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Surface and bulk properties of sputter deposited undoped and Sb-doped SnO_2 thin films

Christoph Körber*, Péter Ágoston, Andreas Klein

Institute of Materials Science, Darmstadt University of Technology, D-64287 Darmstadt, Germany

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ABSTRACT

Electronic surface and bulk properties of sputter deposited polycrystalline intrinsic and Sb-doped SnO_2 thin films have been investigated by a combination of *in situ* photoelectron spectroscopy, electrical four-point conductivity, and optical transmission measurements. The work function and ionization potential of the polycrystalline films increase with increasing oxygen content in the sputter gas by ~1.4 and ~1 eV, respectively. The changes are explained by the different surface terminations known for single crystalline SnO_2. Comparison of surface and bulk Fermi level positions indicates flat band situation for most cases but the presence of a depletion layer for Sb-doped films deposited under oxidizing conditions. Large changes of electrical conductivity depending on the oxygen content in the sputter gas were observed for undoped SnO_2 which can be understood in terms of different concentrations of oxygen vacancies. In contrast, literally no changes occur for SnO_2:Sb, which is attributed to the too high formation energy of compensating defects like oxygen interstitials or Sn vacancies.

1. Introduction

Transparent conducting oxides (TCOs) like SnO_2, In_2O_3 and ZnO, have a wide range of applications in optoelectronic devices, owing to their unique combination of high electrical conductivity and optical transparency in the visible spectrum of the light [1–3]. The requirements for the use of a TCO as an electrode material in optoelectronic devices in brief are optical transparency, high conductivity (high dopability), partially also smooth surfaces and a possibility to tune the work function.

The most popular TCO, used for transparent electrodes, with conductivities up to 10^4 S/cm, is Sn-doped In_2O_3, also referred to as indium tin oxide (ITO) [2,3]. The drawback of ITO is the high price of In, which fortifies the demand on In-free TCOs. Inexpensive alternative TCOs for optoelectronic applications are Al-doped ZnO (ZnO:Al) and F-doped SnO_2 (SnO_2:F). Conductivities $> 10^3$ S/cm can be accomplished with SnO_2:F thin films, prepared via chemical vapor deposition (CVD), using HF for doping [2,4]. Very rough surfaces are obtained from the CVD process. This limits the application of SnO_2:F for organic light emitting devices, where smooth surfaces are required in order to minimize the electrical field at the TCO/organic interface during operation.

Sputter deposition of TCO thin films from ceramic targets provides a method to coat large areas and is therefore highly attractive for commercial applications. Furthermore, this technique often leads to smooth surfaces with a typical rms roughness of ~1–2 nm [5–7]. The most common dopant used for sputter deposited SnO_2 thin films is Sb (Sb_{Sn}), since doped ceramic targets can be readily used and smooth surfaces are obtained. However, Sb-doped SnO_2, so far, has been prevailingly of scientific interest, since its conductivities are in general one order of magnitude smaller than those of CVD SnO_2:F [2,4,8]. The smaller conductivities are most often attributed to a segregation of Sb^{3+}at internal and external interfaces, respectively [9–15].

An important issue for the application of TCOs in optoelectronic devices is the electronic lineup at the TCO/active material interface. For the application in organic light emitting diodes, e.g., the work function of the TCO is crucial for the hole injection into the organic conductor and has been extensively investigated for In_2O_3 and ITO (see, e.g., Refs. [16–21]) as well as ZnO and ZnO:Al (see Ref. [22] and

* Corresponding author. Tel.: +49 6151169661.
E-mail address: ckoerber@surface.tu-darmstadt.de (C. Körber).

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references therein). The work function of a semiconductor can be affected by changes of the Fermi level position and surface dipole, respectively. The latter corresponds to a change in the ionization potential I_P, which is defined as the energy difference between the vacuum level and the valence band maximum. Sputter deposition of TCO thin films provides a possibility to affect the Fermi level position and surface dipole, respectively, by adding reactive gases like, e.g., O_2 to the process gas, allowing for engineering of TCO properties [16,22–25].

SnO_2 is also a very important material used for semiconductor based gas sensors (Taguchi sensors) and has been extensively studied over the past decades [26–33]. The working principle of SnO_2 based gas sensors is the change of resistivity in dependence on atmospheric conditions. A well accepted model for the change of resistivity is the modification of band bending in the near-surface region, induced by adsorption/desorption of gas molecules at the oxide surface [29,30,32,34]. For a n-type semiconductor like SnO_2, the adsorption of, e.g., oxygen, which involves the formation of negative ions (e.g., O_2^-), leads to an upward band bending (depletion layer) at the surface and that effect changes the potential barrier of intergrain junctions in Taguchi sensors [29,30,32,34,35]. Hence, the resistivity of the SnO_2 gas sensor is increased in the near-surface region.

Photoelectron spectroscopy (PES) allows to measure the Fermi level position of a material at the surface [36]. Furthermore, surface potentials such as work function and ionization potential can be directly determined with this technique. In contrast to the highly surface sensitive PES, electrical and optical measurements provide information about the electronic bulk properties of materials. However, the position of characteristic energy levels and free carrier concentrations are most often not directly accessible from electrical and optical data.

In this work we combine surface sensitive PES with bulk sensitive electrical and optical measurements in order to determine surface potentials and reveal the defect structure (doping mechanism) of sputter deposited polycrystalline SnO_2 and SnO_2:Sb thin films, depending on the deposition conditions. We show, that the Fermi level position and surface dipole, i.e., work function and ionization potential, of SnO_2 and SnO_2:Sb can be systematically controlled by changing the oxygen content in the sputter atmosphere. Bulk sensitive electrical conductivity and optical transmission measurements suggest different defect mechanisms for undoped and Sb-doped SnO_2. Furthermore, a depletion layer at the surface of oxidized SnO_2:Sb is revealed in contrast to flat band conditions in the case of undoped SnO_2 and reduced SnO_2:Sb.

2. Experimental

Thin film deposition and photoelectron spectroscopy were performed at the DArmstadt Integrated SYstem for MATerial research (DAISY-MAT). The system provides a central distribution chamber, which combines a Physical Electronics PHI 5700 multi-technique surface analysis system with several preparation chambers, allowing for rapid sample transfer between preparation and analysis chambers without breaking ultrahigh vacuum (UHV) conditions [36,37]. X-ray photoelectron spectra were recorded using monochromated Al Kα radiation with an energy resolution of ~0.4 eV, determined from the Gaussian broadening of the Fermi edge emission of a sputter-cleaned Ag sample, which was also used to calibrate the binding energy scale. UV photoelectron spectra were acquired under normal emission using He I radiation from a gas discharge lamp with an energy resolution of less than 0.2 eV. A sample bias of −1.5 V was applied while recording the UV spectra.

SnO_2 and Sb-doped SnO_2 (3 wt% Sb_2O_5) thin films were deposited from ceramic targets with diameters of 2 in and purity of 99.99%, purchased from Kurt J. Lesker (Hastings, England) and MaTeck (Jülich, Germany), respectively. Pure Ar or Ar/O_2 mixtures were used as sputter gases. Defined Ar/O_2 ratios were established by means of mass flow controllers (MKS, Esslingen, Germany).

All films were prepared via radio-frequency (RF) magnetron sputtering on quartz glass slides. A power of 25 W and target-to-substrate distance of 7.5 cm were employed. The total gas pressure during sputtering in the deposition chamber was 0.5 Pa in all cases. During deposition, substrates were heated using a home-made heater with a commercial halogene lamp and a tantalum reflector shield. Temperature was monitored using two independent thermocouples attached to the sample holder. A substrate temperature of 400 °C was used as a standard for the deposition of the thin films. The base pressure of the deposition chamber was 10^{-6} Pa.

Four-point conductivities were measured at room temperature with linear contact geometry using spring-loaded probes gently pressing on the film surfaces. Currents were applied via a Keithley Precision Current Source (model 6220) and voltages measured with a Keithley Multimeter (model 2700). Different spots on the thin films were probed and various currents applied in order to determine an average conductivity for each specimen. Film thicknesses were determined from optical spectroscopy and range between approx. 300 and 700 nm.

Transmission spectra were recorded using a PerkinElmer Lambda 900 UV/VIS/NIR spectrometer, providing a wavelength range from 180 to 3000 nm. Baseline corrections were applied from the transmission spectrum of an uncoated quartz substrate.

3. Photoemission results

Fig. 1 shows core level and valence band spectra of undoped and Sb-doped SnO_2 thin films, deposited with different oxygen contents in the sputter gas (xO_2). All films were grown at 400 °C substrate temperature. Wide range survey spectra (not shown), recorded with monochromatic Al Kα radiation, revealed no contamination of the deposited thin films.

The Sn $3d_{5/2}$ and O 1s core levels for both undoped and Sb-doped SnO_2 are shifted to lower binding energies with increasing xO_2. For the undoped films, the core level emissions show a symmetric line shape. The Sn $3d_{5/2}$ emissions of the SnO_2:Sb films are asymmetric for low oxygen contents in the sputter gas, due to an additional component at the high binding energy side. This effect is attributed to a screening effect, measured with photoemission, and has been already described for highly doped SnO_2:Sb ceramics [38,39] and ITO thin films [40].

The Sb $3d_{5/2}$ emissions of the SnO_2:Sb films overlap with the O 1s emissions, which complicates the interpretation of those spectra. However, the $3d_{3/2}$ emissions of Sb are clearly resolved. Due to the low concentration of Sb in the SnO_2:Sb films, the signal-to-noise ratio is rather small. Yet, the Sb $3d_{3/2}$ emission lines appear relatively broad, suggesting that more than one component contribute to the overall line shape. Atomic sensitivity factors, which are required for the calculation of the Sb concentration, are only available for the Sb $3d_{5/2}$ emission line. Therefore, the intensity of the $3d_{5/2}$ emission was calculated by multiplying the intensity of the $3d_{3/2}$ emission with the branching ratio of 1.5, according to the degeneracy of the 3d levels. Correspondingly, the intensity of the Sb $3d_{5/2}$ emission was subtracted from the O 1s signal in order to determine the O intensity.

With increasing xO_2, a slight increase of O concentration vis-à-vis with a decrease of Sn concentration at the surface is observed from quantitative analysis of the XP core level spectra (see Fig. 2). In the case of Sb-doped SnO_2, no variation of Sb concentration, within the experimental limits of quantitative XPS analysis (5–15% relative error), is detected. The Sb concentration is consistent with the