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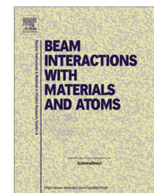

Effects of argon sputtering and UV-ozone radiation on the physico-chemical surface properties of ITO

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A B S T R A C T

X-ray photoelectron spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) were used to evaluate and determine the effects of 1 KeV Ar^+ irradiation (sputtering) on the surface chemical composition and work function of Indium Thin Oxide (ITO). While Ar^+ sputtering removes carbon-based surface contaminants, it also modifies the Sn-rich surface of ITO and leads to a reduction of the oxidation state of Sn from Sn^{4+} to Sn^{2+}. The decrease in the work function of ITO is directly correlated to the decrease of Sn atomic concentration in the Sn-rich top surface layer and the reduction of the oxidation state of surface Sn.

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1. Introduction

Indium Tin oxides are widely used in many device applications requiring transparent conducting oxides (TCOs). High work function of ITO via optimal surface processing and modification leads to more efficient device applications such as organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs). Surface carbon-based contaminants are known to significantly lower the work function of ITO. Many studies investigated the effectiveness of several surface carbon removal methods and their effects on the work function of ITOs [1–3]. These surface processing methods are based on wet chemical etching, oxygen and hydrogen plasmas, and ion sputtering. The wet chemical etching removes some carbon-based contaminants but introduces hydroxyls on the surface of ITO [4] resulting in minor changes to the work function of ITO [2,5]. The plasma processing and ion sputtering results in either introduction of additional oxygen (re-oxidation) or removal of oxygen (deficiencies) on the surface of ITO. The level of oxygen concentration in the surface region has significant impact on the work function of ITO: the work function increases with increased oxygen concentration [2]. Sugiyama et al also concluded that the surface Sn concentration weakly affected the work function of ITO. They attributed the work function change to the change in Fermi level caused by the change of carrier concentration. As an n-type semiconductor, more oxygen vacancies and Sn dopants increase the carrier concentration of ITO. The major charge carrier in ITOs are the donor electrons which are provided by Sn^{4+} in ITOs. To obtain high conductivity, in ITOs, In_2O_3 is heavily doped with Sn. The solubility of Sn in In_2O_3 is lower than 6% [6]. When the Sn doping level is beyond the solubility limit, a Sn-rich phase starts forming at the surface and along the grain boundaries of ITO [7]. The removal techniques of carbon-based contaminants are expected to have significant impact on the atomic composition of Sn-rich surface of ITOs. The changes to the work function of ITO, after surface treatments, were attributed to three factors: the surface carbon-based contaminants, the O/In ratio, and Sn/In ratio [2]. The above studies didn't give importance to the role of Sn-rich surface of ITO, the post processing changes of its make-up and the role it played in degrading the work function. No comprehensive experimental measurements were undertaken to directly correlate the processing induced changes in the Sn-rich surface chemistry of ITOs and their corresponding work function.

In this study, ITO samples were subjected to in-situ 1 KeV Ar^+ sputtering and characterized by XPS and UPS. The ITO samples were exposed to UV-ozone radiation prior to introduction into the ultra-high vacuum (UHV) chamber with in-situ XPS and UPS capabilities. The UV-ozone removed more than 90% of the carbon-based contaminants from the ITO surface. The effects of Ar^+ sputtering on the surface chemistry/atomic composition and the work function is determined. The correlation between the

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Sn-rich surface of ITO, the sputtering induced Sn/In atomic ratio changes and the work function of ITO is elucidated.

2. Experimental

The ITO/glass samples, used in this study, are standard substrate used by many groups for opto-electronic device applications and are obtained from Luminescence Technology Corp. Prior to introduction into the UHV chamber for Ar^+ sputtering studies, the ITO samples are exposed in air to UV-ozone radiation to removes most surface carbon-based contaminants. The UV radiation is generated by a mercury lamp and the distance between the lamp and the sample is fixed at 10 cm. After UV-ozone treatment, the ITO samples are immediately transferred to the UHV chamber to minimize additional contaminations from the atmosphere. The UHV chamber is equipped with Ar^+ sputtering, UPS, and XPS capabilities for in-situ studies. The energy of the Ar^+ sputtering is 1KeV and the background pressure in the chamber is about 10^{-6} Pa during Ar^+ sputtering.

The XPS and UPS data measurements are performed using the PHI 5000 XPS system. The background pressure during XPS measurements is about 10^{-7} Pa. The XPS system used a monochromatic Al K alpha radiation (hυ = 1486.6 eV) as an X-ray source. All XPS Spectra are collected with a pass energy of 11.75 eV and an energy step of 0.1 eV. The ITO samples are loaded on a sample stage capable of Take Off Angle (TOA) ranging from 12° to 90°. The XPS is calibrated with the binding energies of a sputter cleaned high-purity silver foil. As for UPS measurement, the UPS spectra are collected using He I source (hυ = 21.22 eV) with 2.950 eV pass energy and 0.005 eV energy steps. In order to separate secondary edges of ITO samples from that of the analyzer and increase the intensity of the secondary edge, a −9 Volts is applied to the surface of ITO sample during UPS data collection. The UPS is calibrated using the Fermi edge of a sputtering cleaned high purity gold foil.

3. Result and discussion

3.1. Surface contaminant and Tin-rich surface of ITO

The level of surface carbon-based contaminants is examined using XPS measurements of the C1s core-level spectra. To increase surface sensitivity, the C1s spectra are collected at 30° take-off angle (TOA). The C1s spectra for ITO samples with different processing conditions are displayed in Fig. 1(a). After 30 min UV-ozone treatment, the intensity of C1s was significantly reduced. More than 90% of carbon-based contaminants are removed by the UV ozone treatment. After 0.3 min irradiation with 1.0 KeV Ar^+, no C1s peak is visible indicating that the level of carbon-based contaminants (if they exist) are below the detect limit of XPS.

The surface chemistry of ITO is then characterized using angle resolved XPS (ARXPS). To determine the relative concentration depth profiles of In and Sn, the corresponding In3d and Sn3d core-level spectra (not shown here) are collected at take-off angle of 15°, 30°, 45°, and 90°. The intensity ratio Sn/In versus TOA is plotted in Fig. 1(b). The net intensities of $In3d_{5/2}$ and $Sn3d_{5/2}$ core-level peaks are determined by integrating the $In3d_{5/2}$ and $Sn3d_{5/2}$ peaks and using Shirley function for background removal.

The Sn/In peak intensities ratio follows an exponential-like trend as a function of the TOA and is higher at a TOA of 15°. This demonstrates clearly that the Sn atomic concentration is significantly higher at the surface of ITO than in its bulk. Thus, the high atomic concentration of Sn in the surface region confirms the Sn-rich surface of ITO.

3.2. Ar^+ sputtering and reduction of Sn-rich surface of ITO

Complete removal of carbon-based contaminants at the surface of ITO required 30 min UV-ozone radiation followed by 1.0 KeV Ar^+ sputtering for a minimum of 0.3 min. The Ar^+ sputtering, although at very low energy and for very short time, is still expected to significantly impact the surface chemistry of ITO at least through preferential sputtering. The original Sn-rich surface of ITO and its electronic properties are expected to change, and Ar^+ sputtering as a surface treatment may not be an optimal method to remove carbon-based contaminants from ITO surfaces. The effect of Ar^+ sputtering on the surface chemistry of ITO is investigated by XPS and UPS. For comparison, one ITO sample was only exposed to 30 min UV-ozone radiation and the second ITO sample received 30 min UV-ozone radiation followed by 0.3 min Ar^+ sputtering. The XPS spectra for In3d, Sn3d and O1s are collected for both of ITO samples. The $In3d_{5/2}$ XPS peaks for both ITO samples didn't show any visible change in terms of their binding energies and peak shapes and thus are not plotted here. This is probably expected since preferential sputtering would have more effect on Sn and O than In. This justifies the primary focus on the analysis of XPS spectra of $Sn3d_{5/2}$ and O1s. The corresponding superposed

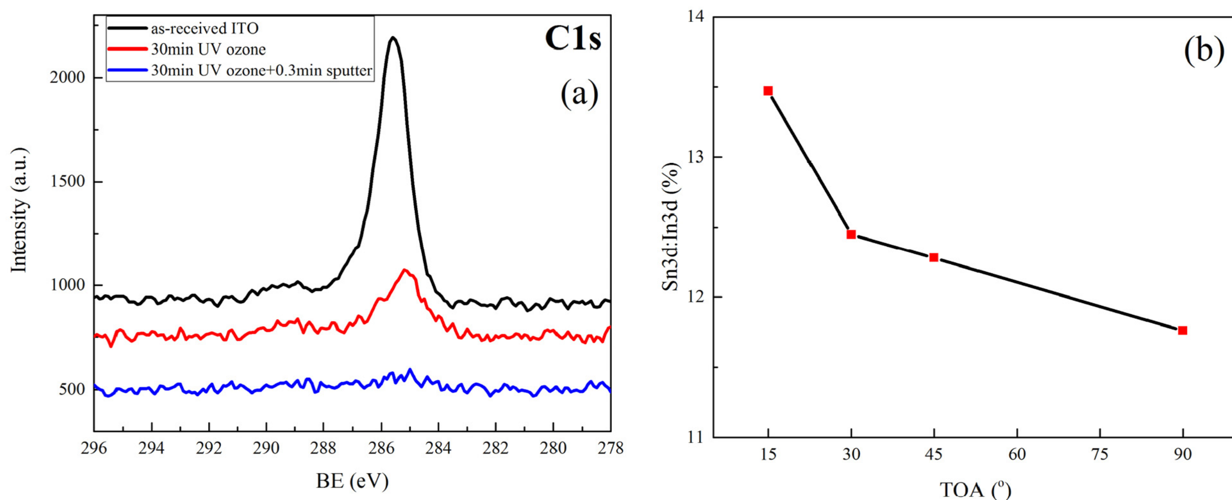

Fig. 1. (a) C1s spectra; (b) Intensity ratio Sn/In versus TOA.

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