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Evidence for surface dipole modifications in In_2O_3 -based transparent conductors

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Surface dipole modifications were identified for contamination-free In_2O_3 -based transparent conducting oxides by ultraviolet photoelectron spectroscopy on both thin film and bulk ceramic specimens. In particular, heating in air was found to result in an increase in ionization potential and work function. The formation of surface dipoles may be related to the unique structure (crystal, defect) of bixbyite-based materials. These findings have important ramifications for the tuning of work functions in In_2O_3 -based transparent conductors. © 2008 American Institute of Physics.

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Transparent conducting oxides (TCOs) such as In_2O_3 , SnO_2 , and ZnO have a wide range of applications in electronic and optoelectronic devices.^{1,2} For the application in organic light emitting diodes, the work function of Sn-doped In_2O_3 is an important issue for hole injection into the organic conductor and has been extensively investigated (see, e.g., Refs. 3–7). The work function of a semiconductor can be affected by changes in the Fermi level position in the band gap and by changes in the surface dipole. 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. It is often not distinguished whether the changes in work function are due to changes in the Fermi level position or due to changes in the surface dipole. Our previous work on surface properties of *in situ* prepared In_2O_3 and tin-doped In_2O_3 (ITO) using photoelectron spectroscopy has shown that changes in work function caused by a variation of oxygen partial pressure during deposition are exclusively due to changes in the Fermi level position.^{8–11} The ionization potentials of *in situ* deposited In_2O_3 and ITO films are essentially constant with values of ~ 7.1 and ~ 7.7 eV, respectively. For In_2O_3 , identical values have been observed for reactively evaporated⁹ and for magnetron sputtered films.^{10,11}

In this contribution, we show that a treatment of In_2O_3 -based TCOs at elevated temperatures in air, which is inherent to ceramic samples, leads to a considerable increase in the ionization potential and thereby also the work function. This modification of the surface dipole is further evident from distinct valence band features. A comparable effect is observed for Zn–Sn codoped In_2O_3 (ZITO) samples, which are highly self-doped alternatives to ITO.¹² It is therefore proposed that the modification is a characteristic for In_2O_3 -based TCOs including ITO, which exhibit the cubic bixbyite crystal structure.¹³

We have determined the work functions and ionization potentials of different specimens using ultraviolet photoelectron (UP) spectroscopy in a Physical Electronics PHI 5700 spectrometer system, which is part of the integrated prepara-

tion and surface analysis system DAISY-MAT.¹⁴ UP spectra are recorded in normal emission with a sample bias of -1.6 V. The binding energies of the valence band maxima (E_{VB}) are derived from linear extrapolation of the leading edge of the valence band emissions. The work functions φ of the samples are derived from the secondary electron cutoffs, taken at the half height of the onset of emission at high binding energy. Ionization potentials are determined by adding the work function and the valence band maximum binding energy.

Thin films of In_2O_3 and ITO were prepared by radio frequency magnetron sputtering, transferred, and measured without breaking vacuum. (Zn,Sn)-codoped In_2O_3 films (ZITO) were prepared *ex situ* by pulsed laser deposition. X-ray diffraction of the ZITO film showed the bixbyite structure. Bulk ceramic pellets,¹⁵ air-annealed In_2O_3 and ZITO samples were measured before and after heating to 400°C in 0.5 Pa of oxygen for 90 min in the sputter deposition chamber. This procedure leads to the removal of hydrocarbon contaminations as verified by x-ray photoelectron spectroscopy analysis.^{10,11}

Valence band spectra of differently prepared In_2O_3 samples are shown in Fig. 1. The valence band features up to 7 eV binding energy of the *in situ* deposited samples are comparable to those reported previously for reactively evaporated and for magnetron sputtered samples.^{9,11} The secondary electron cutoff of the sample deposited in pure Ar, i.e., under reducing conditions, is located at 14.2 eV below the valence band maximum. This corresponds to an ionization potential of 7.0 eV, which is in the range of previously reported values for In_2O_3 .^{9,11} The secondary electron cutoff of the sample deposited in an Ar/ O_2 gas mixture, i.e., under oxidizing conditions, is shifted by 0.1 eV to smaller values.

Noticeable changes in the valence bands with additional features at ~ 2.5 and ~ 4 eV below the valence band maximum are observed for the ceramic In_2O_3 sample and the air-annealed thin film sample. Both samples have been cleaned *in situ* by heating in 0.5 Pa oxygen, a treatment which has been shown not to induce spectral changes. The secondary electron cutoff of the ceramic and the air-annealed In_2O_3 sample is furthermore shifted to lower values resulting

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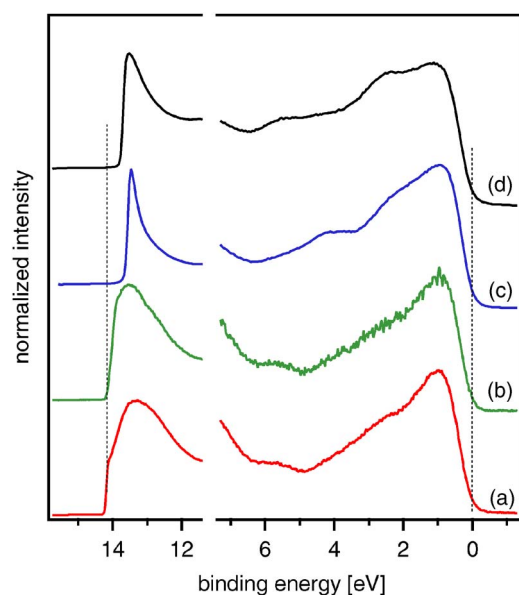


FIG. 1. (Color online) He I excited valence band spectra of different In_2O_3 samples: Films deposited by radio frequency magnetron sputtering *in situ* at 200°C in (a) pure Ar and (b) in a 90% Ar/10% O_2 mixture; (c) ceramic specimen sintered in air; (d) same as (a) heated in air at 400°C for 24 h. Samples (c) and (d) have been cleaned *in situ* by heating in 0.5 Pa O_2 at 400°C for 90 min. To eliminate the shifts induced by different Fermi level positions, the valence band maxima are set to zero binding energy.

in increased ionization potentials of 7.55 and 7.6 eV, respectively.

The variation of valence band features and ionization potential has been reproducibly observed on different TCOs with bixbyite structure. Further examples are presented in Fig. 2. The valence band structure and the ionization potential of *in situ* magnetron sputtered ITO films do not vary with

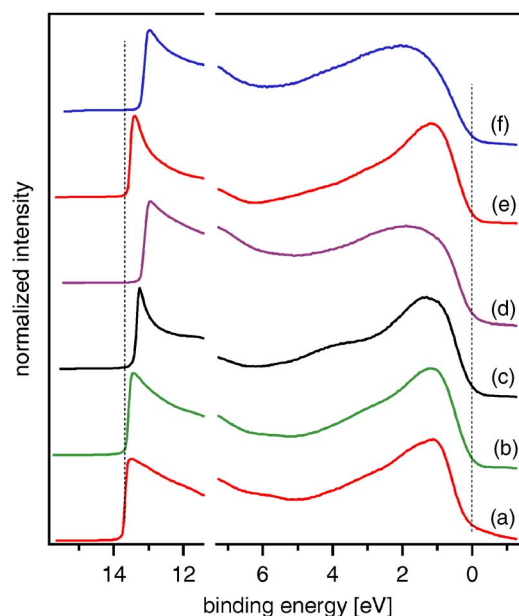


FIG. 2. (Color online) He I excited valence band spectra of differently doped and treated In_2O_3 samples: ITO film deposited by rf magnetron sputtering at 400°C substrate temperature in (a) pure Ar and (b) in a 90% Ar/10% O_2 mixture; (c) same as (a) after air annealing at 400°C for 24 h; (d) same as (a) after ozone treatment; (e) thin film 30% (Zn,Sn)-codoped In_2O_3 ; (f) sintered ceramic 40% (Zn,Sn)-codoped In_2O_3 . Samples (c), (e), and (f) have been cleaned *in situ* by heating in 0.5 Pa O_2 at 400°C for 90 min. The valence band maxima are set to zero binding energy.

oxygen added to the sputter gas, in good agreement with earlier results.^{8,10,11} After air annealing, a slight increase in the ionization potential from 7.7 to 7.9 eV is observed. The widely used illumination with intense ultraviolet radiation in air for 30 min using a UV-ozone photoreactor (PR100) induces an even larger increase in the ionization potential to 8.1 eV. Although the latter sample was transferred to the spectrometer within a few minutes after the ozone treatment, the broadening of the valence band structures for this sample are at least partially related to hydrocarbon surface contaminations.

Spectra recorded from a thin film and sintered ceramic specimen of highly (Zn,Sn)-codoped In_2O_3 are displayed in Figs. 2(e) and 2(f). The thin film ZITO sample shows a rather sharp valence band structure and exhibits an ionization potential of 7.7 eV (work function $\phi=4.85$ eV). A broad valence band structure with additional emissions at ~ 2 and ~ 4 eV below the valence band maximum is observed for the ceramic specimen. The latter exhibits an ionization potential of 8.1 eV (work function $\phi=5.1$ eV).

The presented data show that the surface dipole of In_2O_3 -based TCOs, which exhibit the bixbyite crystal structure, strongly varies with sample preparation. In particular, sintered ceramic specimens have considerably larger ionization potentials, and thus work functions, than typical thin film samples. The close similarity between the ceramic and air annealed thin film samples indicates that the additional valence band emissions and the higher ionization potentials can be induced by a high temperature exposure to oxygen at not too low partial pressure. This suggests that the modification is related to a variation of the surface dipole. Due to the experimental conditions and observed behavior, it is inferred that the modification of the surface dipole involves mainly In and O atoms. In agreement with the changes in the valence band structure a possible explanation might be the presence of a surface peroxide species as proposed by Golovanov *et al.*¹⁶

It is remarkable that adding oxygen during deposition has a significantly different effect than air annealing. Air annealing for 24 h leads to a considerable increase in the work function by an increased surface dipole but has only a small effect on the Fermi level position.¹¹ The small shifts of the Fermi level are consistent with the observed reduction in electrical conductivity from 140 to 20 S/cm (In_2O_3) and from 6000 to 1100 S/cm (ITO) upon air annealing. In contrast, adding oxygen during deposition leads to a large variation of Fermi level position and conductivity without any noticeable effect on the surface dipole.⁸⁻¹¹ The origin of this difference might be related to the different oxygen partial pressures during the treatments. Even with the addition of oxygen during deposition, the oxygen partial pressure never exceeds ~ 0.1 Pa, which is several orders of magnitude lower than the equivalent in air. In addition, the difference may be related to the unique crystal/defect structure of bixbyite-based materials, which can easily accommodate excess oxygen, e.g., the well-known Frank and Köstlin clusters in bulk ITO.¹⁷

For polar materials, a variation of the ionization potential can be due to a variation of surface orientation.^{18,19} However, the surface dipole changes are induced by annealing of thin film samples at only 400°C , which is not expected to change the surface orientation of the films.

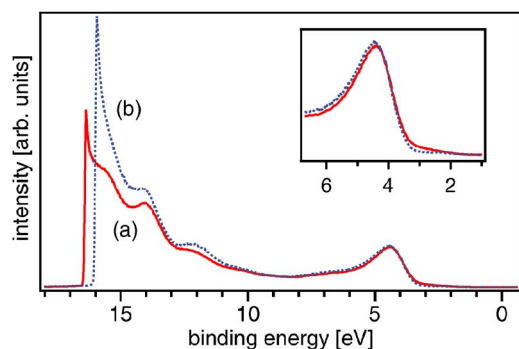


FIG. 3. (Color online) He I excited valence band spectra of nominally undoped SnO_2 films prepared *in situ* by radio frequency magnetron sputtering at 400°C substrate temperature in (a) pure Ar (solid line) and (b) a 95% Ar/5% O_2 gas mixture (dotted line). No intensity normalization or energy shift has been applied to the presented spectra.

Surface dipole changes are well known for SnO_2 , where the surface can be either fully oxidized with all surface Sn atoms in the 4+ oxidation state or in a reduced state with surface Sn atoms in the 2+ oxidation state.²⁰ The reduced surface exhibits considerably less surface oxygen^{20,21} and a strongly reduced ionization potential.²¹ Valence band spectra of nominally undoped SnO_2 films prepared *in situ* by magnetron sputtering are presented in Fig. 3. The valence band structures of films deposited either in pure Ar or in an Ar/ O_2 gas mixture are largely identical. Only a small emission above the valence band maximum is observed for the film deposited under reducing conditions (pure Ar). The emission is due to Sn^{2+} -related surface states, which are well documented and explained in literature (see, e.g., Ref. 20 and references therein). With the addition of oxygen to the sputter gas, the Sn^{2+} -related emissions are suppressed and the secondary electron cutoff is shifted to a lower binding energy, corresponding to an increase in work function by ~ 0.4 eV. As the valence band maximum does not change, this corresponds to an increase in the ionization potential (from 8.2 to 8.6 eV). The difference is in good agreement with literature.²¹

In contrast to the bixbyite materials, SnO_2 films with either oxidized and reduced surfaces and correspondingly different ionization potentials can thus be easily prepared *in situ* by magnetron sputtering at different oxygen partial pressures. In addition, the valence band structure is identical for oxidized and reduced surfaces. Hence, an explanation for the different ionization potentials of the In_2O_3 -based TCOs, which is based on different oxidation states of indium, is not likely. Instead, in accordance with the changes in valence band structure which are dominated by O 2*p* states, we posit that a change in oxygen coordination at the surface, possibly associated with the formation of surface peroxide species, as suggested by Golovanov *et al.*,¹⁶ leads to the change in the surface dipole. In literature, several investigations of the (0001) surfaces of the isoelectronic compounds Fe_2O_3 and Al_2O_3 are available (see Ref. 22 and references therein).

These surfaces correspond to the bixbyite (111) surface, which is probably not relevant in the present case as the deposited thin films have a strong (100) texture. However, the work on (0001) surfaces also considers two different surface terminations—a metal-terminated and a fully oxidized surface, which is similar to the results described by Golovanov *et al.* However, future work has to address the precise nature (structure, surface termination) of bixbyite surfaces.

In summary, we have presented evidence from photoelectron spectroscopy for the modification of surface dipoles on TCOs with bixbyite structure. The surface dipole and thereby the work function can be significantly increased by a high temperature oxygen exposure. These changes involve only In and O atoms, and are probably related to a surface peroxide species. The ability to independently modify both the Fermi level and the surface dipole (and ionization potential) of In_2O_3 -based transparent conductors allows for the tuning of work function, which has important technological ramifications for applications such as organic light emitting diodes and organic photovoltaic devices.

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