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Surface composition and electronic properties of indium tin oxide and oxynitride films

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Abstract

The surface properties of indium tin oxynitride films prepared by rf-sputtering in nitrogen atmosphere were investigated by X-ray and ultraviolet photoelectron spectroscopy as well as electron energy loss spectroscopy and Auger electron spectroscopy depth profiling. The results are compared to reference measurements on conventional rf-sputtered indium tin oxide films. The incorporated nitrogen is present in different chemical environments. Employing these different spectroscopic techniques, it was found that desorption of nitrogen from the ITON structure upon annealing is the origin of the observed drastical changes in the surface composition and electronic structure. The formation of oxygen vacancies and Sn surface segregation upon annealing is linked to improvements in the physical properties (larger spectral range of transmittance and higher conductivity) of the films.

Keywords: Oxides; Oxynitrides; X-ray and ultraviolet photoelectron spectroscopy; Auger electron spectroscopy; Electron energy loss spectroscopy

1. Introduction

Indium tin oxide (ITO) is a n-type degenerate semiconductor with a band gap that varies between 3.7 and 4.4 eV [1,2]. Due to its unique properties, such as high electrical conductivity, very high optical transmittance, high infrared reflectance, excellent hardness and chemical inertness [3], it is used for display devices, solar cells and many other optical applications [4]. ITO has also been employed as transparent ohmic contact on the p-layer of III-nitride based optoelectronic devices [5–8].

In a previous study we have shown that the use of nitrogen as process gas during sputtering of indium tin oxide (ITO) leads to the incorporation of nitrogen in the ITO thin film forming indium tin oxynitride (ITON) [9]. The nitrogen in these films is bound in several chemical states and the surface properties as probed by X-ray photoelectron spectroscopy are well correlated with the electrical properties of the film, like the conductivity and its formation of ohmic contact on p-type GaN [10].

Changes of the surface properties of ITO thin films after various surface treatments, like annealing [11,12], KrF excimer laser irradiation [13], plasma treatments (atmospheric air [14], N_2, Ar or O_2 [15,16]) and UV–ozone exposure [17] have been reported. In these investigations an attempt was made to correlate the observed modifications of the surface properties of the films (chemical composition, chemical states and work function) with their physical properties (roughness, carrier concentration and transmittance).

This work investigates changes in the surface composition and electronic properties of ITON thin films upon annealing up to 800 °C by different electron spectroscopy techniques. Thermally induced changes are discussed

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with respect to electrical properties such as carrier concentration.

2. Experimental procedure

ITO and ITON thin films were fabricated by rf-sputtering (13.56 MHz) in plasma containing Ar or N_2, respectively. The deposition was performed at room temperature on pre-cleaned Si wafers (1–10 Ω cm) in a Nordiko NS2500 system using an indium tin oxide target (80% In_2O_3 + 20% SnO_2, diameter 6 in.). During this procedure the gas flow (Ar for ITO and N_2 for ITON) was controlled by mass flow controllers to maintain a total pressure of 5×10^{-3} Torr in the chamber (base pressure $<1 \times 10^{-9}$ Torr) [9].

The dependence of the surface chemical composition and the surface electronic properties was examined in an UHV system with a base pressure $<2 \times 10^{-10}$ Torr using X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) as well as electron energy loss spectroscopy (EELS). XPS measurements were performed using monochromated AlKα radiation ($h\nu = 1486.7$ eV) produced by a PHI 10-610 X-ray source in combination with an Omicron XM1000 monochromator, while a HIS13 UV source was used for UPS, for the generation of He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) radiation. The energy resolution of this setup with the used experimental settings was determined on an Ag reference sample. The FWHM of the $Ag3d_{5/2}$ peak is 0.6 eV and in UPS the Fermi edge is measured to be <0.1 eV broad. EELS was performed with an EKF 1000 electron gun, resulting in a peak of the elastically scattered electrons with a FWHM varying between 0.6 eV and 0.8 eV for the used primary electron energies E_0 (200–1000 eV). All spectra were recorded with a seven channel EA125 hemispherical electron analyzer operating in the constant pass energy (CAE) mode.

The samples were analyzed directly after loading into the analysis system and after gentle sputtering with Ar^+ ions (2 keV, 30 min) for the removal of surface contaminants. Changes upon annealing of the ITO and ITON samples were investigated after *ex situ* rapid thermal annealing (RTA) (ramp ~45 K/s, $t = 1$ min, $T = 400$ °C, 600 °C) in a N_2 atmosphere (flow 450 sccm) and subsequent UHV analysis as well as after *in vacuo* heating of the samples combined with a monitoring of the gas desorption using residual gas analysis (RGA) and subsequent surface characterization. Auger-electron spectroscopy (AES) and depth profiling measurements have been carried out in a separate UHV system.

The AES system (Thermo Microlab 350) is equipped with a high spatial resolution field emission electron beam column and a high energy resolution hemispherical analyzer. The primary electron beam (5 keV, 14 nA) had an incidence angle of 45° with respect to the surface normal and sputtering was carried out by a conventional scanned ion beam gun (Ar^+ ions, 1 keV, incidence angle of 47°).

3. Results and discussion

First, the surface topography was characterised by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Briefly, due to the used deposition method the sample surfaces consist of a closed polycrystalline film with a typical rms roughness between 3 nm and 5 nm, equal to already reported results [9]. The grain size increases slightly with deposition power as well as post-growth rapid thermal annealing. However, the grain size as measured by AFM and SEM remained well below 100 nm in all cases and no indication for other lateral inhomogeneities across the sample was found. Thus the lateral homogeneity of all films is typical for samples prepared by sputtering techniques.

The analysis of the surface chemical composition of ITON and ITO reference samples prepared by rf-sputtering was performed by XPS. The typical core level peaks related to the detected elements have their maximum intensity at a binding energy (BE) of 18.4 eV, 26.2 eV, 444.7 eV, 486.5 eV, and 530.2 eV with respect to the Fermi energy for the In4d, Sn4d, $In3d_{5/2}$, $Sn3d_{5/2}$, and O1s state, respectively. As expected nitrogen was also detected in the ITON thin films; however, it is vertical not uniformly distributed through the films. As deposited ITON films possess a nitrogen content of ~9 at.%, which varies slightly with deposition power. The nitrogen atoms are found to be in different chemical states at 396.7 eV, 398.3 eV and ~404.0 eV (not shown here). For directly loaded samples an additional peak at 400.0 eV is found. A detailed discussion of these nitrogen structures can be found elsewhere [10]. Briefly, the peak at 400.0 eV is removed after the Ar^+ ion bombardment and is attributed to N–O bonds located directly on the surface. The structures at 398.3 eV and ~404.0 eV are identified as oxynitride bonds and incorporated unbound nitrogen, respectively. Both peaks disappear after annealing above ~550 °C. The state at 396.7 eV is related to nitrogen bound to metal atoms.

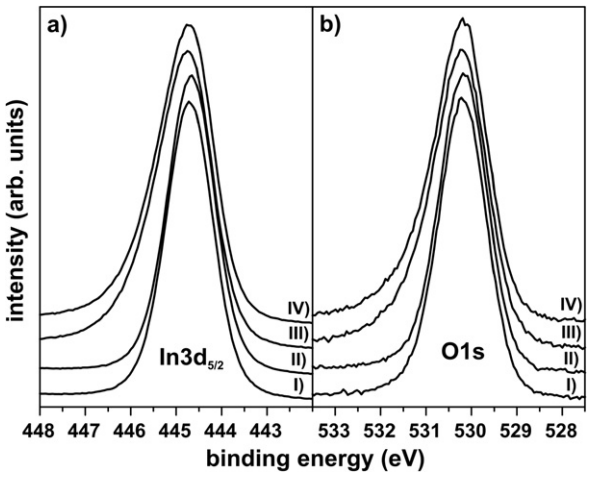

Fig. 1. $In3d_{5/2}$ and O1s core level spectra of a series of ITON samples with varying annealing temperatures: (I) as deposited, (II) 400 °C, (III) 600 °C and (IV) 800 °C.