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ScienceDirect
Thin Solid Films 516 (2008) 3841–3846
www.elsevier.com/locate/tsf

Reactively sputtered TiO_2 layers on SnO_2:F substrates: A Raman and surface photovoltage study

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Received 17 October 2006; received in revised form 22 May 2007; accepted 28 June 2007
Available online 6 July 2007

Abstract

DC reactively sputtered TiO_2 layers on SnO_2:F substrates were investigated by Raman and surface photovoltage spectroscopy. The stoichiometry and layer thicknesses were investigated by elastic recoil detection analysis. The deposition temperature, the $O_2/(O_2+Ar)$ ratio and the deposition time were varied systematically. With increasing temperature, the layers become crystalline with the rutile modification dominating. Rutile phase preferentially forms on vertical facets of SnO_2 crystallites. Anatase phase starts to form during prolonged deposition and at lower $O_2/(O_2+Ar)$ ratios. The energy of the exponential absorption tails below the band gap, a measure of the defect density of the films, is determined by the deposition temperature and not by other parameters if the deposition temperature is relatively high, irrespective of the content of crystalline phases or the value of the band gap. Charge separation takes place at length scales significantly shorter than the layer thicknesses (diffusion length less than 6 nm). TiO_2 films sputtered at 380 °C show rectifying behaviour with a carbon contact.

Keywords: Titanium oxide; Thin films; Direct current reactive sputtering; Surface photovoltage spectroscopy; Raman spectroscopy; Elastic recoil detection analysis

1. Introduction

TiO_2 layers are of great interest for very different applications in fields as gas sensors [1], photovoltaics [2], photocatalysis [3] or ultraviolet photosensing [4] with Pt/TiO_2 Schottky-diodes [5]. TiO_2 films can be prepared by various methods. One of them is the relatively simple reactive DC sputtering technique from elemental targets which allows, for example, an excellent control of stoichiometry under very pure conditions [6]. Reactively sputtered TiO_2 layers are also suitable for photocatalysis [7] or application in dye sensitized solar cells [8].

The structure, chemical bonds and electronic properties of reactively sputtered TiO_2 layers depend on the sputter parameters as deposition temperature, total sputtering power, discharge power or oxygen content in the sputtering gas. The correlation of the electronic properties of reactively sputtered TiO_2 layers with the morphology and the content of TiO_2 phases (amorphous, rutile, brookite and anatase) is a major issue of the current research. For example, phase transitions from amorphous TiO_2 to the anatase phase can be stimulated by the plasma parameters concomitant with substrate heating. It has been shown, that crystalline TiO_2 phases start to form at relatively low substrate temperatures (below 200 °C) during reactive DC sputtering [8]. For comparison, the phase transition from anatase to rutile proceeds typically at temperatures of the order of 600 °C under equilibrium conditions while the phase transformation of the surface region of anatase nanoparticles demands significantly higher temperatures [9]. Theoretical studies predict phase and shape transitions of TiO_2 nanoparticles controlled by surface chemistry [10]. For reactive sputtering, the impact of energetic particles, like sputtered atoms and ions from the plasma, additionally influences the chemical processes.

In this work, we correlate qualitatively structural with electronic properties of reactively DC sputtered TiO_2 layers. The deposition temperature, the oxygen content in the sputtering gas, and the sputtering time were varied systematically in our experiments. The electrical quality of the sputtered TiO_2 layers is demonstrated by current–voltage characteristics of SnO_2:F/TiO_2/graphite structures. Raman spectroscopy is applied to identify the phases of rutile and anatase in the TiO_2 layers from the specific

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doi:10.1016/j.tsf.2007.06.172

Raman modes [11]. Surface photovoltage spectroscopy (SPS) [12] is used to characterize the surface work function, the surface photovoltage amplitude, the optical band gap of TiO_2 (E_g), and the so-called Urbach-energy (E_t) of the exponential absorption tails below the band gap [13].The value of E_g amounts to 3.06 eV for the rutile phase [14]. For the anatase phase, E_g is increased by 0.2 eV in comparison to rutile [15]. It has to be noted that by SPS studies, E_t is only related to optical transitions into states from which charge separation is possible. It will be shown that different growth modes may play a role at different facets on the substrates surface and lead locally to preferential formation of anatase or rutile phases.

2. Experimental details

2.1. Deposition of TiO_2 layers by DC magnetron sputtering

The TiO_2 layers were deposited by reactive DC magnetron sputtering from a pure Ti target on glass substrates covered with SnO_2:F (TEC8). Before deposition, the substrates (1×1 in.^{2} size) were cleaned in C_2H_5OH:H_2O = 1:1 solution in an ultra-sonic bath and dried with N_2 gas. For the TiO_2 layer deposition, a home made sputtering and evaporation system (basic pressure $5 \cdot 10^{-5}$ Pa) has been used. The Ti sputter target (3 in. diameter, 99.7% purity) was pre-sputtered for three minutes before reactive sputtering onto SnO_2:F substrate layers was performed. The distance between the sputter target and the substrate was 66 mm for all depositions. The sputter plasma was generated at a constant power of 100 W (DC).

The deposition temperature, the oxygen content in the sputter gas, and the deposition time were systematically varied. The substrates were heated with a halogen lamp (up to 380 °C). The oxygen content in the gas flow was changed by variation of the $O_2/(O_2+Ar)$ ratio from 0.032 to 0.120 while the standard Ar flow was 48 sccm. The purities of the Ar and O_2 gases were 99.999 and 99.99%, respectively. The pressure during the deposition was about 0.4 Pa. The deposition times varied between 5 and 60 min. The thickness of the sputtered TiO_2 layers has been changed over one order of magnitude.

2.2. Sample characterization

The morphology of the sputtered TiO_2 layers (lateral views and cross-sections) was investigated with a LEO 1530 (Gemini) *field emission scanning electron microscope*. The acceleration voltage was kept at 10 kV.

For thin layers, the ERDA (elastic recoil detection analysis) technique gives information about the areal density of the different atomic masses. The Berlin time-of flight ERDA setup at the Hahn-Meitner-Institute [16] was applied for the investigation of the stoichiometry and of the areal densities of Ti, O, Ar, Si, Fe, C, H in the sputtered TiO_2 layers. Areal density of Ti and corresponding TiO_2 thickness with sputter times for TiO_2 layers prepared at deposition temperature of 380°C and $O_2/(O_2+Ar)$ ratio of 0.08 are given in Table 1. The thickness scales vary well with the deposition time. The areal density of oxygen atoms was two times larger than the areal density of Ti atoms, i.e. stoichiometry of TiO_2 was reached. The thickness depends as well on $O_2/(O_2+Ar)$ ratio. For $O_2/(O_2+Ar)$ ratio of 0.04 and deposition time of 30 min, a 45 nm TiO_2 layer was obtained. The total concentration of Ar, C, Fe and Si atoms was less than 5% for the long sputter times and about 10% for the sputter time of 5 min. If assuming a density of TiO_2 equal to 4 g/cm^3 (rutile: 4.25 g/cm^3, anatase: 3.89 g/cm^3), the thicknesses of the TiO_2 layers amount to 6, 15, 32 and 65 nm for sputter times of 5, 15, 30 and 60 min, respectively (deposition temperature 380 °C, $O_2/(O_2+Ar)$ ratio 0.08).

Table 1
Areal density of Ti and corresponding TiO_2 thickness with sputter time

Sputter time (min)	Areal density of TiO_2 ($\times 10^{17}$ Ti/cm^2)	TiO_2 thickness[a] (nm)
5	0.28	6
15	0.78	15
30	1.60	32
60	3.50	65

Deposition temperature and $O_2/(O_2+Ar)$ ratio for sputtered TiO_2 layers were 380 °C and 0.08, respectively.
[a] Assumed the density of TiO_2 = 4 g/cm^3 (rutile: 4.25 g/cm^3, anatase: 3.89 g/cm^3).

Some electrical properties of the sputtered TiO_2 layers were checked by using small area SnO_2:F/TiO_2/graphite structures (area about 4 mm^2) which were manually fabricated with carbon ink. Current–voltage measurements were performed at room temperature in the dark with a source-measure unit (Keithley, SMU 237).

The anatase and rutile phases of TiO_2 were identified by Raman spectroscopy. A Raman spectrometer with a HeNe laser (wavelength 632.8 nm) for excitation has been used. The spectrometer was calibrated with the phonon line of Si. The accumulation time was 300 s for all spectra. The spectra were normalized to the substrate (glass/SnO_2:F).

The work function of the sputtered TiO_2 layers was measured in air with a Kelvin probe (Besocke). Surface photovoltage spectra were obtained as the light-induced change of the work function. The SPS measurements were performed at room temperature. A quartz-prism monochromator (SPM2) with a Xe-lamp (1000 W) has been used for illumination (photon energies between 2.5 and 4.5 eV were used, the spectral resolution was better than 30 meV). Before starting the SPS measurements, the samples were kept in the dark until the value of the work function became stable. Values of the forbidden energy band gap and of the energy of the exponential defect tails below the band gap were obtained from the analysis of the surface photovoltage spectra.

3. Results and discussion

3.1. Morphology and electrical properties

Fig. 1 shows a typical cross-section of a TiO_2 layer sputtered on SnO_2:F at 380 °C. The thicknesses of the SnO_2:F and TiO_2 layers are about 500 and 50 nm, respectively. The large grains are related to the polycrystalline SnO_2:F substrate layer (thickness about 500 nm). The most striking feature of Fig. 1 is the presence of two distinct local regions A and B (marked by the circles in Fig. 1). Region A is characterized by an excellent TiO_2 coating on SnO_2 facets with angles of the order of 45°. The thickness of the