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Influence of V^+-implantation on structural, chemical, optical and nanomechanical properties of TiO_2 films

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ABSTRACT

TiO_2 thin films were deposited by sol-gel method. V^+ ions were implanted by using metal vapor vacuum arc implanter at 40 kV. The dose of implanted V^+ ions was chosen as 6×10^{15}, 1×10^{16}, 3×10^{16} and 6×10^{16} ions/cm^2. The investigations of structural, optical, nanomechanical and chemical characterizations of implanted thin films were carried out. The grain size of as deposited TiO_2 film was about 23 nm, and the size was reduced after implantation. Implantation had no influence on the lattice parameters "*a*" and "*c*" of the films. Band gap of as deposited TiO_2 film was estimated as 3.45 eV. The band gap of implanted films was found to decrease with increasing the dose of implanted ions. The refractive index of the implanted films increased with increasing the dose of implanted ions.

1. Introduction

TiO_2 films have been studied extensively due to their applications in a variety of fields such as photocatalysis, dye sensitized solar cells, gas sensor, biomedical material, etc. [1–3]. Because of its wide band gap, TiO_2 can only be excited by UV light irradiation. Up to now, great efforts have been utilized to develop the visible light sensitivity of TiO_2 in order to make use of solar energy more efficiently in practical applications [4–8]. Modification of TiO_2 films by using transition metals ion implantation is a useful method, which has been studied for improving photocatalytic ability on the degradation of organic pollutants under visible light irradiation [9–13]. It is known that many important applications of TiO_2 depend on its chemical, structural and optical properties. Those properties of ion implanted TiO_2 films will be influenced strongly by the process of implantation and implanted ions.

Among TiO_2 films preparing techniques sol–gel method is an economical and simple way to produce the films. The influence of V^+ ion implantation on photocatalytic activity of TiO_2 films prepared by sol–gel method has been discussed in previous work [11]. So we undertook a comprehensive study of chemical, structural, nanomechanical and optical properties of TiO_2 films which were prepared by the sol-gel method and modified by V^+ ion implantation in this work.

2. Experimental

2.1. Preparation of V^+ ion implanted TiO_2 films

All the films were prepared by sol–gel method [11] with dipping procedure for chemical and structural studies and spin-coating procedure for nanomechanical and optical studies. In dipping procedure, the substrates used to deposit TiO_2 films were soda lime glass slides. Twelve layers were coated with the withdrawing speed of 2 mm/s. In spin-coating procedure, the substrates were quartz glass. The spinning was performed in two stages with a speed of 500 rpm for 15 s and 3500 rpm for 30 s respectively. The procedure of spinning was repeated three times to have an approximately 180 nm thickness of the film, which was measured by profile meter of XP-2. After each coating the film was heated for 10 min in atmosphere at 80 °C and later annealed to 450 °C at a rate of 1.5 °C/min. After calcined at 450 °C for 30 min, the films cooled naturally.

A *MEVVA* (metal vapor vacuum arc) implanter was used to perform the implantation of V^+ ions at 40 kV. The dose of implanted V^+ ions was chosen as 6×10^{15}, 1×10^{16}, 3×10^{16} and 6×10^{16} ions/cm^2. After the implantation, TiO_2 films were annealed at 450 °C for 4.5 h.

2.2. Characterization techniques

The surface structure was studied by a field emission scanning electron microscope (FESEM, Hitachi S4800). The X-ray photoelectron spectra of the V^+-implanted films were measured by an

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ESCA750 X-ray photoelectron spectroscope equipped with MgKα excitation. A Rigaku X-ray diffractometer with monochromatized CuKα radiation ($\lambda = 0.154056$ nm) in a 2θ range of 15–90° was used to analyze the structure of the films. The optical transmittance spectra of samples were recorded in the wavelength range of 250–1000 nm using a Shimadzu UV–Vis spectrophotometer. The nanoindentation hardness of the films was investigated by a MTS nanoindenter using continuous stiffness measurement (CSM) technique in XP mode.

3. Results and discussion

3.1. Morphology and XPS analysis

The deposited TiO_2 films were uniform. A thickness of 1.8 μm was attained in 12 cycles dipping coat (Fig. 1(a)). Fig. 1(b) shows that the as deposited TiO_2 film has homogeneous porous structure. Fig. 1(c) reveals that the surface structure of V^+-implanted TiO_2 film had become smooth, which was most likely the reason for focusing problems due to the loss of surface roughness. It is obvious that the surface of the film has been polished by ion implantation.

The chemical states of vanadium were evaluated by XPS as shown in Fig. 2, and the dose of implanted ions was 6×10^{16} ions/cm^2. The V2p$_{3/2}$ XPS spectrum was analyzed in details by the deconvolution using Gaussian mixture peak fitting, in which the fitted peaks appeared at 516.1 eV and 517.3 eV indicated the existence of both V^{4+} and V^{5+} [14,15]. Because the signal of characteristic peaks of vanadium was very weak, and XPS can only measure the elements on the most outer surface, only very little vanadium was on the surface of the TiO_2 films indicating most vanadium located inside TiO_2.

For more information of implanted V ions, a depth profile was taken for the sample with dose of 6×10^{16} ions/cm^2 (Fig. 3). It was chosen to take only 5 different measurements, including one measurement at the surface. The figure shows the implantation depth is deeper than intended (60 nm, calculated by SRIM2000) so that the same number of implanted ions is distributed over a larger range.

The O1s XPS spectra are shown in Fig. 4. The O1s peak could be decomposed into two contributions. The dominant peak at about 529.9 eV was attributed to Ti–O. The O1s peak at 531.9 eV was assigned to the surface hydroxyl [16]. The calculated results indicated that the hydroxyl content of the as deposited TiO_2 film could be negligible. However, the amount of the surface hydroxyl O increased notably in the TiO_2 film with dose of implanted ion at 6×10^{16} ions/cm^2. The photocatalytic mechanisms of TiO_2 presented that the increase of the surface hydroxyl would lead to the enhancement of the performance of TiO_2. Thus the method of ion implantation would improve the properties of photocatalytic oxidation of TiO_2 films.

3.2. Structural analysis of the films

The XRD patterns of films implanted at different ion dose are shown in Fig. 5. It is clear that all the peaks were associated with anatase TiO_2 and the phase transformation was not induced by V^+-implantation and subsequent annealing. Furthermore, it is obvious that the intensity of (101) peaks of V^+-implanted films was weaker than the as deposited TiO_2 films.

The influence of V^+ ion implantation on grain size was evaluated using the full width at half maximum (FWHM) of the intense (101) diffraction peak of anatase TiO_2 according to the Scherer equation

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the crystallite size in nm, $k = 0.9$ which is a constant, λ is the wavelength of incident X-ray (CuKα = 0.154056 nm), and β is the FWHM in radians, θ is the half diffraction angle. The calculation results are presented in Fig. 6. It can be seen that the grain sizes decreased as the dose of implanted V^+ ions was increased. The estimated crystallite size of as deposited TiO_2 film was about 23 nm

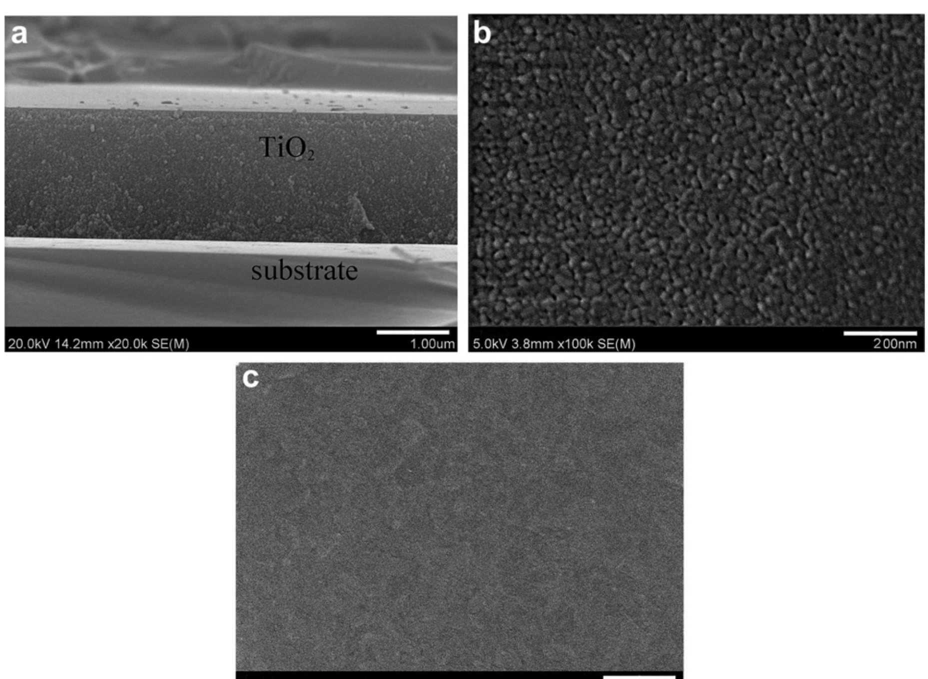

Fig. 1. SEM images. (a) Cross-sectional image of as deposited TiO_2 film; (b) Top view of the as deposited TiO_2 film; (c) Top view of the V^+-implanted TiO_2 film with dose of 6×10^{16} ions/cm^2.