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Strain-induced optical band gap variation of SnO₂ films

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Abstract

Thickness dependent strain relaxation effects are utilized to study the impact of crystal anisotropy on the optical band gap of epitaxial SnO₂ films grown by pulsed laser deposition on (0001)-oriented sapphire substrates. A X-ray diffraction analysis reveals that all films are under tensile biaxial in-plane strain and that strain relaxation occurs with increasing thickness. Variable angle spectroscopic ellipsometry shows that the optical band gap of the SnO₂ films continuously increases with increasing film thickness. This increase in the band gap is linearly related to the strain state of the films, which indicates that the main origin of the band gap change is strain

relaxation. The experimental observation is in excellent agreement with results from density functional theory for biaxial in-plane strain. This work demonstrates that strain is an effective way to tune the band gap of SnO₂ films and suggests that strain engineering is an appealing route to tailor the optical properties of oxide semiconductors.

Keywords: Tin oxide; Epitaxial, Pulsed laser deposition; X-ray diffraction; Optical properties; Strain, Bandgap, DFT

1. Introduction

Epitaxial oxide thin films are of tremendous importance due to their promise across a wide range of technological fields including optical, electronic, optoelectronic and biological areas [1]. Semiconducting metal oxides are particularly attractive due to their chemical and thermal stability and potential use in photovoltaic or photocatalytic devices [2]. Thus, the optical band gap of these materials is considered to be one of the most critical values in terms of applications. Band gap engineering [3] in these materials is typically accomplished by controlling the composition of alloys or constructing layered materials with alternating compositions [4]. Changes of optical properties can also be induced by the creation of holes [5], the modification of the surface structure [6], or by the introduction of defects [7]. In the last decade, researchers have studied the effects of strain on properties of metal oxides. Strain has direct effects on the structure in terms of bond length and bond angle changes. These structural changes can alter the electronic structure of materials. For example, epitaxially grown films are biaxial strained to a substrate ip and show oop strain due to the Poisson effect. This kind of strain engineering provides a potentially disorder-free route to enhance the electron mobility in transistors [5], increase

catalytic activity [8], alter band structure and significantly increase superconducting [9], as well as ferromagnetic and ferroelectric transition temperatures of thin films [10]. The standard techniques used for tuning the band gap in thin films are oxygen vacancy [11] and nitrogen doping [12], and interfacial interactions [13]. Strain has been proposed as an alternative to standard techniques [3, 14, 15, 16]. Tin oxide (SnO_2) is an important n-type semiconductor oxide with high optical transmission in the visible range due to its wide band gap of 3.6 eV, which can be grown epitaxial through various methods [17]. Strain-engineering of the band gap of SnO_2 has been studied theoretically and demonstrated experimentally for SnO_2 films [18]. Here, we grow SnO_2 thin films on single-crystalline (0001)-oriented sapphire substrates with different thicknesses that differ in their strain state due to in-plane strain relaxation. We find that the optical band gap of the SnO_2 films increases linearly with increasing out-of-plane strain and determine a sensitivity of 0.38 eV per percent strain. This result is in excellent agreement with density functional calculations for films with varying biaxial in-plane strain.

2. Experimental

SnO_2 thin films with thickness of 8-126 nm have been grown on single-crystalline (0001)-oriented sapphire substrates using pulsed laser deposition. A stoichiometric SnO_2 target has been used. The growth temperature and laser energy was 700 °C and 2.0 J/cm², respectively. The growth has been carried out in an oxygen pressure of $p_{\text{O}_2} = 50$ mTorr and the films were annealed for 20 min and subsequently cooled in 0.5 atm O_2 to ensure a good oxygen stoichiometry. Structural characterization of the films has been carried out by X-ray diffraction (XRD) and reflectivity using a *X'Pert Panalytical MRD* diffractometer, Atomic force microscopy

(AFM) was used in order to investigate the topography of the as grown films and determine their surface roughnesses. The optical properties of the SnO_2 films have been determined by variable angle spectroscopic ellipsometry (VASE). The ellipsometric data was collected with a *J.A. Woollam Co.* ellipsometer working in a rotating analyzer mode in the energy range of $1.2 \text{ eV} < h\nu < 5.0 \text{ eV}$ at incidence angles 65° , 70° and 75° and at room temperature. The data on the wavelength-dependent ellipsometric angles Ψ and Δ has been fitted by a two-layer model consisting of the substrate and the film in order to determine the optical refractive index n and extinction coefficient k of the thin film material.

3. Results and Discussion

3.1 Structural properties

Figure 1 (a) shows wide angle θ - 2θ X-ray diffraction patterns of the films with various thickness. All films show only substrate reflections and the (200) and (400) peaks of the tetragonal rutile SnO_2 structure. This means that all films are epitaxial with the a -axis oriented out-of-plane (oop) and that no impurity phases are present within the detection limit of XRD. This is important to note, as previous work has shown the degradation of the film crystallinity [18] and the appearance of (101) oriented domains for thicker films [19]. XRD scans around in-plane reflections (not shown) reveal that the films grow with a SnO_2 [010] // Al_2O_3 $\langle 110 \rangle$ epitaxial relationship. This is in agreement with previous studies [13, 19] and means that SnO_2 forms crystallographic domains of about equal portion with the bc plane of the unit cell rotated 120° with respect to each other.

Figure 1 (b) shows the θ - 2θ scans around the (400) SnO_2 peaks. Laue fringes are observed for all films, which indicates excellent structural film uniformity and quality. The XRD peaks

monotonically shift to lower angles with increasing film thickness, which is consistent with an increase of the oop lattice parameter a . The most obvious origin of this lattice parameter change is strain relaxation. Thinner films are partially strained to the substrate, but with increasing thickness the film tends to release the in-plane (ip) strain to obtain its strain-free bulk lattice parameter. The non-linear strain-dependence on the film thickness is in agreement with theoretical considerations on elastic energies of strained thin films and with experimental observations in numerous thin film thickness studies [20].

It has been predicted that the optical response of SnO₂ to strain depends on the type of lattice deformation applied [21]. Experimentally, pure oop tensile strain without any changes of ip lattice parameters has been experimentally shown to reduce the optical band gap of SnO₂ films [21], whereas oop tensile strain induced by ip strain relaxation increases the band gap [18]. It is therefore important to discuss the strain relaxation scenario that occurs in SnO₂ films with increasing thickness. It should be noted that the hexagonal lattice of sapphire Al₂O₃ imposes asymmetric ip stress on the tetragonal lattice of SnO₂. For a -axis oriented SnO₂ films, the lattice mismatch is about +1% along the b axis and as large as +13.8% along the c axis, which can lead to different strain relaxation mechanisms along both ip lattice directions [22]. The lattice parameters of the thickest film were determined from 2θ scans on ip and oop reflections and are given as $a = 4.669 \pm 0.001$ Å, $b = 4.73 \pm 0.01$ Å and $c = 3.16 \pm 0.01$ Å. Both ip parameters, b and c , are smaller than what is expected for coherent growth on c -cut sapphire (JCPDS file 46-1212, $a = 4.758$ Å, $c = 12.991$ Å, $c/a = 2.730$). This indicates that partial strain relaxation took place along both lattice axes and suggests that strain relaxation is not uniaxial along one lattice direction. However, unfortunately we are not able to quantify the ip strain states of thinner films with sufficient accuracy to confirm this assumption. The reason is the poor ip epitaxy of the films due to the large asymmetric lattice mismatch, which leads to broad XRD ip peaks with low intensity.

The errors of the ip parameters of the films were too large provide a clear trend as function of the film thickness.

3.2 Topographic properties

Figure 2 (a) and (b) show topographic $5\mu\text{m} \times 5\mu\text{m}$ AFM images of the 15 nm and 126 nm film, respectively. Both images demonstrate the excellent film growth of SnO_2 via PLD. For the thinner film, step-edge terraces of the sapphire substrate are visible. The film is nearly atomically flat with a root mean square (rms) roughness of only 0.1 nm, which is much smaller than what has been reported for SnO_2 films deposited on a- and m-cut sapphire [23]. Even for the thickest film the rms roughness is only of the order of 0.2 nm.

3.3 Optical properties

Figure 3 (a) shows the wavelength dependent ellipsometric angles Ψ (top) and Δ (bottom) measured for all sample thicknesses. The substrate and the layer are approximated by a Kramers-Kronig consistent B-spline with 16 data points over the full energy range. This two-layer model is justified by the flat interfaces and surfaces of the SnO_2 films, as shown in the previous section. The optical band gaps of the films are determined by extrapolating the linear part of the absorption α to zero, where the absorption is plotted as $(\alpha h\nu)^2$ vs $h\nu$ (Tauc-plot). This method is the standard technique for determining the optical band gap of direct band gap semiconductors, such as SnO_2 . The model fits that were used to determine the optical properties are plotted as solid black lines and demonstrate an excellent match with the experimental data. The resulting optical refractive index n and extinction coefficient k are shown in Figure 3 (b). The optical properties of the films are in agreement with values reported in previous bulk or thin film studies [23]. The films have a low k , below 3 eV, due to their transparent nature, but the absorption is

significantly increasing at higher energies due inter-bandgap transitions. This absorption band is also reflected in a peak of n and was attributed to transitions from the valence band, composed of O 2p states, to the conduction band, which consists of hybridized O 2p and Sn 5s states [9,20].

In order to determine the optical band gaps of the films, the absorption coefficient $\alpha = 4\pi k/\lambda$ was plotted in a Tauc plot as α vs the energy $h\nu$ (Figure 4), where the direct band gap is given by extrapolating the linear section of the curves to zero. The band gap is continuously increasing with increasing film thickness. The thickness dependence of the band gap is shown in Figure 5 (b). This thickness dependence is non-linear and resembles the thickness dependence of the strain that was determined from the XRD data and is shown in Figure 5 (a). It is therefore natural to suppose that the changes of the optical band gap are mainly strain driven. Figure 5 (c) shows the optical band gap as a function of oop strain. The linear dependence implies that compressive oop strain reduces the band gap of SnO₂ films. We find that the sensitivity to oop strain is about 0.38 eV/ % strain. We should note here that the sign of this strain sensitivity is opposite to our previous study on single axis oop strain induced by low-energy He implantation [20]. Zhou *et al.* [17] reported an increase of the band gap with increasing film thickness as seen in this study, but with a larger strain effect. However, it is unclear whether this large strain response was caused purely from strain effects or if a loss of crystallinity contributed.

In order to clarify the different response of SnO₂ films to strain we compare our experimental data with DFT calculations [21]. For the calculations, the pseudopotential Quantum ESPRESSO code was deployed. First, geometric optimization of the rutile bulk structure was carried out using the Perdew- Burke-Ernzerhof (PBE) exchange functional within the generalized gradient approximations (GGA). The optimized SnO₂ structure has the lattice parameters $a_{\text{the}} = 4.78 \text{ \AA}$ and $c_{\text{the}} = 3.21 \text{ \AA}$, which are only slightly larger than the experimental lattice parameters.

The overestimation is typical for GGA calculations. After the determination of the stress-free bulk structure a symmetric biaxial strain along the bc plane was applied and the lattice was kept free to relax along the a direction. In order to get reliable band gap values, the hybrid PBE0 functional has been applied for the final DFT calculation after structural relaxation within the given constraints. The Hartree-Fock portion was tuned to match the electronic band gap of the relaxed structure with the experimentally determined optical band gap of the thickest film. The red solid line in Figure 5 (c) shows the result of the calculations. The DFT data is in excellent agreement with our experimental data. We therefore hypothesize that the ip strain relaxation in our SnO_2 films with increasing thickness is biaxial, as indicated by the XRD data, and results in a significant enhancement of the optical band gap.

4. Conclusion

A thickness dependent series of SnO_2 films grown by PLD was studied. The films have been grown epitaxial on sapphire substrates with high structural quality and very low surface roughness. It was found that the films are partially strained along both ip lattice axes and strain relaxation occurs with increasing film thickness that results in the release of compressive oop strain. The optical band gap of the films was found to linearly depend on the oop strain. Compressive strain of 1% reduces the band gap by about 0.38 eV. The experimental results are compared with DFT calculations and shown to be in excellent agreement. This work demonstrates that strain is an effective way to tailor the optical band gap of SnO_2 films.

Acknowledgments

The work of SFR was performed within the Nucleu program, supported by the ANCSI. The author gratefully acknowledge financial support from PN 16 14 02 04. The work by TZW and

AH was supported by the US Department of Energy (DOE), Office of Basic Energy Sciences (BES), Materials Sciences and Engineering Division, with user projects supported at ORNL's Center for Nanophase Materials Research (CNMS) which is also sponsored by DOE-BES.

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Figure captions

Figure 1: Structural characterization: (a) Wide-angle out-of-plane θ - 2θ XRD scan of the 126 nm SnO₂ film that demonstrates phase-pure epitaxial growth. (b) θ - 2θ scans around the 400 SnO₂ reflection of films with various thickness. The arrow illustrates the peak shift as a result of the out-of-plane strain relaxation with increasing film thickness.

Figure 2: Sample topography: AFM images of the SnO₂ surfaces for the (a) 15 nm and (b) 126 nm thin film. Both films show a smooth surface with a rms roughness below 0.3 nm.

Figure 3: VASE data: (a) Ellipsometric parameters angles Ψ (top) and Δ (bottom) for the films of various thicknesses in dependence of the photon energy. The color code is shown in (b). The grey dashed lines show the fits to the data for the two-layer model that was used to calculate the refractive index n and extinction coefficient k . (b) Shows the optical constants n and k as a function of the photon energy for the thinnest (8 nm, green) and thickest (126 nm, black) film. The blue arrow illustrates the blueshift of the maximum of n that is related to the optical band gap shift, as it is discussed throughout the text.

Figure 4: Optical band gap: Optical band gap change as determined by the linear extrapolation of the absorption coefficient $\alpha = 4\pi k/\lambda$ in the $(\alpha h\nu)^2$ -Tauc plot. The band gap is continuously increasing with increasing film thickness.

Figure 5: Relation between strain and optical band gap: (a) oop strain as function of film thickness. The strain was calculated in respect to the lattice parameter of the thickest film. (b) Optical band gap as function of film thickness. (c) Optical band gap as function of oop strain (blue open symbols). The red solid line shows the dependence of band gap on oop strain as calculated by DFT for biaxial ip strain relaxation. An excellent agreement of experimental and theoretical data is found.

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