OPTICAL PROPERTIES OF SnO_2 FILM

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Abstract

A SnO_2 epitaxial thin film with thicknes of 25 nm is grown by the PLD technique on a (111) orientated $SrTiO_3$ (STO) substrate. The effects of epitaxial growth on the lattice structure, microstructure and optical properties of oxide thin film has been studied. The film is out-of-plane epitaxial oriented to the substrate. The XRD difractograms show only tin dioxide peaks which can be assigned to the (002) and (004) reflexes of the tin dioxide phase. The thickness of the film is calculated from the distance of X-ray reflectivity oscillations. The observation of clear thickness fringes is an indication for a low surface roughness of the film. Atomic force microscopy (AFM) was also used to investigate the surface of the films. AFM images reveal a film surface that shows a flat film surface. Variable angle spectroscopic ellipsometry (VASE) has been used to determine the optical properties of the SnO_2 film.

Introduction

The aim of the present project is to extend the knowledge acquired to date to study the main parameters for obtaining epitaxial films by various methods, determine optimum conditions necessary and analyze the phenomena involved during deposition, so that the structural and optical properties of the films they have finally qualify for applications in the energy and environmental industries.

In the literature, metal oxides such as SnO_2 are of major interest in solar and environmental applications, and it is necessary to deepen the studies in this field.

Tin oxide in its pure form is an n-type semiconductor [Chowdhury, 2011]. Its results in terms of electrical conductivity are due to the existence of punctual defects (native and foreign atoms) acting as donors or acceptors. Some unique properties make this material extremely useful for many applications. Thus, increased attention is paid to studies on tin oxide, particularly with regard to the preparation methods, its electrical and optical properties.

Experimental

The tin dioxide thin film was deposited on commercial (111) oriented $SrTiO_3$ (STO) substrate using the pulsed laser deposition (PLD) technique. The substrate was ultrasonically washed using acetone and methanol before deposition The PLD technique includes a relatively simple concept of ablation using laser pulses on the target material. With each pulse, an amount of material is removed and transported in the direction of the substrate via the plasma. Stoichiometric transfer of the target material to the substrate, mass propagation time comparable to crystallization and growth processes, atomic scale growth control of the film,

allow the formation of well-defined, layered structures. One of the most fascinating features of PLD, is a nearly stoichiometric transfer from the SnO_2 target through the ablation process [Díaz, 2012]. During the laser ablation process, photons penetrate into the surface layers of the target material in accordance with the optical absorption depth and, first, by removing some of the atoms' valence electrons (in the PS duration). These surface-valent electrons oscillate in the electromagnetic field of the laser and collide with atoms and ions by neighbors, transferring some of their energy to the crystal lattice. Once the particles have reached the surface of the substrate, diffusion occurs until the atoms reach low energy levels. Since each pulse emits less than one layer of deposited material, sequential ablation from multiple lenses can be used to increase the material. PLD is considered to be one of the most widely used flexible research techniques for filming large-scale films. A KrF excimer laser (248 nm wavelength and 23 ns pulse width, Lambda Physics) was used for ablating the tin dioxide target with an energy density of about 2 J/cm^2 and a repetition rate of 3 Hz. The films were deposited at a substrate temperature of 700 °C using an oxygen pressure of 50mTorr. After growth the films were annealed for 20 min and cooled down to room temperature at an oxygen pressure of about 0.5 atm O_2. Film quality and structural properties were investigated by X-ray diffraction (XRD) using a high resolution thin film diffractometer. Different measurements were made: (1). Reflection in order to estimate the thickness of the films, (2) Normal Bragg-Brentano geometry to obtain information about the phase and structural order of the films. Before every XRD analysis, the sample alignment was performed on STO (111) peaks of the substrate in order to avoid the peak shift due to the sample misalignment. Atomic force microscopy (AFM) has been employed to investigate the surface of the films. A *DI Nanoscope III* AFM in tapping mode was used for this purpose. In order to study the optical properties of thin films the ellipsometry technique will be employed. Ellipsometry is a non-destructive optical technique used in this paper for optical characterization of thin film, in which the sample to be characterized is illuminated with a beam of polarized light.

Results and discussion

1. XRD results of the SnO_2 film

The SnO_2 film was grown by on-axis pulsed laser deposition from the SnO_2 target on STO (111). In figure 1a) the reflectivity curve of the film grown on STO (111) substrate is shown. The thickness of the films is calculated from the distance of the oscillations. The observation of clear thickness fringes is an indication for a good surface roughness of the films. We calculate the thickness to be 25 nm.

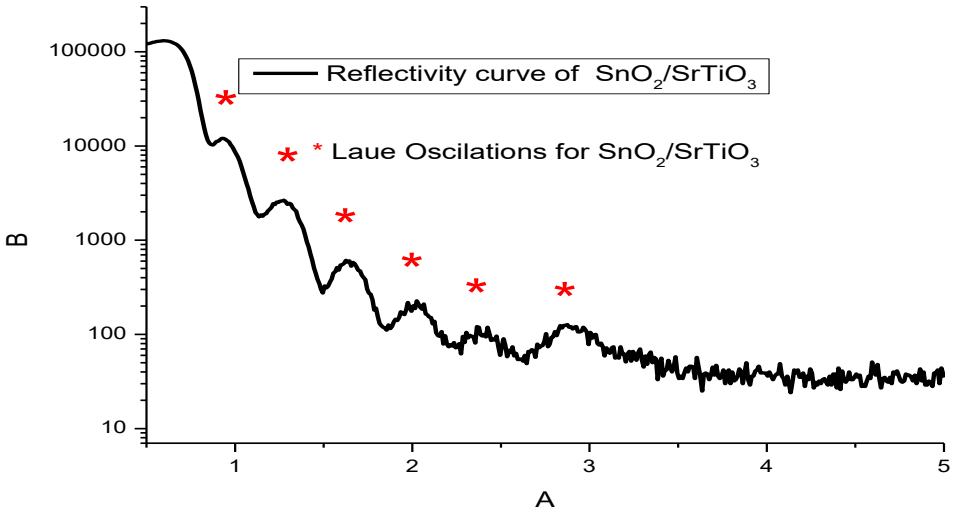

Figure 1. The reflectivity curve of the film grown on STO (111) substrate.

Laue oscillations remain observable for SnO_2 thin film which indicate that the structural quality of the film is not deteriorated.

Wide angle θ-2θ XRD scans of the film grown on STO (111) has been recorded to investigate the phase-purity and epitaxial nature of the films and are plotted in figure 2a). The scans show only (111) substrate peaks and peaks that can be assigned to the (00l) reflexes of SnO_2. The films are out-of-plane epitaxial oriented to the substrate. There are no peaks corresponding to other phases or impurities of films.

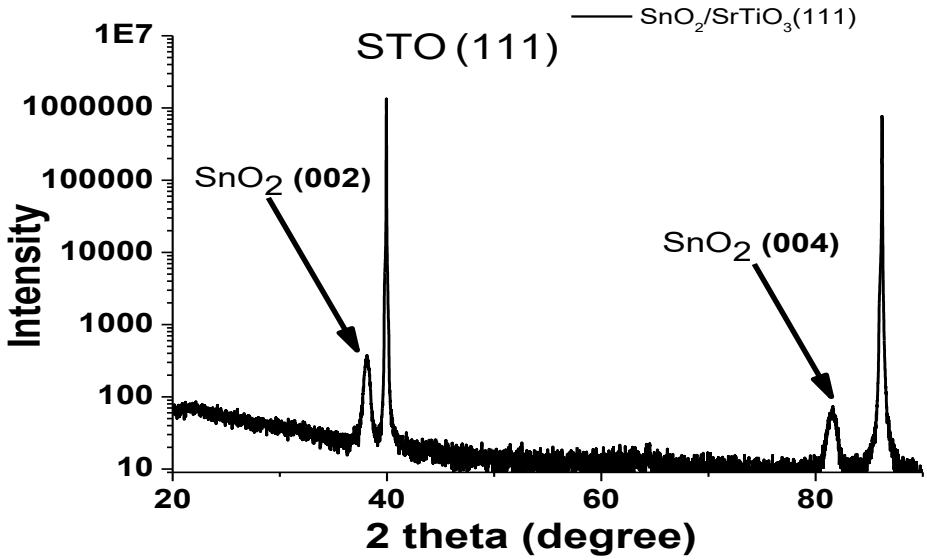

Figure 2.a) X-ray diffraction patterns (Bragg-Brentano θ-2θ) of the 25 nm film grown on STO (111).

Figure 2.b) shows X-ray diffraction (XRD) ω-2θ Bragg scans along the 002 reflection of the as-grown film. We determined the out of plane lattice parameter to be 4.716 Å, which is close to that of bulk SnO_2 (c = 4.73 Å)

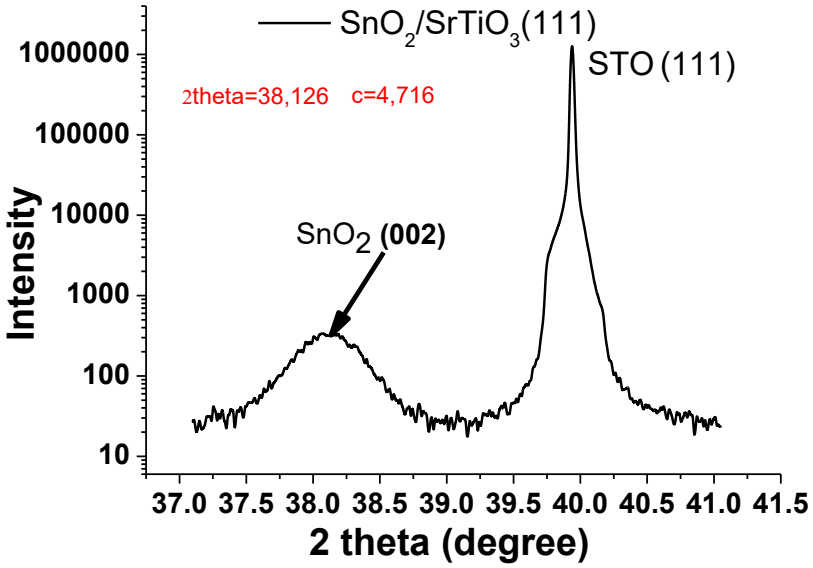

Figure 2. X-ray diffraction (XRD) ω-2θ Bragg scan around the 002 reflections of the SnO_2 film and the STO (111) substrate.

2. Topography of the SnO_2 film

Atomic force microscopy (AFM) was used to investigate the surface of the films. AFM images reveal a film surface that shows a flat film surface and with no visual droplets of defects.

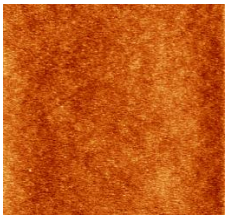

Figure 3. Surface morphology images of 25 nm films of SnO_2 deposited on STO (111).

3. Optical properties of the film

Ellipsometry measures the change in polarization state of the measurement beam induced by reflection from (or transmission through) the sample. The change in polarization state is commonly characterized by the ellipsometric Psi (Ψ) and Delta (Δ) parameters. In Spectroscopic Ellipsometry (SE), Ψ and Δ values are acquired as a function of wavelength. However, to extract sample parameters such as film thickness and optical constants from the measured SE data set, an optical model must be built to fit the data. The CompleteEASE software provides a graphical user interface for building models and displaying measured data and model fits. It also provides a simple interface to the SE hardware, making acquisition of accurate SE data fast and easy.

The optical constants of the STO substrate have been determined by a VASE measurement on the bare substrate and have been fixed in the two-layer model system. The SnO_2 layer was fitted by a Kramers-Kronig consistent B-spline model. In figure 4a) we show the Tauc-plot of the optical absorption spectrum for 25 nm thin film. This plot allows for the determination of direct optical band gap by extrapolating the linear parts of the curves to zero.

The inset presents ellipsometric Ψ parameter function of wavelength recorded for 3 different angles (65, 70 and 75 degree) together with the fitting calculated curves. The band gap energy of the 25 nm thin SnO_2 film deposited by on-axis pulsed laser on STO (111) substrate is 4.18 eV.

It is observed that the band gap energy can be tunable to be bigger than the values observed by other researchers [Mishra, 2009]

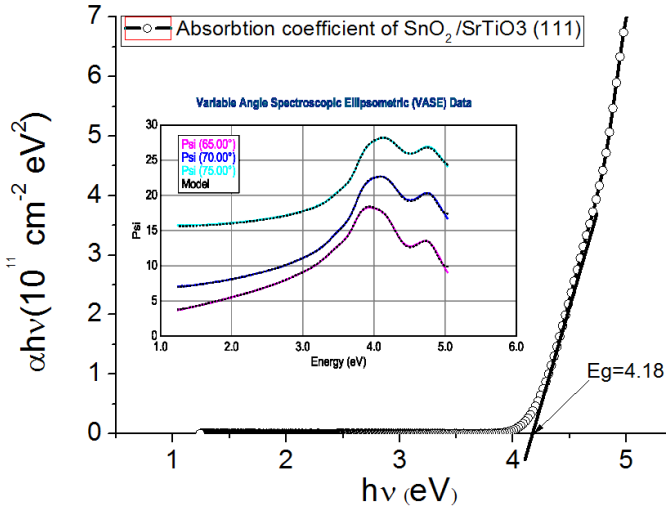

Figure 4.a) Tauc-plot of the optical absorption spectrum for 25 nm thin SnO_2 film. In the inset ellipsometric Psi (Ψ) and Delta (Δ) parameters function of wavelength were recorded for 3 different angles.

The refractive index (n) and extinction coefficient (k) for the 25 nm SnO_2 film calculated with Complete EASE software are presented in figure 4b). The inset presents the average values for n and k parameters of the film.

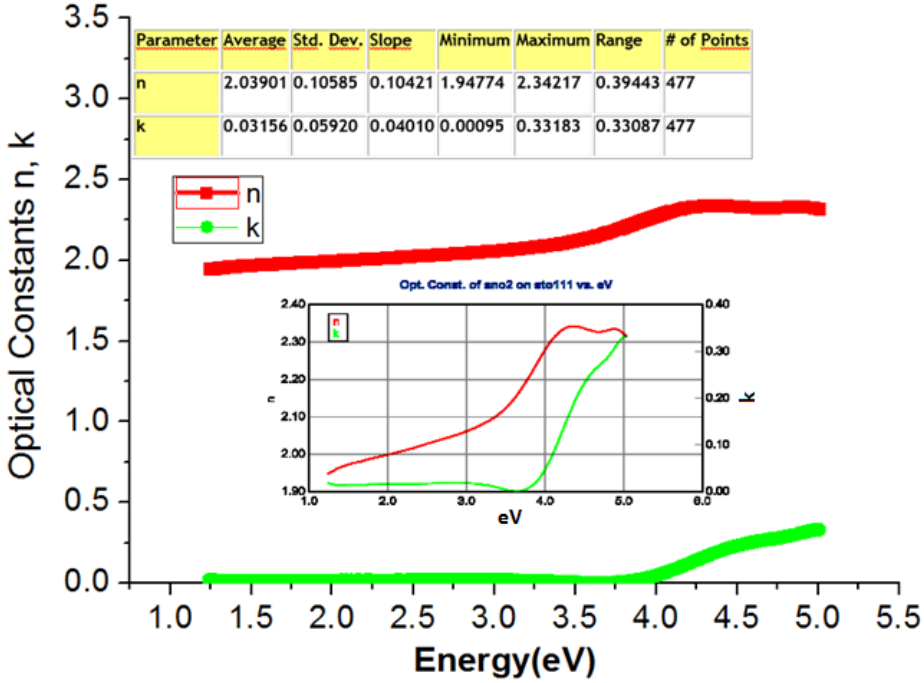

Figure 4. b) Optical constants (n, k) of 25 nm SnO_2 film. The results are in accordance with

the findings of Baco et al. [Baco, 2012]

Conclusion

Epitaxial films of SnO_2 have been grown by on-axis pulsed laser deposition from the SnO_2 target on (111) oriented crystalline $SrTiO_3$ substrate with a band gap energy of 4.18 eV. The results demonstrate that epitaxial strain can be deployed to change optical properties of oxide films. This could potentially be used to produce films with properties designed for specific application.

Acknowledgements

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References

F.R. Chowdhury, S. Choudhury, F. Hasan, T. Begum, Optical properties of undoped and indium-doped tin oxide thin films, *Journal of Bangladesh Academy of Sciences*, Vol. 35, No. 1, 99-111, 2011

E.C. Díaz, A. Duarte-Moller, J.M. Camacho, R. Castro-Rodríguez, *SnO_2 thin films grown by pulsed Nd:YAG laser deposition*, Applied Physics A, Volume 106, Issue 3, 619–624, 2012

R.L. Mishra, S.K. Mishra, S.G. Prakash, Optical and gas sensing characteristics of tin oxide nano-crystalline thin film, *Journal of Ovonic Research*, Vol. 5, No. 4, 77 – 85, 2009

S. Baco, A. Chik , F.M. Yassin, Study on Optical Properties of Tin Oxide Thin Film at Different Annealing Temperature Journal of Science and Technology, Vol 4, No 1, 61-71, 2012.