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Properties of heavily W-doped TiO_2 films deposited on Al_2O_3-deposited glass by simultaneous rf and dc magnetron sputtering

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Abstract

TiO_2 films were heavily doped with W (TiO_2:W) by simultaneous rf magnetron sputtering of TiO_2, and dc magnetron sputtering of W. The advantage of this method is that the W content could be changed in a wide range. The coexistence of TiO_2, WO_3 and $TiWO_5$ in the TiO_2:W film was detected by XPS analysis. Besides, tungsten in TiO_2:W film on the bare glass may form mixed valence of W^{0+} and W^{6+}. Electrical conductivity was primarily due to the contribution of oxygen vacancies and W donors ($W_{Ti}^{\bullet\bullet}$). When the film thickness increased, the TiO_2:W film showed higher carrier concentration and higher mobility. Furthermore, the resistivity and the transmission decreased obviously with film thickness. On comparing with the TiO_2:W film deposited on the bare glass, the TiO_2:W film on the Al_2O_3-deposited glass exhibited lower surface roughness, lower resistivity, higher optical energy gap, higher optical transmission, and lower stress-optical coefficient.

Keywords: Film; Sputtering; Resistivity; Optical energy gap

1. Introduction

Titanium dioxide is a material widely used in the ceramic, cosmetic, coating, automobile and pigment industries. Nowadays it has been one of the most extensively studied oxides because of its remarkable optical and electrical properties [1,2]. Compared with other semiconductors, the great advantages of TiO_2 lie in the fact that it possesses appropriate flat band potential and high chemical stability. To date, TiO_2 is still the leading photocatalyst because it can mineralize a large range of organic pollutants [3,4]. However, due to its large band gap energy (typically < 380 nm), TiO_2 can only absorb ultraviolet light rather than visible light that occupies the great part of solar light. Furthermore, the overall quantum yield rate can be influenced by the low rate of electron transfer to dissolved oxygen and a high rate of recombination between electron–hole pairs [5]. Thus, much effort has been made to decrease the band gap energy of TiO_2 by doping TiO_2 with main group elements including carbon, nitrogen and sulfur [6–8], transition metal elements such as W^{6+}, Fe^{3+}, Zr^{4+}, V^{5+} and Mo^{6+} [9–12]. Among transition metal elements, W^{6+} ion can substantially reduce the recombination process between dopant cation and TiO_2 matrixes. It seems to be an interesting dopant to extend the absorption threshold toward the visible range. Besides, Jo et al. [13] studied WO_3 doped TiO_2 thick film deposited by screen printing, and reported an electrical interaction between WO_3 and TiO_2 for high temperature gas sensors.

Different methods, such as chemical, physical deposition processes, and ion implantation can be selectively employed to dope TiO_2 films [14]. Among the physical vapor deposition (PVD) techniques, magnetron sputtering has the advantage of being scalable to large-area industrial processes and has shown to be an efficient way to prepare and dope high-quality TiO_2 films [15]. Because doped films generally can be caused to have very stable optical and electrical properties [16]. Furthermore, studies of the conduction mechanism in heavily W-doped TiO_2 (TiO_2:W) thin films prepared by magnetron sputtering have not been reported. In this work, the TiO_2 films

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were heavily doped with W (TiO_2:W) by simultaneous rf magnetron sputtering of TiO_2, and dc magnetron sputtering of W. The advantage of this kind of deposited method is that the W content could be changed in a wide range.

Aluminum oxide is a very promising layer material because of its interesting optical properties and low cost [17]. The formation of fibered morphology of Al_2O_3 film was dominated by low Ar pressure, and was good for optical properties [18]. Besides, the glass has been widely used in optical devices and has many important applications. Thus, the Al_2O_3 film exhibiting fibered morphology was deposited on the glass and acted as the substrate in this study. The characteristics of films are affected by the preparation conditions such as working pressure, substrate temperature, types of substrates, and the thickness of the films [19,20]. The influence of types of substrates (bare glass and Al_2O_3-deposited glass) and film thickness on optical and electrical properties of TiO_2:W films was investigated.

2. Experimental procedures

The Al_2O_3-deposited glass and TiO_2:W films were prepared by magnetron sputtering. The targets used in this study were sintered stoichiometric Al_2O_3 (99.99% purity, 5 cm diameter, 5 mm thickness, Target Materials Inc., USA), sintered stoichiometric TiO_2 (99.99% purity, 5 cm diameter, 5 mm thickness, Target Materials Inc., USA) and metallic W (99.95% purity, 5 cm diameter, 5 mm thickness, Target Materials Inc., USA).

The dimension of the glass substrates (Corning 1737) was 24 mm × 24 mm × 1.1 mm. Before deposition, the substrates were ultrasonically cleaned in alcohol, rinsed in deionized water and dried in nitrogen. For the deposition of the films, the sputtering was performed in a pure Ar with a target-to-substrate distance of 15 cm. The substrate was not heated and no external bias voltage was applied to the substrate. The rotating speed of the substrate was 20 rpm.

A turbo-molecular pump backed by a rotary pump, was used to achieve a base pressure of 1.3×10^{-4} Pa. At a working pressure of 0.29 Pa, an rf power (13.56 MHz, RGN-1302, ULVAC, Japan) of 200 W was supplied to the Al_2O_3 target and the Al_2O_3 film was deposited to a thickness of 100 nm. On the Al_2O_3-deposited glass, the TiO_2:W film with a thickness of 20–300 nm was deposited at a working pressure of 1.5 Pa. An rf power (13.56 MHz, RGN-1302, ULVAC, Japan) of 50 W was supplied to the TiO_2 target, and a dc power (DCS0052B, ULVAC, Japan) of 6 W was applied to the W target.

Film thickness was measured using a surface profiler (Alpha-Step 500, TENCOR, Santa Clara, CA). Surface morphologies and surface roughness were examined by atomic force microscopy (AFM; Agilent 5500, Santa Clara, CA). Elemental compositions were investigated by X-ray photoemission spectroscopy (XPS; PHI 5000 VersaProbe, Japan). The optical transmission spectra of films in the ultraviolet–visible–near infrared (UV–VIS–NIR) region were obtained using a spectrophotometer (HP 8452A diode array spectrophotometer, Hewlett Packard, Palo Alto, CA). The resistivity, mobility, and carrier concentration were measured by a Hall Effect Measurement System (HMS-2000, ECOPIA, USA). Linear refractive indices of samples were recorded using a spectrometer (MP100-ST, Fremont, CA). Young's modulus was measured by the Nano Indenter XP System (MTS Systems Corporation, MN, USA).

Fig. 1 shows the Moiré deflectometry experimental set-up that is used to measure the nonlinear refractive indices of TiO_2:W films on the bare glass and the Al_2O_3-deposited glass. Lens L_1 focused a 5-mW He–Ne laser beam (wavelength of 632.8 nm), which was re-collimated by lens L_2. The focal lengths of lenses L_1, L_2 and L_3 were all –250 mm. Two similar Ranchi gratings, G_1 and G_2 with a pitch of 0.1 mm were used to construct the Moiré fringe patterns. The distance between the planes of G_1 and G_2 was set to 64 mm, which is one of the Talbot distances of the used gratings. The Talbot distances satisfy $z_t = tp^2/\lambda$ where p is the periodicity of the grating; λ is the wavelength of light, and t is an integer. In this work, the Moiré fringes were clearly formed at a Talbot distance of $z_{t=4} \approx 64$ mm. The Moiré fringe patterns were projected onto a computerized CCD camera by lens L_3, which was placed at the back of the second grating.

3. Results and discussion

3.1. The effect of Al_2O_3-deposited glass substrate

Fig. 2 shows the morphologies of (a) Al_2O_3-deposited glass, (b) TiO_2:W film on the Al_2O_3-deposited glass (sample A) and (c) TiO_2:W film on the bare glass (sample B). In Fig. 2a, the fibered morphology is a consequence of the nucleation of grains that grow geometrically and impinge laterally. It is a result of a competition during deposition between the rate of arrival of new Al_2O_3 species on the surface and the concurrent redistribution over the surface by diffusion. Hence, the fibered morphology may be due to the nonequilibrium growth [18]. The advantages of Al_2O_3 film with fibered morphology were described in a previous paper [18]. According to Fig. 2b and c, sample A and sample B were composed of irregular grains with island structures, but sample A exhibited lower roughness. The roughness values were very close to the morphologies of growing films [21]. Generally, the surface roughness could affect the carrier mobility [22].

The bonding conditions of oxygen on the surfaces of TiO_2:W films were investigated by XPS spectra. Fig. 3 shows Ti 2p photoelectron peaks in the XPS spectra of (a) TiO_2:W film on the Al_2O_3-deposited glass (sample A) and (b) TiO_2:W film on

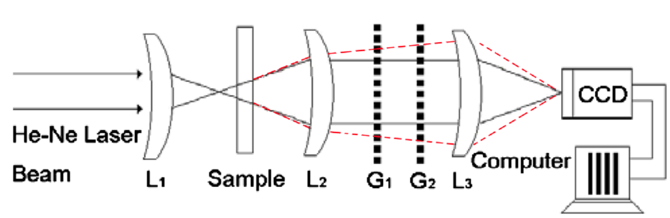

Fig. 1. The experimental set-up for measuring nonlinear refractive index by the Moiré deflectometry technique.