Strain-induced optical band gap variation of SnO$_2$ 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 SnO$_2$ films grown by pulsed laser deposition on (0001)-oriented sapphire substrates. An 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 SnO$_2$ 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 SnO$_2$ films and suggests that strain engineering is an appealing route to tailor the optical properties of oxide semiconductors.

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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 [3,14–16]. 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/cm^2, respectively. The growth has been carried out in an oxygen pressure of $pO_2 =$ 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 eV < $h\nu$ < 5.0 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 determine the optical refractive index n and extinction coefficient k of the thin film material.
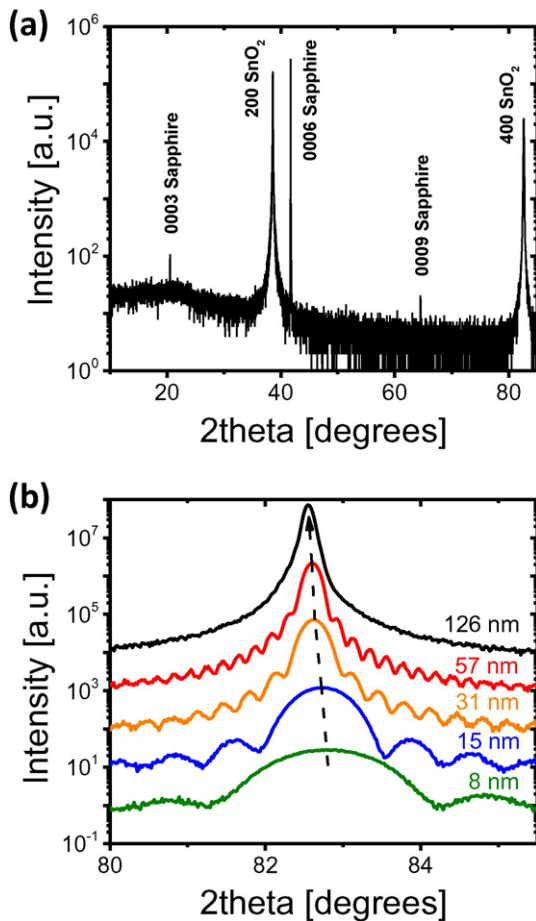
Fig. 1. Structural characterization: (a) Wide-angle out-of-plane θ-2θ XRD scan of the 126 nm SnO_2 film that demonstrates phase-pure epitaxial growth. (b) θ-2θ scans around the 400 SnO_2 reflection of films with various thickness. The arrow illustrates the peak shift as a result of the out-of-plane strain relaxation with increasing film thickness.

3. Results and discussion

3.1. Structural properties

Fig. 1(a) shows wide angle θ-2θ X-ray diffraction patterns of the films with various thicknesses. 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]//Al2O3 ⟨110⟩ 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.

Fig. 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 SnO_2 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 SnO_2 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 SnO_2 films with increasing thickness. It should be noted that the hexagonal lattice of sapphire Al_2O_3 imposes asymmetric ip stress on the tetragonal lattice of SnO_2. For *a*-axis oriented SnO_2 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 ± 0.001 Å, $b = 4.73$ ± 0.01 Å and $c = 3.16$ ± 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

Fig. 2(a) and (b) show topographic 5 μm × 5 μm 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.