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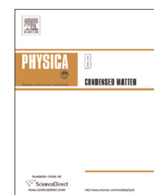

Properties of sputtered TiO_2 thin films as a function of deposition and annealing parameters

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ABSTRACT

The influence of sputtering parameters and annealing on the structure and optical properties of TiO_2 thin films deposited by RF magnetron sputtering is reported. A pure TiO_2 target was used to deposit the films on Si(100) and glass substrates, and Ar/O_2 gas mixture was used for sputtering. It was found that both the structure and the optical properties of the films depend on deposition parameters and annealing. In all cases the as-deposited films were oxygen deficient, which could be compensated by post-deposition annealing. Changes in the Ar/O_2 mass flow rate affected the films from an amorphous-like structure for samples deposited without oxygen to a structure where nano-crystalline rutile phase is detected in those deposited with O_2. Annealing of the samples yielded growth of both, rutile and anatase phases, the ratio depending on the added oxygen content. Increasing mass flow rate of O_2 and annealing are responsible for lowering of the energy band gap values and the increase in refractive index of the films. The results can be interesting towards the development of TiO_2 thin films with defined structure and properties.
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1. Introduction

Titanium dioxide films find a very wide range of applications in various fields like gas sensing, photocatalysis, dye sensitized solar cells etc. [1–3]. They show excellent chemical inertness, high photocatalytic activity, optical transmittance with high refractive index in the visible range and good mechanical hardness, the rutile and anatase phase of this material are non-toxic [4–7]. This all makes TiO_2 films a suitable candidate for many optical applications. As photocatalyst compound it has a large application in the coating industry due to its efficiency in dissociating organic pollutants under UV irradiation [8,9].

It is generally considered that TiO_2 in the anatase form is the most photoactive and the most practical of the semiconductors for widespread environmental application such as water purification, wastewater treatment, hazardous waste control, air purification, and water disinfection. However, there are reports that in certain circumstances TiO_2 in the rutile form exhibits a higher photocatalytic activity, and in some cases anatase–rutile mixture is more efficient, having some properties not seen in either of the single phases [10–12]. Photo-catalytic oxidation of organic compounds is of interest for environmental applications and in particular for the control and elimination of hazardous wastes. The complete mineralization (i.e., oxidation of organic compounds to CO_2, H_2O, and associated inorganic components such as HCl, HBr, SO_4^{2-}, NO^{3-}, etc.) of a variety of aliphatic and aromatic chlorinated hydrocarbons via heterogeneous photo-oxidation on TiO_2 has been reported [13]. In addition to organic compounds, a wide variety of inorganic compounds are sensitive to photochemical transformation on semiconductor surfaces. Examples include ammonia, azide, chromium species, copper, cyanide, gold, halide ions, iron species, manganese species, mercury, nitrates and nitrites, nitric oxide and nitrogen dioxide, nitrogen, oxygen, ozone, palladium, platinum, rhodium, silver and sulfur species among others [13]. However, due to a high the band-gap value, ~3 eV for rutile and ~3.2 eV for anatase, the photocatalysis property emerges only for UV radiation. This limits the use of solar light as a sustainable energy source for TiO_2 activation, because only 5% of the incoming solar energy on the Earth's surface is in the UV range [9]. To overcome this constraint one must try to tune the energy band gap by deposition on heated substrates, post annealing of thin layers, doping, implantation and other techniques that can influence the electronic properties of the films.

The phase being formed during deposition of TiO_2 on unheated substrates strongly depends on mass flow and partial pressure of oxygen in the chamber [14,15]. Magnetron sputtering of TiO_2 films

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is of special interest, because it is an industrial process applicable to large area deposition, and high quality TiO_2 films can be achieved even at low substrate temperatures [16]. In this work, we concentrate on deposition of TiO_2 on unheated substrates, of Si and glass, which can extend the range of application on polymers and plastic surfaces. Annealing effects and changes of sputtering parameters on the structure and the optical properties of TiO_2/Si thin films deposited by RF magnetron sputtering are studied and discussed.

2. Experimental details

Thin films of TiO_2 were deposited by RF magnetron sputtering on glass and Si(100) substrates at room temperature from a 99.99% pure TiO_2 target. Prior to deposition, the glass and Si substrates were cleaned in acetone, isopropanol and deionized water for 5 min. The base pressure in the chamber was about 1.6×10^{-5} Pa. The target-substrate distance was maintained at 40 cm. The sputtering gas was Ar, and via the same feed-through oxygen could be added to the system. The Ar/O_2 ratio was controlled by measuring the mass flow rate. Working pressure during deposition was at 1.1 Pa. The Ar/O_2 ratio was varied in the range from 80/0 sccm (no oxygen added to the system) to 30/1 sccm (maximum amount of oxygen added to the system). The sputtering power was kept constant at 200 W and the deposition times were varied between 10 and 22 min. Parameters of deposition and the measured thickness of the deposited films are summarized in Table 1. After deposition, the films were annealed in Ar (5.0) atmosphere at 400 °C for 2 h, in a tube furnace.

Structural and compositional characterization of the thin films was carried out by X-ray diffraction (XRD), glow discharge optical spectroscopy (GDOS) and transmission electron microscopy (TEM). For XRD analysis we used Siemens D5000 X-ray Diffractometer with automatic data acquisition. Diffraction patterns were recorded in the range of diffraction angles 2θ from 20° to 100° at a fixed angle of incidence of 3° in grazing incidence (GIXRD) configuration. Step width for scanning was 0.02° with 2 s dwell time. Reference patterns used for identification of reflections were JCPDS cards [021-1272] and [021-1276] for TiO_2 and JCPDS card [023-1078] for TiO. GDOS analysis was used to study the elemental depth profiles. GDOS was performed on a GDA 750, Spectruma Analytik GmbH, with RF source of 2.5 mm and with discharge parameters of $U = 680$ V and $p = 5$ hPa [17]. Before GDOS measurement, calibration was done on sample of well known thickness. The analyzing gas was Ar (5.0). TEM analyses were performed with a Philips XL30 microscope, operated at 200 kV. The samples were prepared for cross-sectional analysis by ion beam thinning. TEM was also used to control the thickness of the deposited films, which was initially measure by a profilometer.

Optical properties were studied by UV/VIS measurements, performed on a spectrophotometer Cary 5000 (Varian GmbH). It was used to collect transmittance spectra of both the films and bare substrate. Optical transmittance spectra were measured at normal incidence in the spectral ranges of 250–1500 nm with a scan rate of 300 nm/min, using a bare substrate as a reference.

Table 1
Deposition and annealing parameters for TiO_2/Si thin films, measured thicknesses and thicknesses calculated by PUMA.

Sample	*m*(Ar/O) (sccm)	*t* (s)	*d* (nm)	*d* (nm) PUMA	T_{an} 2 h (°C)
A(80/0)	80/0	600	195	180	400
B(80/1)	80/1	1320	120	112	400
C(60/1)	60/1	1320	105	108	400
D(30/1)	30/1	1320	80	80	400

Band gap energies were determined from transmission spectrum employing Tauc plots [18].

Refractive indexes were obtained numerically, using Pointwise Unconstrained Minimization Approach (PUMA) [19,20]. This method is very useful in obtaining optical data for samples of small thicknesses, for which transmittance does not display a fringe pattern in a highly transparent spectral region. The accuracy of the method has been shown by reconstructing transmittance spectra from calculated thickness (d), refractive index (n) and extinction coefficient (k) by this method and compared to measured transmittance obtained by UV/VIS measurement.

3. Results

The results of the film compositional analyses have shown that despite of using a pure TiO_2 target the deposited films are oxygen deficient with respect to the Ti:O = 1:2 stoichiometry. It is believed that smaller O_2 partial pressures, shorter substrate to magnetron distances and greater RF power produce an environment of reduced reaction of sputtered Ti species with O_2, and to result in the formation of non-stoichiometric rutile structures [21]. In order to improve this, oxygen was added during sputtering. As can be seen in Table 1, this results in a reduced deposition rate as there is a difference in the thicknesses of the deposited films, depending on the Ar/O_2 mass flow ratio. Sample which was deposited without introducing oxygen into the chamber, for 600 s, has a thickness of 195 nm. Other samples were deposited with additional oxygen flow into the chamber at different Ar/O_2 mass flow ratio. Time of deposition for them was set to 1320 s. The evaluated deposition rates of the TiO_2 films as a function of total mass flow of Ar/O_2 gases is plotted in Fig. 1. It can be observed that highest deposition rate is when there is no additional oxygen in the system. With introduced oxygen in the system deposition rate significantly drops. For samples deposited with introduced oxygen, deposition rate shows linear dependence of total mass flow rate. Such behavior can be due to a lower concentration of Ar as the sputtering gas, and partial lowering of the target sputtering rate because of a dynamic surface passivation by the introduced oxygen. Similar conclusions were reported by Ohsaki et al. [22].

As an example, the depth profiles deduced by GDOS from as-deposited samples deposited with mass flow ratios of Ar/O_2: 80/1 and 60/1 are shown in Fig. 2. The profiles indicate that in the initial stage of deposition the composition of the films is close to TiO_2

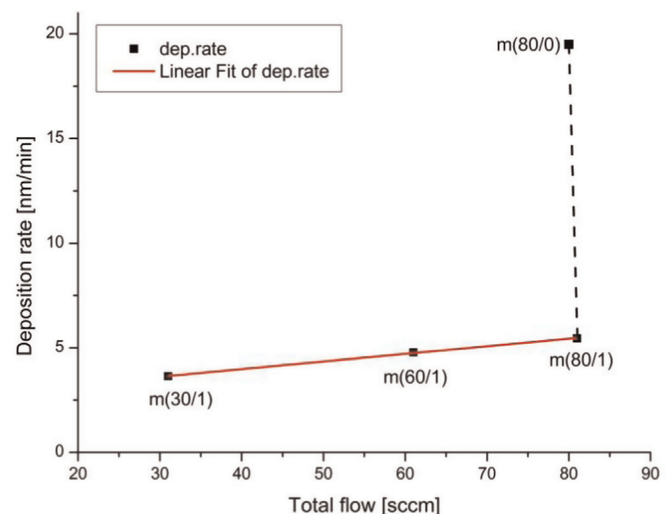

Fig. 1. Deposition rates of TiO_2 films as a function of the total mass flow rate of Ar/O_2 gases.

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