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A novel technique for increasing electron mobility of indium-tin-oxide transparent conducting films

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Abstract

Indium-tin oxide (ITO) films are used as transparent electrodes in display and other optoelectronic devices. Despite the reasonably high free electron concentration in these films, their electrical conductivities are much lower than that of metals. This is due in part to the reduced electron mobility caused by the high concentration of trapping centers created by structural defects in the ITO film. In this article, a simple technique is proposed for post-deposition treatment of ITO films to improve their properties. It has been found that exposure of ITO films to atomic-hydrogen plasma produces a significant increase in the electrical conductivity of the films. Under optimum conditions, over a three-fold increase in electrical conductivity is observed. The hydrogenation process does not affect optical transparency of the samples adversely. In fact a slight improvement over the visible range is seen.
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Keywords: Indium-tin oxide; Transparent conducting thin films; Hydrogen plasma; Hydrogenation process; Dangling bonds; Electrical passivation of structural defects

1. Introduction

Tin-doped indium oxide or ITO is the most widely used transparent-conducting material. Such transparent-conducting thin films are in widespread use as electrodes in a variety of optoelectronic devices, as heat-mirror coatings in 'smart windows' for buildings, in automobile and airplane windshields, in incandescent light bulbs, in flat-plate and concentrating solar collectors, and in a wide range of other applications [1–3]. Indium oxide is a wide-bandgap oxide semiconductor ($E_g = 3.75$ eV), which absorbs UV radiation (due to band-to-band transitions) and reflects in the IR region (due to free-electron oscillation). In between these two limits it has a transparency window covering the visible spectrum and near-IR (see Fig. 4). Transition between the transmitting and reflecting regions takes place at a wavelength λ_P, called the plasma reflection edge. The location of λ_P in an ITO film depends on the free-electron concentration n_1. As n_1 is increased, λ_P moves towards shorter wavelengths.

Tailoring the surface and bulk properties of ITO is of considerable importance in current display devices as well emerging applications such as organic optoelectronic devices. For example, changing the work function of the material is essential for controlling the charge injection properties of light emitting diodes fabricated on organic semiconductors [4].

The free-electron density in ITO films is normally quite high (up to $\sim 10^{21}$ cm^{-3}) [2], but the drift mobility (~ 10–70 cm^2 V^{-1} s^{-1}) is much lower than that of conventional semiconductors such as Si. Hence their electrical conductivity still remains significantly lower than that of a typical metal [2]. The reason for the low drift mobilities is the presence, in large concentration, of structural defects such vacancies, interstitial atoms and grain boundaries in these films. These defects act as scattering and trapping centers in ITO films. The effect of atomic hydrogen in passivation of structural defects in amorphous and polycrystalline silicon and

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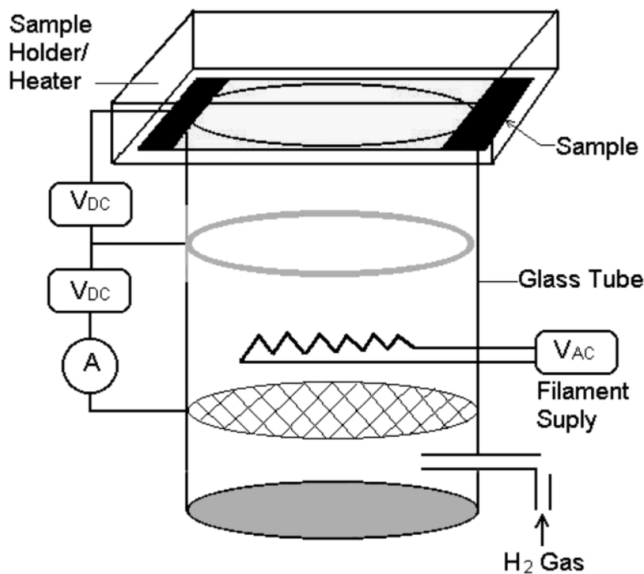

Fig. 1. Configuration of the plasma source.

hence improvement in their electronic properties is well known [5,6]. Passivation of structural defects in ZnO transparent-conducting films has been reported recently [7].

In this paper we report on enhancement of drift mobility, and hence electrical conductivity, of ITO films by a simple post-deposition hydrogenation treatment.

2. Experimental procedure

ITO films were deposited by the spray-hydrolysis technique. A solution of indium chloride and tin chloride was sprayed onto heated glass-slide substrates. The deposition conditions are as follows: Substrate temperature = 480 °C; Sn/In atomic ratio = 2.5%; volume of solution sprayed = 15 cm^3; nozzle-to-hot plate distance = 40 cm; carrier gas N_2 at 2 atmospheres; furnace preheating temperature = 150 °C. Rectangular aluminum electrodes were evaporated onto the two ends of each sample as ohmic contacts for measuring sheet resistance (and resistivity) of the sample, and to make electrical connection to the sample during the hydrogenation process.

Atomic-hydrogen plasma was obtained using the setup illustrated in Fig. 1. The plasma source consisted of a glass tube with a tungsten filament, heated by an AC power supply, as the electron source. This filament was placed between two metal rings. The lower ring (anode) and the upper ring (cathode) were connected to the accelerating DC power supply. A second DC supply was used for adjusting the hydrogen ion energy. The sample was placed on top of the plasma source.

A sample holder with a resistance heater was used for heating the sample during the hydrogenation process. The sample temperature was controlled with a thermocouple sensor and a temperature-controller circuit. This set-up was placed inside an Edwards E306A vacuum coating unit. High-purity (99.99%) hydrogen gas was fed into the system from the lower end of the plasma source. H_2 flow was controlled by inlet valve of the coating unit. Sheet resistance and electrical conductivity of each sample were measured before and after the hydrogenation process. Current–voltage (I–V) plots of the samples were obtained with an interface card inside a personal computer, which measures 4100 fixed points for each plot. The data are then plotted and saved in the computer. Standard Hall measurements were used to determine the electron mobility. The optical transmission data of the films were also recorded before and after the hydrogenation step with a Perkin-Elmer Lamda-9 double-beam spectrophotometer. Film thickness was measured from the interference peaks.

3. Results

An ITO film (400 nm thick) with a sheet resistance (R_S) of 59.4 Ω/□ was chosen for the hydrogenation treatment. It was hydrogenated at a substrate temperature T_{Sub} = 100 °C for 45 min. The sample was allowed to cool down and its R_S was measured. Then the hydrogenation step was repeated for the same sample but at T_{Sub} = 150 °C. This process was repeated for five different substrate temperatures. Fig. 2 shows the results.

As seen in Fig. 2, R_S is reduced to 21.6 Ω/□ after hydrogenation at T_{Sub} = 200 °C, which indicates a relative increase of 175% in electrical conductivity of the film. We believe the increase in sheet resistance for $T_{Sub} > 200$ °C is due to diffusion of mobile alkali metal impurities from the glass substrate into the ITO film. We have also observed a similar increase in sheet

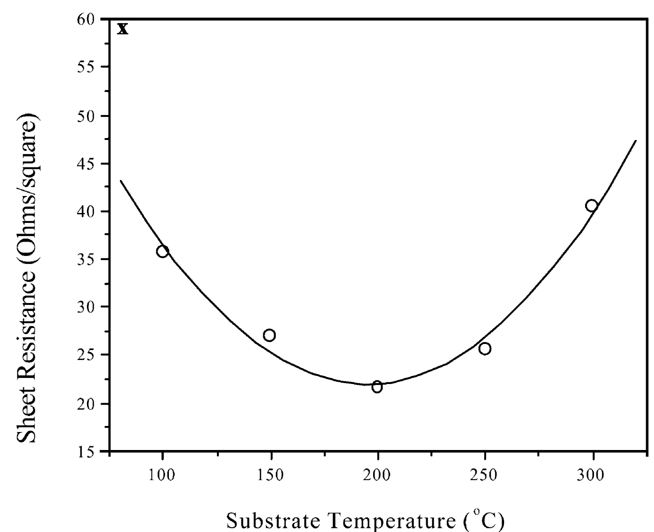

Fig. 2. Variation of sheet-resistance (Ω/□) of an ITO film with substrate temperature during the hydrogenation process ('x' denotes RS of the sample before hydrogenation).

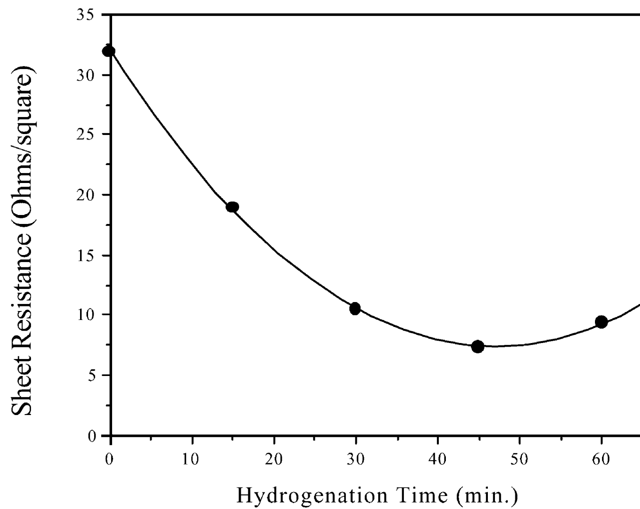

Fig. 3. Dependence of sheet resistance of an ITO sample on hydrogenation time (at $T_{sub}=200$ °C).

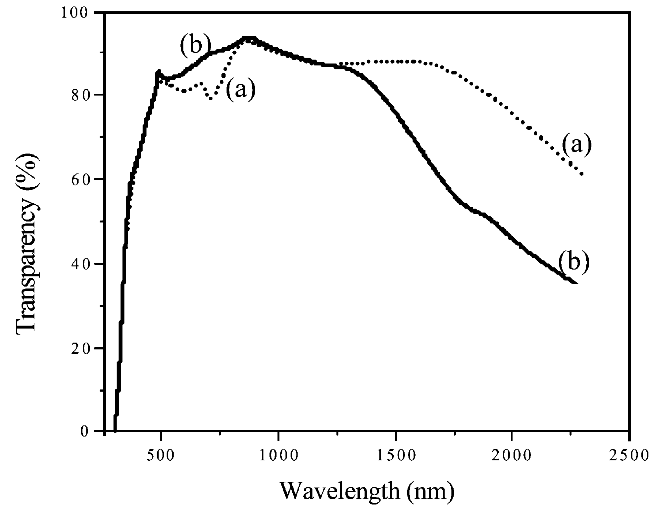

Fig. 4. Transmittance spectra of (a) an as-deposited ITO sample, and (b) after hydrogenation at $T_{sub}=200$ °C for 45 min.

resistance of the films when heated in vacuum at temperatures of 200 °C and above. To study the effect of hydrogenation time, another ITO sample (with an as-deposited R_S of 31.85 $\Omega/\square$) was hydrogenated at different times. The substrate temperature was fixed at 200 °C. The results are plotted in Fig. 3. As this figure shows, hydrogenation for 45 min produced the lowest sheet resistance (7.35 $\Omega/\square$). This is equivalent to a relative increase of 330% in electrical conductivity of the sample.

In another series of optimization tests, it was found that when the H-ion energy was fixed at 15 eV and the sample current was set in the range of 0.17–0.20 mA, best results were obtained. We would like to note that our technique of repeated hydrogenation of the same sample, followed by measurement on cool-down to room temperature, provides an accurate assessment of the influence of hydrogen treatment, with no concerns about sample-to-sample variations.

The optical reflection and transmission spectra were obtained on all the hydrogenated samples as well as unhydrogenated control. The transmission spectra of the ITO film before and after hydrogenation (to the optimal level for minimum resistance) are shown in Fig. 4. It is seen that the transmission in fact is improved above the absorption edge following hydrogenation. The reduction in transmission in the long wavelength regime arises from increased IR reflectance. The latter is to be expected in view of the increased electrical conductivity arising from hydrogenation.

4. Discussion and conclusions

As the experimental results indicate, the hydrogenation process produced a three-fold increase in the electrical conductivity of ITO films. More importantly, as seen in Fig. 5, this conductivity change arises essentially from an increase in mobility, with the free electron concentration remaining practically unchanged under hydrogenation. This phenomenon is in stark contrast to the well-known hydrogen-induced dopant deactivation phenomenon seen in a variety of commonly used semiconductors; typically atomic hydrogen treatment causes reduction of free carrier concentration by up to several orders of magnitude in materials as varied as Si, GaAs, InP and CdTe [8].

We believe that the changes observed in our ITO films can be explained in a manner analogous to that in amorphous and polycrystalline silicon. ITO films that are deposited at moderate substrate temperatures

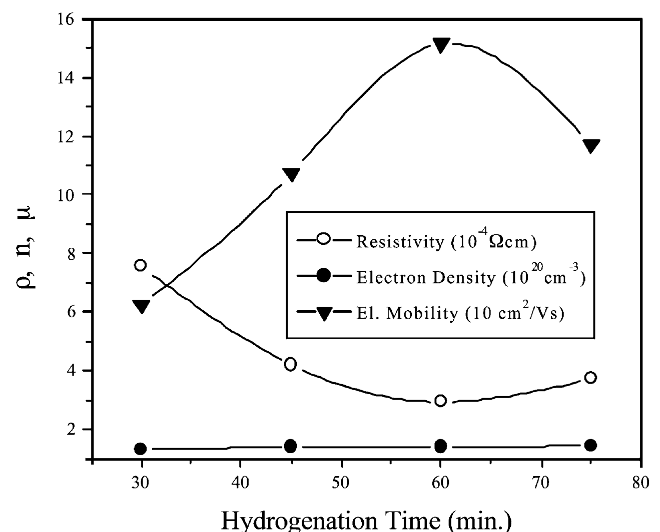

Fig. 5. Variations of electrical resistivity (ρ), free-electron concentration (n), and electron mobility (μ) with hydrogenation time for an ITO film hydrogenated at $T_{sub}=200$ °C.

(~400–500 °C) have polycrystalline structure, with very small crystallite sizes. Hence these films contain a high density of structural defects such as grain boundaries, interstitial atoms, and vacancies, along with some impurity atoms. A great many electrically active 'dangling bonds' might be expected in these films. With their small size, hydrogen ions can readily diffuse into the bulk of the film and passivate these dangling bonds. This will result in a considerable increase in carrier mobility and hence electrical conductivity of the film. Hydrogenation at low substrate temperatures will result in passivation of traps mainly in the surface layers, whereas at higher temperatures the bulk of the film is passivated. In our experiments, hydrogenation at T_{sub} = 200 °C produced the best results.

It is well known that the hydrogenation process, by itself, can create some structural defects in silicon [5]. This is the reason why hydrogenation by a single hot-filament has attracted attention recently. Our experimental results for the case of ITO films also show that prolonged hydrogenation could have negative effects on electrical conductivity of the films (Fig. 3). Also hydrogenation at high sample currents has negative effects on the electrical conductivity of ITO films. Further work is needed for a full investigation of these effects.

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