

Valence band and band gap photoemission study of (1 1 1) In_2O_3 epitaxial films under interactions with oxygen, water and carbon monoxide

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Abstract

Synchrotron radiation ultraviolet photoemission experiments at photon energies of 150 and 49 eV were performed on an epitaxial layer of (1 1 1) In_2O_3 with good crystallinity as established by a standard scanning probe and diffraction methods. Valence band (VB) and band gap photoemission spectra were monitored under separate oxygen, water and carbon monoxide exposures (100 L) at different activation temperatures within the range utilized for chemiresistive gas sensors (160–450 °C). Large changes in photoemission response within the whole VB were observed for all gases. Regular shifts of the valence band edge relative to the Fermi energy were found under gas exposures on two kinds of surface (partially reduced or partially oxidized), and are interpreted as changes of surface potential. Treatments in oxygen resulted in upward band bending (~ 0.5 eV at $T = 320$ °C). Regardless of activation temperature, treatments in water resulted in downward band bending, but with small changes (< 0.1 eV). Reduction properties of carbon monoxide were observed only at high temperatures of $T \geq 370$ °C. At temperatures of 160 and 250 °C unusual “oxidizing” behavior of CO was observed with upward band bending of ~ 0.7 eV (160 °C). Oxidizing and reducing effects of the gas interactions with the (1 1 1) In_2O_3 surface in all cases were accompanied by a corresponding behavior, i.e., a decrease or increase in photoemission response from so-called defect states in the band gap near the top of the valence band. The increases of photoemission within a band gap with maxima at binding energies (BE) of 0.4 (O_2 -induced peak) and 1.0 eV (CO-induced peak) were, respectively, found for interactions with O_2 and CO for low temperatures ($T = 160$ and 250 °C). These responses were ascribed to acceptor-like electronic levels of O_2 and CO chemisorption states, respectively. A definite split of the top VB peak (BE ~ 4.0 eV) was found under CO dosing at 160 °C. Established knowledge of the CO interaction with the (1 1 1) In_2O_3 surface explains earlier revealed acceptor-like behavior of In_2O_3 film conductivity during CO detection at operational temperatures lower than 250 °C through the formation of acceptor-like electronic levels of adsorbed CO molecules.

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1. Introduction

Indium oxide is one of the basic oxides, and has been extensively studied due to its prominent applications in

optoelectronics, gas sensors and as a modeling material, and possesses some interesting chemical and structural peculiarities. Its unique catalytic conversion properties for some pollutants should be mentioned. Like conductometric gas sensor materials, In_2O_3 demonstrates enhanced sensitivity to oxidizing gases (O_3 , NO, etc.) [1–4]. Despite great efforts to develop a basic understanding, there is no

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generalized pattern for describing gas sensitivity and catalytic mechanisms on this oxide. Among the issues to be resolved is which kind of gas sensitivity mechanism, chemisorption or “redox”, is realized in a given case. Thus far, even simple questions about the position of the Fermi level on the surface, its evolution under different ambient conditions, and the corresponding band bending pattern remain unanswered. These are fundamental questions.

There appear to be big differences in crystalline structure (syngony, complicated body centered unit cells, polar surfaces, systematic anion vacancies) and gas sensing properties between In_2O_3 and SnO_2 , which is considered a reference material in the field of gas sensors. Of course these differences should also become apparent in the surface region. The problem of the surface vicinity composition in In_2O_3 and In_2O_3 -based materials, closely related with surface band structure, has therefore evoked rather deep interest. Nevertheless, the composition pattern remains debatable. Harvey et al. [5] suggested the idea of a chemical depletion layer due to a bixbyite structure. As a consequence, oxygen diffusion is favored and an oxygen enriched surface results in a decrease in electron concentration at definite oxygen pressures and temperatures of a film's deposition. This was experimentally demonstrated for ITO films [6,7] and is explained using the Frank and Köstlin model [8] through the formation of neutral point complexes $(\text{Sn}_{\text{In}})_2\text{O}_i$ between substituting Sn_{In} atoms with interstitial O_i atoms positioned at systematic structural vacancies.

For pure In_2O_3 , our photoemission experiments [9–11] on textured nanocrystalline films with (100) preferable orientation suggest a considerable deficiency of oxygen from the stoichiometric value within the probing depth of both X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). Ion surface scattering results also confirm this. The deficiency only slightly decreases with annealing up to 900 °C in an oxygen atmosphere and the composition approximates its stoichiometric value only after 1000 °C [12]. Synchrotron radiation photoemission study [13] of the band gap region with a photon energy $h\nu = 150$ eV in the aforementioned polycrystalline films has shown that the emission response extends throughout the band gap up to the Fermi level. This response ascribed to surface oxygen vacancies, or more correctly to In derived states (5s–5p) arising from broken In–O bonds [14], practically disappeared in our experiments after oxygen treatment in UHV conditions [13].

For the behavior of core level peaks (O 1s, O 2s) and their components under O_2 and CO treatments in UHV, their interpretation remains ambiguous and some conclusions from XPS and UPS are contradictory.

The abnormal effect in undoped In_2O_3 thin films was revealed during gas response experiments [15]. This is the so-called acceptor-like behavior for reducing gases, which means the electrical conductivity decreases (not increases) under gas (CO , H_2) interactions with In_2O_3 thin film. This effect is observed in the temperature range of 150–250 °C.

At higher operational temperatures there is only a standard donor-like effect.

The experiments on photoconductivity measurements near the fundamental absorption edge (FAE) for In_2O_3 nanocrystalline films with preferred (111) faceting of crystallites [16] demonstrate a noticeable peak in the spectral response with a maximum at photon energy $h\nu = 2.9$ eV under an ozone admixture and operational temperature $T = 250$ °C. This peak is part of the developed spectral tail extending from the FAE up to 2.4 eV. This spectral feature is fully reversible with the appearance of ozone. We related this feature with the existence of oxygen chemisorbed states, the electronic levels of which may constitute a surface sub-band below the conduction band and determine optical transitions from the VB to this sub-band. One of the goals of this work [16] was to show that the mechanism of surface photoconductivity appears in many respects to be analogous to a conductometric gas sensitivity mechanism, controlled by the adsorption/desorption of oxygen [17]. This was evidenced by a comparative kinetic study of both processes, i.e., photoconductivity and conductivity responses to oxygen changes in the atmosphere.

These aforementioned previous studies of polycrystalline In_2O_3 -based thin films have shown a rather complicated and so far unclear pattern of surface reactivity and adsorption towards common probing gases like O_2 and CO. Therefore, further systematic efforts in this direction and surface experiments on well-characterized monocrystalline samples are required.

Usually the indium oxide nanocrystallite habit exhibits two stable surfaces with (100) and (111) orientations. The distinct differences in geometry and in surface atomic structure of these planes should affect, in the case of monocrystalline film, other surface properties like electronic, adsorptive and reactivity properties.

Our photoemission study of In_2O_3 epitaxial thin films with these two orientations has shown an interesting and unusual behavior for (111) films in comparison with (100) films. The results for (111) films presented below, on the one hand, reveal the electronic states below the Fermi energy (BE ~ 0.3 – 0.4 eV) induced by oxygen exposure, which may be ascribed to chemisorbed states. This result confirms the hypothesis proposed in the photoconductivity cycle of experiments. On the other hand, carbon monoxide exposure at a sample temperature of 160 °C leads to considerable upward band bending even greater than that under oxygen exposure. Some states near a BE of 1.0 eV originating from CO exposure can be considered as electronic chemisorbed states of CO. Such states induced by O_2 and CO adsorption were not found on the film with (100) orientation, indicating an adsorption selectivity for different surface planes. The observation of CO chemisorbed states strongly confirms the aforementioned acceptor-like behavior of the CO conductance response on polycrystalline films. We also present results on VB spectra evolutions with the appearance of unknown spectral contributions under interactions of the (111) In_2O_3 surface

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