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Stannic oxide thin film growth via ion-beam-sputtering

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ABSTRACT

Stannic oxide (SnO_2) is of great technological interest as a member of the important family of oxide materials that combine low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum.

Tin oxide thin films are grown on sapphire substrates by ion beam sputtering method with varying heater temperature from 100 to 750 °C at constant gas flux. Enhancement of crystallinity of thin films with temperature is observed from X-ray diffraction and Raman spectroscopy studies. Morphological studies by atomic force microscopy reveal changes in grain size with variation in substrate temperature.

1. Introduction

Tin dioxide (SnO_2) crystallizes in a rutile-type structure with two equivalent a-axes (4.7382 Å) and a shorter c-axis (3.1871 Å), and it has a wide band gap of 3.59 eV which makes it belong to the class of transparent conductive oxides. Stoichiometric pure SnO_2 is an insulator, while nonstoichiometric SnO_2 displays n-type conductivity due to oxygen vacancies or doping with elements such as antimony or fluorine. Therefore SnO_2 has been recognized as promising material for technological applications, e.g. (i) gas sensors [1–3], (ii) solar cells [4,5] or (iii) electromagnetic shielding maintaining transparency [6]. In this work we refer to a sputtering technique utilizing a self-designed ion source, offering significant advantages over other kinds of sputtering, among them the control of ion energy, flux, species and angle of incidence — nearly independently of each other. Furthermore the gas discharge of the ion source is contained and separated from the rest of the deposition system, avoiding problems arising from sensitive substrates. Advantages of the self-designed sources, among others are the robust mechanical embodiment, the modest electronic demands and most notably the long lifetime resulting from the absence of filaments in the discharge plasma. A high density RF plasma is generated feeding the pre-mixed gas composition into a discharge chamber surrounded by the RF-induction coil of the RF-generator (2 MHz). The inductively coupled eddy electromagnetic RF-field generates a self-sustaining, electrodeless ring discharge. The ion extraction is accomplished by a multihole three-grid extraction system using the accel–decel technique. These ion sources are excellently suited to be operated with reactive as well as with nonreactive gases. For further details concerning the ion source the reader might be referred to [7].

2. Experimental details

SnO_2 layers were produced using the system described above with intentional heating the substrate up to 750 °C from a 3″ diameter metallic tin target of 99.999% purity (*Kurt J. Lesker Company*) in an atmosphere of argon and oxygen gases, both of which have 99.999% purity. The chamber is pumped to a base pressure of 2×10^{-4} Pa. The RF launch power was chosen to be 200 W, whereas the extraction voltages were chosen to be +2.4 kV and −0.2 kV to yield a homogeneous impingement onto the 3″ target with a current density of 16 mA/cm^2. Films were fabricated on the (001) and (012) surfaces of α-Al_2O_3 (sapphire) at a constant gas mixture of 5 sccm argon and 10 sccm oxygen. The substrates were subject of exposure for 60 min.

The microstructure and morphology of deposited films were characterized using X-ray diffraction (XRD) and atomic force microscopy (AFM). For the X-ray diffraction studies, θ–2θ scans were carried out in Bragg–Brentano geometry on a SIEMENS D5000 diffractometer with Cu K_α radiation. AFM studies were performed on an AIST-NT SmartSPM, operating in non-contact mode. Thickness and optical transmittance were determined using a PerkinElmer Lambda 900. The UV–visible transmission data were then used to extract the optical band-gap (E_g) by following Tauc's method [8]. Raman measurements were performed on a Renishaw InVia microscope system. The spectra were recorded in backscattering geometry at room temperature. A polarized 525 nm excitation laser was focused onto the sample surface using a 50× objective. The same objective was used to collect the scattered light, which was then dispersed by a spectrometer with a focal length of 250 mm and recorded by a CCD detector. The system's spectral resolution is about 1.5 cm^{-1}, whereas the power of the incident laser is 7.5 mW. To avoid a wrong interpretation due to unintentional affection with the laser, spectra with lower laser power were taken and compared before and after full power observation.

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3. Results and discussion

To optimize the properties of tin oxide thin films, a series of tin oxide samples was prepared on c-cut and r-cut sapphire by varying the heater temperature. The effect of this deposition parameter on film properties will be discussed here.

X-ray diffraction pattern taken from the layers indicated that the SnO_2 films grow epitaxially on both orientations of sapphire with the relationships of SnO_2 (200)||Al_2O_3 (001) and SnO_2 (101)||Al_2O_3 (012), respectively. This is consistent with previous results for SnO_2 deposited on the same sapphire substrate orientations [9–11]. Fig. 1a shows X-ray diffractograms obtained from thin films grown on c-cut sapphire, Fig. 1b those from layers deposited on r-cut sapphire. Since no K_β filter was applied, additional reflections of this radiation overlay with the K_α lines. The vertical lines indicate the position of different lattice planes taken from the ICDD PDF 00-041-1445 for SnO_2. It can be observed that on both substrates a shift towards the bulk position can be observed with increasing the substrate temperature. Such a shift can be interpreted in terms of lower stress or better stoichiometry. Consequently the interplanar spacing calculated from the 2θ values and the lattice constants get closer to the bulk values. In case of r-cut sapphire the interplanar spacing can be calculated from the K_α (101) peak position and changes with increasing temperature from 2.67 Å at 450 °C to 2.65 Å at 700 °C (d_{101} = 2.6427 Å from ICDD PDF 00-041-1445). In this case no calculation of the single crystal parameters is possible, since the (101) reflection is the only one visible in the diffractograms. When c-cut sapphire is used as a substrate, a calculation of lattice constant *a* is possible from evaluating the (200) reflection. Values observed differ less than 2% from the bulk value (4.74 Å) even for the lowest temperature applied to the substrate holder. At temperatures above 450 °C hints of a (101) reflection can be used to calculated lattice constant *c* using the values already known for *a*. Considering the uncertainty of the (101) peak position resulting from an overlay with the (200)K_β line a maximum separation of 1% from the bulk value (3.1871 Å) can be stated. Grain sizes could be estimated following the Scherrer approach increasing from 90 to 120 nm in case of 450 °C heater temperature up to 200–250 nm for the process at 700 °C. Higher temperatures are crucial to obtain crystalline SnO_2. A heater temperature below 500 °C seems to be too low to provide the energy necessary on the surface for the sputtered particles to yield a favored position and create an ordered crystal lattice — the existence of amorphous material might be probable. This assumption is consistent with other works concerning the deposition on substrates without intentional heating. Das et al. [12] observed amorphous tin oxide at substrate temperatures of 150–

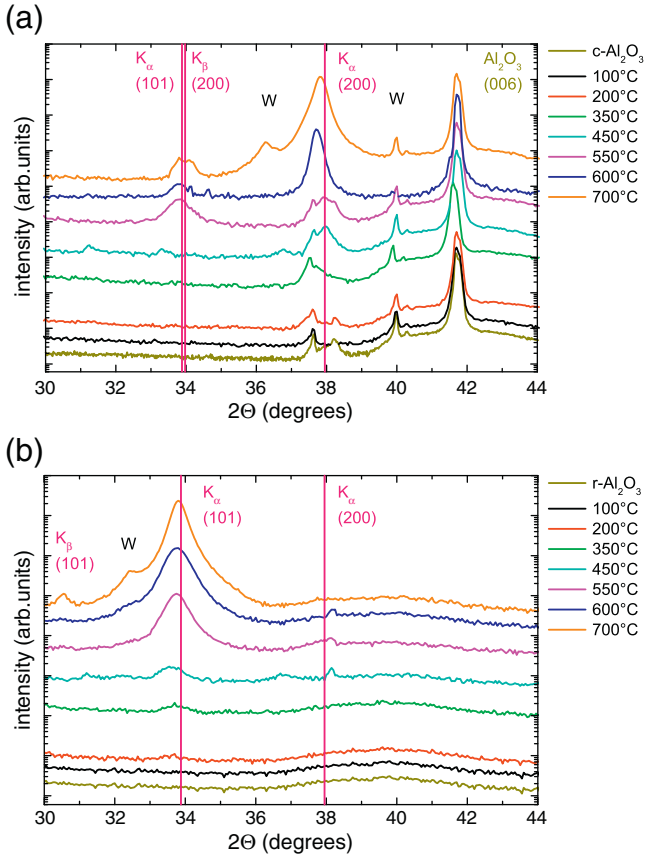

Fig. 1. X-ray diffraction analysis: waterfall diagram of samples deposited on c-cut sapphire (a) and r-cut sapphire (b) at elevated temperatures. Reflections denoted by "W" originate from tungsten L-radiation indicating a degradation of the X-ray tube.

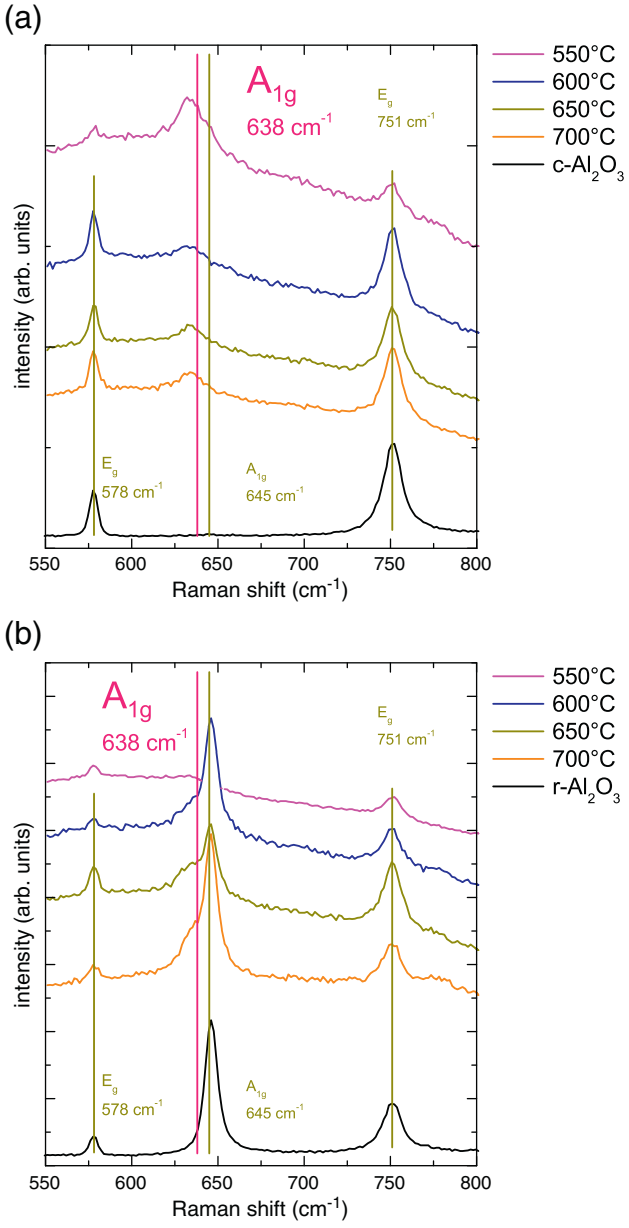

Fig. 2. Raman spectra of SnO_2 deposited on c-cut sapphire (a) and r-cut sapphire (b) at different heater temperatures. The assignments were done according to reference [15] for sapphire and [16] for SnO_2.