Increase Mechanism of Indium-Tin-Oxide Work Function by KrF Excimer Laser Irradiation

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In this study, the increase mechanism of the indium-tin-oxide (ITO) work function (ϕ_W) by KrF excimer laser irradiation was investigated. From the observed x-ray photoelectron spectroscopy (XPS) results and four-point probe measurements, it is suggested that the surface chemical changes and the laser irradiation time had strong effects on the ϕ_W of ITO. Incorporation of oxygen atoms near the ITO surface during laser irradiation induced a peroxidic ITO surface, increasing ϕ_W. The induced increase of the ITO ϕ_W by laser irradiation could be useful for the enhancement of the hole injection in organic light emitting diodes.

Key words: Indium-tin-oxide (ITO), work function, excimer laser

Indium-tin-oxide (ITO) is an important material. Recently, in organic light emitting diodes (OLED), ITO was used as a transparent for injection of holes into the highest occupied molecular orbits of organic semiconductors due to its high work function (ϕ_W, ~4.7 eV).[1–3] The ϕ_W of ITO is very critical to the performance of OLED because it affects the energy barrier height at the interface of ITO with the organic semiconductors, playing a role in reducing the operating voltage of devices.[3–5] Consequently, studies of ITO surface modification for the purpose of enhancing hole injection are plentiful, with a focus on understanding how the ϕ_W is altered by passivation with surface-active species or by acids, bases, or O_2-plasma cleaning procedures.[3,6–8] The possibility to tailor the ITO ϕ_W by various methods is of great interest in the fabrication of optoelectronic devices where Ohmic charge injection is desired. Simple ways of tuning the ϕ_W to match the organic energy levels are of technological importance. In this study, we report the variation of the ITO work function after KrF excimer laser irradiation. Four-point probe and x-ray photoelectron spectroscopy (XPS) were employed to examine the changes in the resistance (R) of ITO, surface chemical bonding states of ITO, and surface atomic compositions of ITO after laser irradiation.

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The ITO samples with the film thickness of 26 nm and the sheet resistance of 71.38 Ω/□ were used in this work. The ITO samples, which were purchased from Wintek Corporation, were, respectively, irradiated in air for 10 and 15 min by a single pulse from a KrF excimer laser. The laser was operated at 248 nm with pulse duration of approximately 50 ns. The incident laser fluence was 26 mJ/cm^2 and the repeat rate was 50 Hz.

According to the observed result from four-point probe measurements, we find that the R of ITO increases with an increase in the irradiation time. The value of R was obtained directly from Ohm's law.[6] Following the demonstration by Swint and Bohn[6] that treatment of ITO surfaces with solutions of varying pH can be followed through changes in the in-plane resistance, this work addresses the link between the n-type depletion layer depth and in-plane resistance in thin (15–30 nm) ITO films. Swint and Bohn indicated that the change in in-plane resistance upon acid or base treatment was attributed to the net effect of surface charge and adsorbed dipole layer magnitude.[6] The relationship between the change in the resistance of ITO (ΔR) and the change in the effective thickness of ITO (Δt_{eff}) is expressed as[6]

$$\frac{\Delta R}{R_o} \sim \frac{\rho l}{\Delta t_{eff} w} \quad (1)$$

where R_o is the resistance of the nontreated ITO sample, ρ is the film resistivity, l is the length of the film, and w is the width of the film. The assumption of unchanging resistivity in the carrier-containing section of ITO is viable, because of the small values of Δt_{eff} observed (<1%).[6] In this study, we found that the laser irradiation caused the resistance to increase and the R increased with an increase in the irradiation time, as shown in Fig. 1. This implied that the laser irradiation led to an increase in the depletion layer thickness and the reduction of t_{eff}, resulting in increased R and ϕ_W.

In order to clarify the surface chemical changes of ITO after laser irradiation, the valence band spectra and XPS spectra of In $3d_{5/2}$, Sn $3d_{5/2}$, O 1s, and C 1s were measured via XPS. In Fig. 2, we can see that the Fermi level (E_F) shifted toward the valence band edge by 0.3 eV for 10-min-irradiated samples and the Fermi level shifted toward the valence band edge by 0.7 eV for 15-min-irradiated samples. The E_F shift corresponds to an increase in the upward surface band bending of the ITO sample, the depletion layer thickness, and the ϕ_W, consistent with the observed result from four-point probe measurements.

After laser irradiation, the surface band bending increased to 0.3–0.7 eV. This could be attributed to the formation of the O-rich surface condition by laser irradiation, as shown in Fig. 3. In ITO, an oxygen vacancy provides two free electrons, causing the degenerated n-type conductivity.[3,9,10] In Fig. 3, the O/(In + Sn) ratio with the step of the laser irradiation was plotted with the detection angle (θ). In this work, the exact sensitivity factor for ITO was not known, so the observed O/(In + Sn) ratio of the nontreated sample at the angle of ~0° was taken as 1. The O/(In + Sn) ratio increased after laser irradiation, and the increase was more pronounced. In addition, in Fig. 3, we find that the O/(In + Sn) ratio

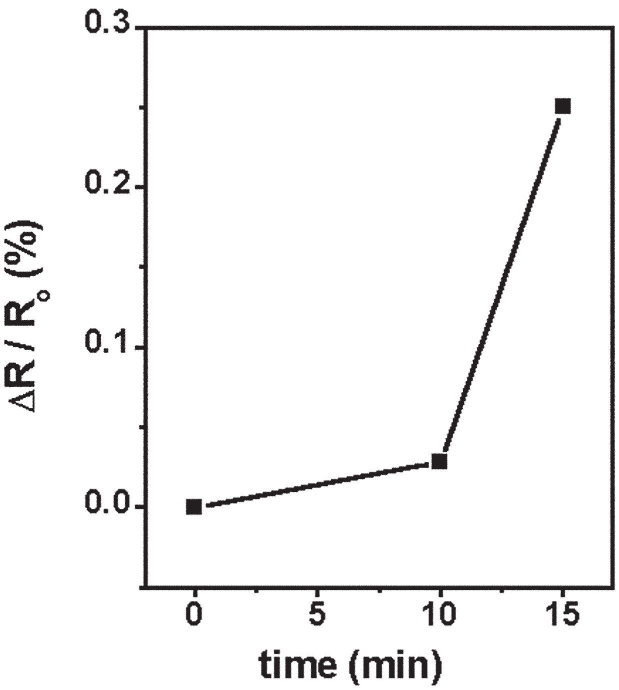

Fig. 1. Plot of the normalized resistance change $\Delta R/R_o$ as a function of the irradiation time.

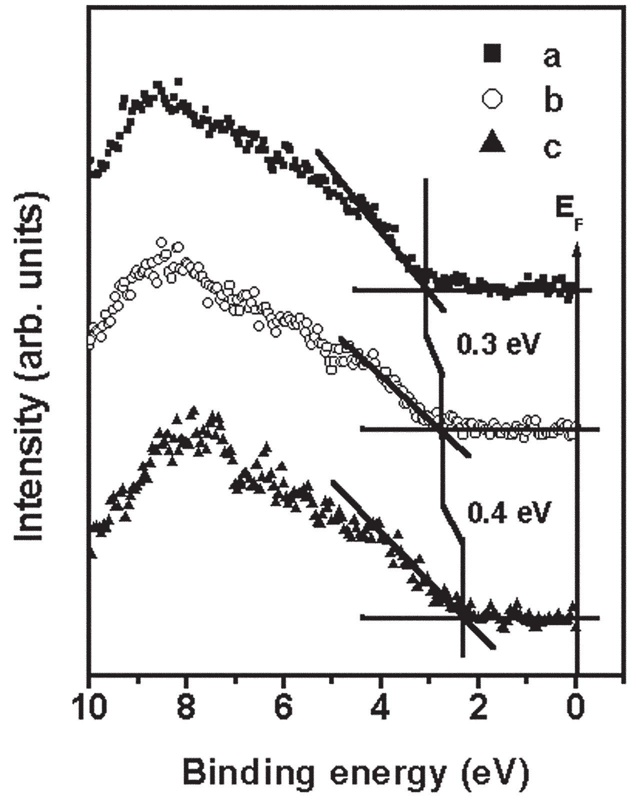

Fig. 2. Valence band spectra for the (a) nontreated, (b) 10-min-irradiated, and (c) 15-min-irradiated ITO samples.

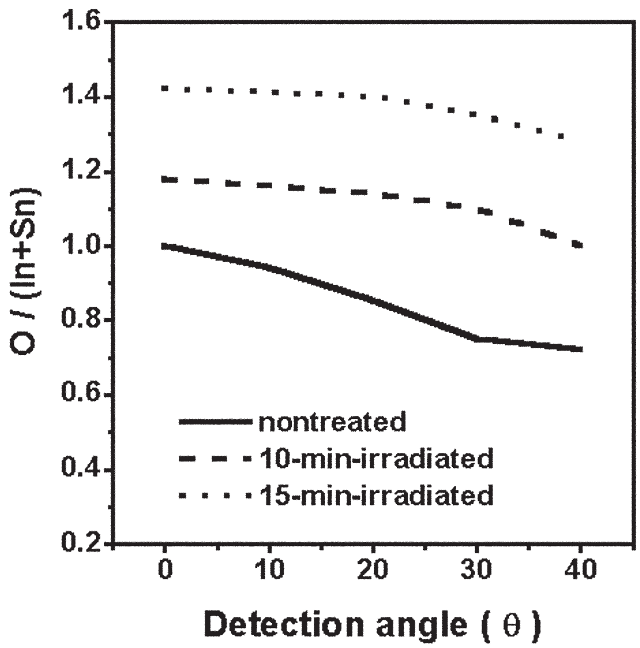

Fig. 3. Change of relative atomic ratio (O/(In + Sn)) on the surface of ITO as a function of detection angle.

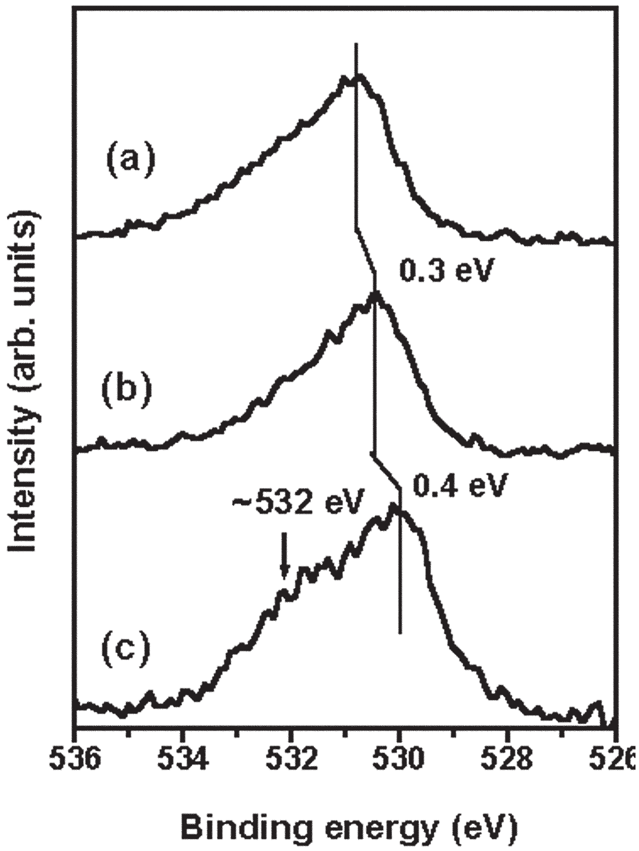

Fig. 4. XPS spectra of O 1s core level for the (a) nontreated, (b) 10-min-irradiated, and (c) 15-min-irradiated ITO samples

increases with an increase in the irradiation time. According to the experimental results shown in Fig. 3, we deduced that an increase in the ϕ_W of the laser-irradiated ITO samples was deeply related to the oxygen enrichment near the ITO surface. That induced oxidation of ITO by the laser irradiation might be adequate to effect beneficial changes in its electrode properties provides a rational guideline for development of new processing methodologies to enhance ITO-based optoelectronic devices.

Figure 4 shows XPS spectra of O 1s core level for ITO samples with and without laser irradiation. The O 1s spectra exhibited very similar behavior in peak shifts by the laser irradiation, indicating rigid changes in surface band bendings of the ITO samples.[3] We found that the peaks shifted toward the lower binding energies after laser irradiation. This corresponds to the shift of the surface E_F of ITO toward the valence band edge, namely, an increase of the ITO work function near the surface.[3] On the other hand, the increase in the intensity of the peak located at ~532 eV[3] was more pronounced after 15-min irradiation, as shown in Fig. 4c. Lee et al. have suggested that the increase of the peak intensity could be due to the adsorption or incorporation of $(O_2)^{-2}$ peroxo species near the ITO surface.[3]

In summary, the effects of KrF excimer laser irradiation on the chemical composition and ϕ_W of the ITO surface have been investigated. The XPS and four-point probe measurements were carried out to investigate changes in surface atomic composition and ϕ_W of ITO by the surface treatment using laser irradiation. We found that the ITO ϕ_W increases with an increase in the irradiation time and an increase in the O/(In + Sn) ratio. The laser irradiation yields work-function shifts as high as 0.3–0.7 eV compared to the nontreated ITO sample. The ϕ_W increase caused by the laser irradiation could be useful for the enhancement of the hole injection in OLED.

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