_2 thin films find a wide range of applications in various fields like photocatalysis, gas sensing, antireflective and protective coatings, antibacterial and optical coatings, dielectric films for a new generation field effect transistors, etc.

TiO_2 is a photosensitive semiconductor. When it is illuminated with light of energy higher than the band-gap, an inter-band transition can be induced and electron-hole pairs are generated. Some of these photogenerated pairs achieve charge separation and diffuse to the TiO_2 surface, react with air or water and eventually generate OH radicals, O anions, which attack the organic compounds adsorbed on the TiO_2 surface and remove them by transforming into CO_2 and H_2O. Thus the TiO_2 surface converts into a strong oxidizer and can act as a photocatalyst, or to attack and clean the water and air by photodestruction of adsorbed contaminants.

TiO_2 can exist in three basic crystalline phases - anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and an amorphous phase. The first two phases have excellent photocatalytic and antibacterial properties when exposed to UVA light (320-400 nm). The rutile phase (ΔE_g = 3,0÷3,1 eV) is thermodynamically stable at high temperatures, but has a lower photocatalytic activity, the anatase phase (ΔE_g = 3,2 - 3,3 eV) is metastable but has a higher photocatalytic activity and under suitable conditions can be converted to the rutile. Some authors [1-3] believe, that the simultaneous presence of three phases - anatase, rutile and amorphous phase leads to better degradation activity, and amorphous TiO_2 films also have a good photocatalytic properties.

Various deposition methods are used to prepare titanium films – physical methods: DC or RF magnetron sputtering, E-beam evaporation, physical vapor deposition (PVD), thermal evaporation, chemical methods: sol-gel method, anodic oxidation, spray pyrolysis, chemical vapor deposition (CVD), etc.

In this work some results for optical properties of TiO_2 thin films deposited by thermal evaporation and cathode arc plasma deposition are presented.

EXPERIMENTAL

Conventional thermal evaporation of thin films in a low pressure chamber is a widely used method. The produced coatings are homogeneous, with greatest cleanliness and lower roughness. Major advantages are the simplicity of the evaporation technique, the higher deposition speed and the possibility for obtaining nanostructure of titanium films. The adhesion of Ti films was improved by substrate heating. Films structures strongly depend on the substrate temperature T_s during the deposition process. Ti thin films formed at room temperature of the substrate or at temperature below 150ºC usually are amorphous and obtain crystallinity after annealing. Authors give various references for the range of substrate temperatures T_s = 50-400ºC. TiO_2 was formed by high temperature annealing (oxidation) of Ti films. After annealing of Ti films the visual aspect of the received TiO_2 films changes to fully transparent.

The second method is cathode arc plasma deposition, i.e. ion-plasma sputtering, which improves the films' cleanliness, uniformity and adhesion. Cathode arc deposition uses a Ti (or TiO_2) target in an argon medium, or in an argon-oxygen medium, most frequently followed by annealing. Using a Ti target in argon-oxygen medium and low deposition velocity, TiO_2 films with a rutile phase are formed; when using a TiO_2 target, TiO_2 films with mixed phases are formed [4, 5].

Ti thin films were deposited by us through two methods: conventional thermal evaporation and cathode arc plasma deposition on optical glass, quartz glass, glass ceramic (sital) and silicon substrates at substrate temperatures in the range of 20 - 200ºC. TiO_2 was formed by high temperature oxidation of Ti films, after their annealing in dry air, using a muffle furnace at various temperatures in the range of 450-750ºC for 1 - 4 hours. TiO_2 films were nanosized, with thicknesses 100 - 300 nm. The films show a rather smooth and compact surface in both deposition methods. Some authors [6] believe, that annealing at T_{ann} = 500 - 600ºC anatase phase is formed, and at T_{ann} > 700ºC rutile is formed. Scotch and scratch tests indicate that the TiO_2 films have a good adhesion, excellent especially for Si and quartz substrates. The adhesion was improved with the increasing of the annealing temperature.

RESULTS AND DISCUSSION

The optical properties of the deposited TiO_2 thin films were studied on the basis of transmittance measurements using the UV-VIS spectrophotometer SPECTROMOM 195D. Transmittance spectra were measured in the wavelength range of 300 - 900 nm. The TiO_2 films spectra exhibit high visible transmittance, up to 95 %, for the thermally evaporated films, which decreased slightly to 85 % for cathodic arc deposited films, because the film surfaces for this (CAD) method become rougher, and the light losses and the absorption in the films grow up.

The crystallographic and optical properties of the deposited films were dependent on the deposition conditions: substrate temperature Ts, film thickness and annealing temperature Tann, for both deposition methods. Fig. 1 present transmittance spectra of films deposited at substrate temperatures 20ºC, 100ºC, 150ºC, 170ºC and 200ºC for samples 1, 2, 3, 4 and 5, respectively. Transmittance spectra of TiO_2 films deposited on quartz substrates and annealed at different temperatures: 450ºC, 600ºC and 750ºC for samples 1, 2, and 3, respectively are presented in Fig. 2. The films thickness is in the range of 100 - 300 nm.

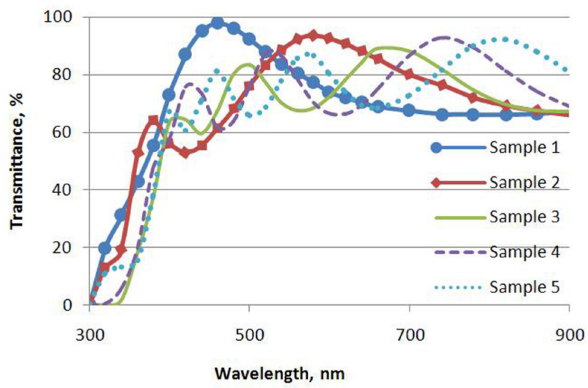

Fig.1. Transmittance spectra of TiO_2 films, deposited at different substrate temperatures.

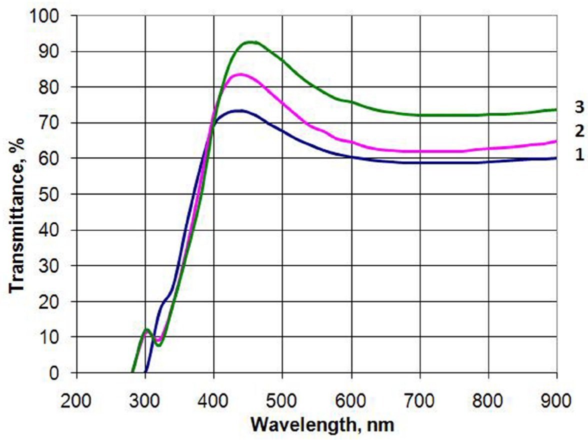

Fig. 2. Transmittance spectra of TiO_2 films, annealed at T_{ann}: 450ºC, 600ºC and 750ºC.

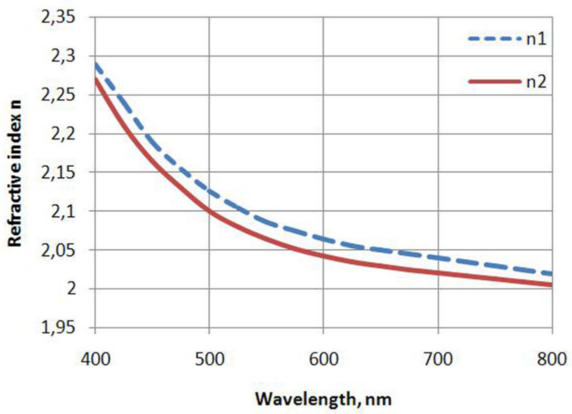

Fig. 3. Variation of the refractive index, n for TiO_2 films with thickness n 1 ~ 150 nm; n 2 ~ 300 nm.

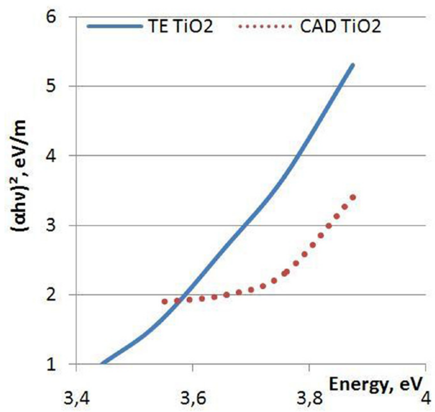

Fig. 4. Direct transitions energy of TiO_2 films.

The absorption coefficient α and the band gap energy of TiO_2 films were evaluated using the optical transmittance spectra. The absorption coefficient was calculated using Eq.(1) [2]:

$$\alpha = [\ln(1/T)]/d, \text{ eVm}^{-1} \qquad (1)$$

where T is transmittance, d is the film thickness.

If the films are with thickness d considerably lower than the thickness of a transparent substrate (optical glass or quartz), Eq. (2) and (3) involving the interference minima and maxima of the transmission curves can be used [7]:

$$\text{for } T_{min}: \quad nd = \lambda/4[(2m + 1)] \qquad (2)$$

$$\text{for } T_{max}: \quad nd = \lambda/4[(2m + 2)] \qquad (3)$$

where n is the refractive index of TiO_2, d is the film thickness, λ is the wavelength of the adjacent maxima and minima; m = 1, 2, 3, … is the order of the interference minima and maxima.

The dispersion of the refractive index, n for films with thicknesses n 1~150 nm and n 2~300 nm is presented in Fig. 3.

The band gap energy ΔE_g for direct and indirect transitions was obtained by plotting the optical absorption $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ versus photon energy (hυ) and extrapolating the linear portion of the TiO_2 transmittance curves in the UV region to 0 [7, 8].

The band gap energies ΔE_g, for both thermal (TE) and cathodic-arc (CAD) evaporated samples, were evaluated by eq.(1) for direct transitions (Fig. 4, TE and CAD). The band gap energy, ΔE_g for thermally (TE) evaporated samples was 3,42 eV at T_{ann}= 450ºC and 3,47 eV with the increase of annealing temperature up to T_{ann} = 600ºC. The band gap energy, ΔE_g for cathodic-arc (CAD) deposited samples was 3,55 eV at T_{ann} = 600ºC.

CONCLUSIONS

The observed band gap value of t5he direct transitions energy 3,47 eV (T_{ann}= 600ºC) after thermal evaporation and 3,55 eV (T_{ann}= 600ºC) after cathode arc deposition support an assumption for an anatase phase.

The observed band gap values of annealed samples are in good agreement with the results for the band gap values of TiO_2 thin films deposited, by the magnetron sputtering method [6, 7], as well as for sol-gel derived TiO_2 films [8] and cathodic arc deposition [9]. The represented values of the direct transition energy for a TiO_2 anatase phase are about 3,4 eV for direct and about 3,2 eV for indirect transitions.

The band gap width differences are connected with increasing of the crystallites dimensions and the surface alterations after annealing; with presence of rutile phase or possible alterations of anatase-rutile correlation, with disturbance oxygen stoichiometry or in presence of an oxides mixture, such as TiO or Ti_2O_3 [7].

TiO_2 thin films deposited by the conventional thermal evaporation and cathodic arc deposition and post-annealing lead to good results corresponding to the crystal phase anatase.

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