Enhancement of drift mobility of zinc oxide transparent-conducting films by a hydrogenation process

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Abstract

Transparent-conducting thin films of zinc oxide were prepared by vacuum evaporation and spray-pyrolysis techniques. A simple set-up for production of atomic-hydrogen plasma was designed and made. ZnO samples were hydrogenated at different substrate temperatures and for different hydrogenation times. Hydrogenation at a substrate temperature of 250°C for 45 min considerably increased the electrical conductivity of ZnO films (approx. by 340%). Hall measurements showed that the hydrogenation process did not change carrier concentration in the films greatly. Thus the increase in the conductivity can be essentially attributed to a considerable increase in carrier drift mobility. This in turn, is attributed to deactivation of 'dangling bonds' associated with the structural defects in ZnO films by hydrogen ions. It was also found that the hydrogenation process did not noticeably affect optical transparencies and microstructure of the films. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zinc oxide; Transparent-conducting films; Atomic-hydrogen plasma; Hydrogenation process; Structural defect passivation; Dangling bonds

1. Introduction

Transparent-conducting films have found a wide range of applications in several fields. They are used in optoelectronic devices as a 'transparent electrode', in photovoltaic solar cells as part of the heterojunction or as an efficient counter-electrode and/or antireflection coating, in 'smart windows' and photothermal solar collectors as a 'heat-mirror' coating, in gas sensors, and in a variety of other applications [1,2]. So far, indium oxide doped with tin (also called ITO) has been the most popular transparent-conducting material. ITO films have the best combination of high electrical conductivity and high optical transparency in the visible spectrum. However, ZnO films have attracted a lot of attention recently [3–16]. The main advantage of ZnO is its material cost, which is much lower compared with

indium oxide and tin oxide. Optical properties of ZnO films, including percent transparency in the visible region, band-to-band absorption edge, and plasma-reflection edge, are comparable with those of ITO films. However, so far, the highest electrical conductivities obtained in ZnO films are approximately one order of magnitude lower than the highest conductivities found in ITO films. Consequently, in applications where the high electrical conductivity is not essential, e.g. in heat-mirror coatings and in gas sensors, ZnO films can readily substitute ITO films. But in applications such as optoelectronic devices and solar cells where the lowest sheet resistance is required, ZnO films do not perform as good as ITO films. In this article, we report a relatively simple post-deposition hydrogenation technique for increasing the electrical conductivity of ZnO films by more than 300%. Obviously, this can have a major effect on widening the applications of ZnO films. This treatment procedure does not affect optical transparencies of the films adversely. In fact, the treated samples showed slight increase in certain visible wave-

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lengths. There have been reports on the beneficial effects of H_2 post-treatments on ZnO films [17–20]. However, in all of those cases, H_2 gas was used, whose effects are believed to be in connection with desorption of oxygen atoms from the films, and etching of small grains on the surface of the films [20]. However, a hydrogen-plasma treatment (which produces atomic hydrogen) affects the film properties in a different way, which is discussed in Section 5.

2. Experimental details

Zinc oxide samples were prepared using two methods. Evaporated ZnO films were deposited by thermal evaporation of ZnO powder in vacuum (using a tungsten boat). The evaporation rate was between 3 and 3.5 Å/s at 150 Å boat current. Glass slides were used as substrates. ZnO samples were also prepared using spray-pyrolysis technique. A solution of zinc acetate was sprayed onto heated substrates. In order to produce the best compromise between electrical conductivity and optical transparency of the films, all of the deposition parameters were optimized. The best samples were prepared under the following conditions: concentration of zinc acetate in the solution was 0.15%; indium (donor impurity) to zinc atomic ratio was 4%; substrate temperature during the deposition was 390°C; and the carrier gas (N_2) pressure was 1 atmosphere. Aluminum electrodes were evaporated on both ends of each sample (see Fig. 1). These were used 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 produced by a set-up, which is schematically shown in Fig. 2. The plasma source consisted of a glass tube with a tungsten filament, heated by a 6 V 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. Another DC power supply was used for adjusting hydrogen ion energy. Sample was placed on top of the plasma source. The whole set-up was placed inside a vacuum coating unit (Edwards E306-A). High purity (99.99%) hydrogen gas was fed into the source through its lower end. H_2 gas flow was controlled by the inlet valve of the coating unit. A sample holder with a resistance heater, a thermocouple, and a temperature-controller circuit was used for heating the sample during the hydrogenation process. The accelerating voltage in the plasma source was set between 376 to 405 V; and the decelerating voltage between sample and plasma source was set in the range of 350 to 390 V. The hydrogen ion energy was between 20 and 25 V, and the current passing through the sample was in the range of 0.11–0.18 mA. Sheet resistance and electrical conductivity of each sample was
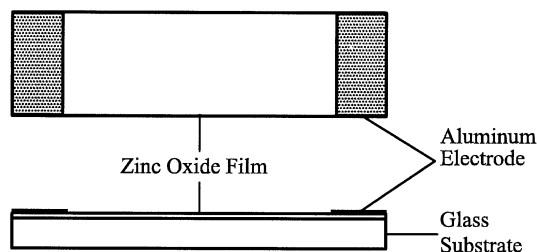

Fig. 1. Basic configuration of the samples.

measured before and after the hydrogenation process. A board inside a personal computer (which measures 4100 fixed points for each I/V plot) produced the I/V plots of samples. Film transparency spectra were recorded before and after the hydrogenation process by a double-beam spectrophotometer (Perkin-Elmer, model Lamda-9). Hall-effect measurement was done for measuring free-carrier concentration in the films. Scanning electron microscopy by a Cambridge Instruments S360 SEM was used for studying microstructure of the samples before and after the hydrogenation process.

3. Results

First, an evaporated ZnO sample (470 Å thick) with a sheet resistance (R_s) of 1450 $\Omega/\square$ was hydrogenated for 60 min at room temperature. After the hydrogenation process, the sample's sheet resistance was reduced to 1191 $\Omega/\square$. The same sample was hydrogenated again for another 60 min; but this time the sample was heated to 200°C during the process. Its sheet resistance dropped to 551 $\Omega/\square$. Repeating the same process with a substrate temperature (T_{Sub}) of 250°C reduced R_s to 327 $\Omega/\square$. However, further increases in T_{Sub} did not reduce R_s any further; at $T_{Sub} = 300$°C the film's sheet resistance increased to
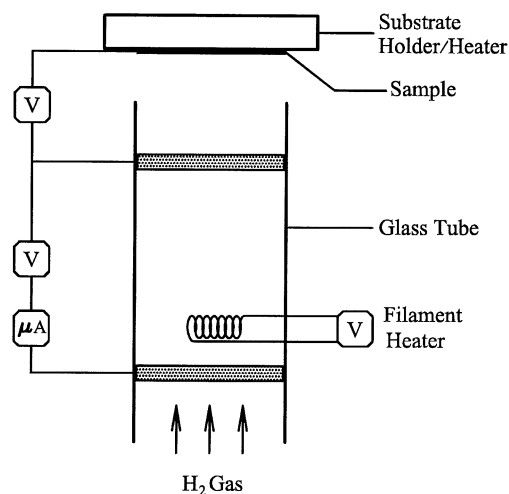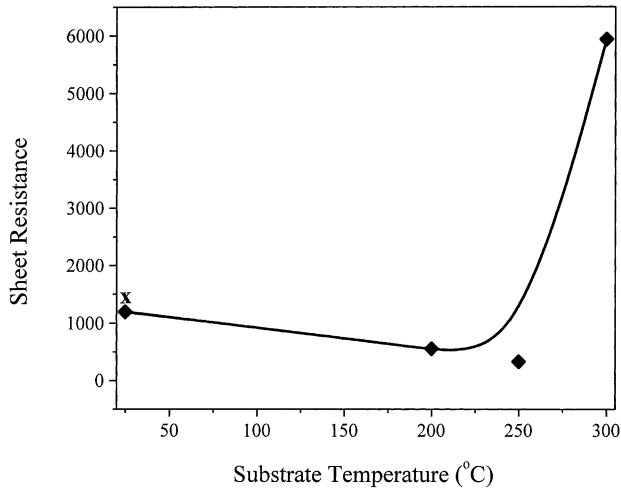

Fig. 2. Configuration of the plasma source.

Fig. 3. Variation of sheet resistance ($\Omega/\square$) of a ZnO film with substrate temperature during the hydrogenation process ('*x*' denotes R_s of the sample before hydrogenation).

Fig. 5. Dependence of sheet resistance of a ZnO film on hydrogenation time (at $T_{Sub} = 250°C$).

5933 $\Omega/\square$. Fig. 3 shows variations of R_s with respect to T_{Sub}. I/V plots of the sample after each hydrogenation step are shown in Fig. 4. A sprayed ZnO sample (0.59 μm thick) with R_s of 505 $\Omega/\square$ was chosen for the second series of experiments. In these tests, the substrate temperature was fixed at the optimum value of 250°C. After 15 min hydrogenation time, the sample was allowed to cool down to room temperature, and its I/V plot and transmission spectrum were recorded. Then, the hydrogenation process was done for another 15 min. This process was repeated five times. The variation of R_s with hydrogenation time is shown in Fig. 5, and I/V curves are plotted in Fig. 6. As these figures show, hydrogenation of approximately 45 min produced the lowest sheet resistance. Optical transparency (T) spectra of the sample after each hydro-

genation step did not show any significant changes. However, a slight increase in T in certain wavelengths in visible region, and a small decrease in T for some wavelengths in the NIR was observed. Two of these spectra are shown in Fig. 7. Hall-effect measurements showed that the hydrogenation process did not considerably affect free-electron concentration in a ZnO film. However, the electrical resistivity of the film decreased noticeably. Fig. 8 shows the variations of free-electron concentration (N), electrical resistivity (ρ), and electron mobility (μ) as a function of hydrogenation time for a ZnO film hydrogenated at $T_{Sub} = 250°C$. SEM studies of the surface topography and fracture cross-section of ZnO samples before and after the hydrogenation process did not indicate noticeable change in the microstructure of the samples.
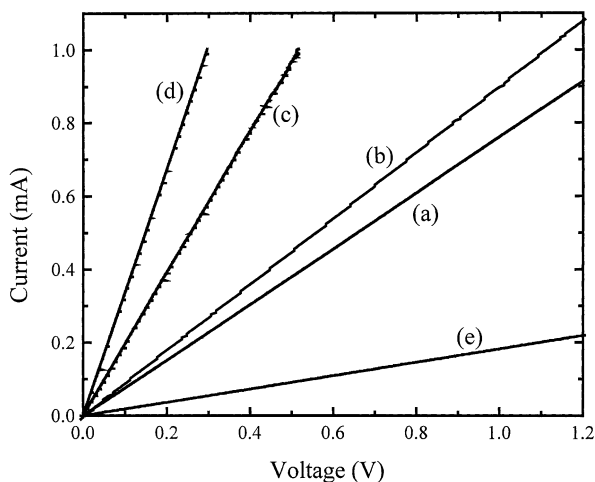

Fig. 4. I/V plots of a ZnO film: (a) as deposited, and after hydrogenation for 1 h (each step, as described in the text) at substrate temperatures of: (b) 25°C, (c) 200°C, (d) 250°C and (e) 300°C.
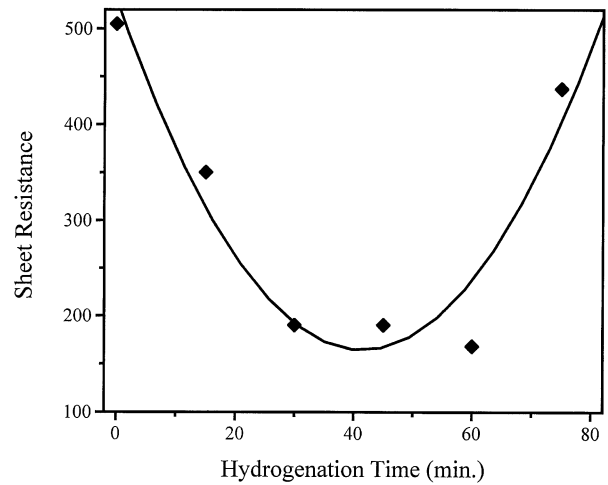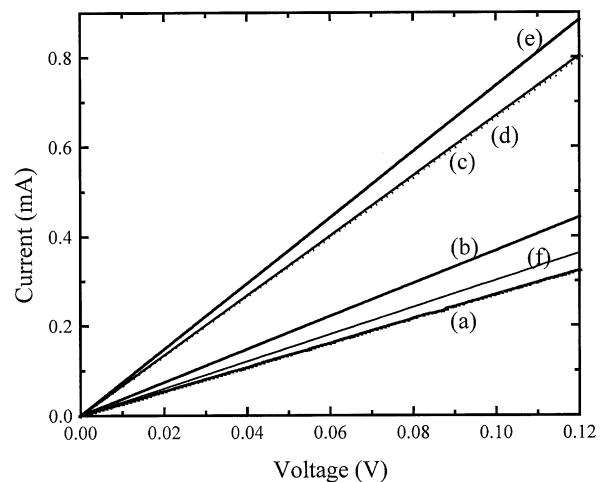

Fig. 6. I/V plots of a ZnO film: (a) as deposited, and after hydrogenation at $T_{Sub} = 250°C$ for: (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min and (f) 75 min.
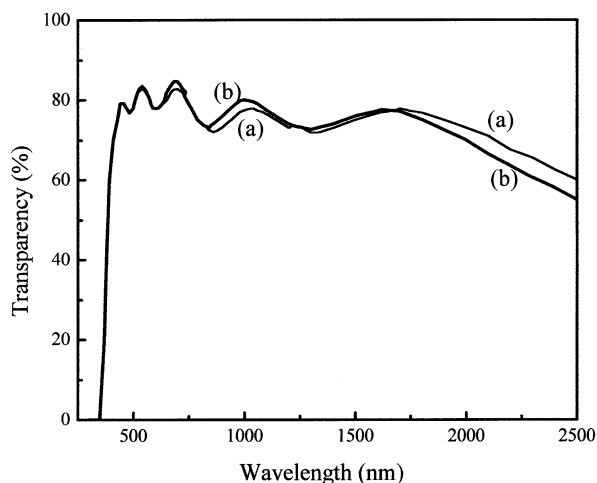
Fig. 7. Transparency of a sprayed ZnO film: (a) as-deposited, and (b) after hydrogenation for 60 min at $T_{Sub} = 250°C$.

4. Conclusions

The experimental results clearly indicate that the hydrogenation process was quite effective in increasing electrical conductivity of ZnO films. The hydrogenation at optimum conditions reduced R_s of the evaporated sample to 22.5% of its initial value, and for the sprayed sample, R_s dropped to 33.3% of its original value. Since the film thickness was fixed, we can say that the relative increases in the electrical conductivity of the films were 343% and 200%, respectively.

5. Discussion

We believe that the observed effect is analogous to the effect of atomic hydrogen in amorphous and poly-crystalline silicon case [21–23]. Obviously, there is a
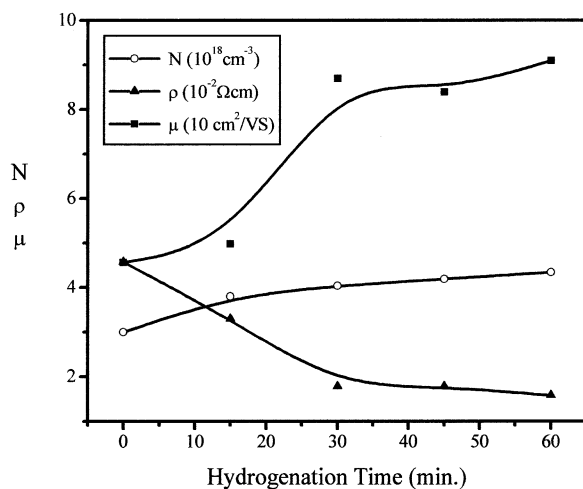

Fig. 8. Variations of free-electron concentration (N), electrical resistivity (ρ), and electron mobility (μ) with hydrogenation time for a ZnO film hydrogenated at $T_{Sub} = 250°C$.

great concentration of structural defects such as vacancies, interstitial atoms, grain boundaries, etc., in a thin ZnO film. Clearly, this concentration is greater for films deposited at lower substrate temperatures. Having a small size, hydrogen ions can readily diffuse into the bulk of a film, and deactivate the 'dangling bonds' associated with the structural defects. This will result in a considerable increase in carrier mobility, and hence lifetime of electrons in the film.

Hydrogenation at low substrate temperature was not very effective in deactivating charge-carrier traps. This is due to the fact that hydrogen ions need to diffuse into the bulk of the ZnO film in order to deactivate a large number of traps. As the experimental results indicate, hydrogenation at $T_{Sub} = 250°C$ was most effective.

However, hydrogenation at higher substrate temperatures did not produce better results. Considering H–Zn and H–O bond energies (~ 0.89 and 4.44 eV, respectively), one can conclude that these bonds stay stable at temperatures that we did our tests (up to 300°C). So the increase in film resistivity at $T_{Sub} = 300°C$ (Fig. 3) cannot be attributed to the hydrogen-bond breakup. We believe that the main reason is due to the diffusion of alkali ions (e.g. Na^+ and K^+) from the glass substrate into the ZnO film. Since these act as acceptor impurities in ZnO, they reduce the free-electron concentration and hence, increase the film resistivity. In fact, we have observed this effect in several other independent cases (as well as for some other transparent conducting materials). The increase of film resistivity at $T_{Sub} = 250°C$ in longer hydrogenation times (see Fig. 5) can also be explained by the diffusion of the mobile alkali impurities into the ZnO film.

Acknowledgements

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