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Robust room temperature persistent photoconductivity in polycrystalline indium oxide films

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We have investigated the effects of UV irradiation on the electrical and optical properties of polycrystalline In_2O_3 films. We found that UV illumination at a peak wavelength of 365 nm leads to a sharp drop in resistance and increase in carrier concentration. This highly conductive state persists for a timescale of hours in air at room temperature after illumination. We observe distinct changes in the optical absorption spectra and the associated change in carrier concentration, which is consistent with a Burstein–Moss shift of ~ 0.1 eV. The relaxation rate of this persistent conducting state depends strongly on temperature. We find that the conductance relaxation in an oxygen-free environment can be described by a stretched exponential while the behavior of the samples in air is better described by a logarithmic relaxation, both of which may be associated with glassy behavior. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3159623]

Indium oxide is one of very few materials possessing both high electrical conductivity at room temperature and high optical transparency in the visible region of the spectra.[1] It is widely used mainly in the form of doped indium tin oxide, in light emitting diodes, liquid crystal displays, and solar cells.[1] However, despite these numerous applications, some fundamental properties of indium oxide remain unclear. Even the nature of the band gap in In_2O_3 remains the subject of intense debate. Early measurements of the optical absorption edge[2] indicated a direct energy gap of 3.7 eV while the gap of 2.6 eV has been ascribed to indirect phonon-assisted transitions.[3] However, recent calculations[4] as well as x-ray photoemission spectroscopy measurements[5] are inconsistent with these conclusions and very recent measurements on high quality epitaxial films[6] give a lower value of ~ 2.6 eV for the direct gap.

Persistent photoconductivity (PPC), a light-induced change in conductance persisting after irradiation has stopped, has been observed in a variety of semiconductors[7] including wide gap semiconductors such as ZnO.[8] One common explanation for PPC, which is intimately connected to the band structure, is associated with the donor complex (DX) model, and the DX centers,[7] the defects whose energy depends on whether they are neutral or negatively charged. The energy of the center is lowered by removing electrons from a donor, resulting in a metastable state that is separated by a fraction of an eV from a neutral donor, promoting the induced conductance.[9] In another model the origin of PPC is explained by charge separation due to traps by random potential fluctuations, which may be related to the microstructure of the films.[10] An entirely different mechanism, oxygen photoreduction, has been proposed for amorphous[11] or noncrystalline[12] In_2O_3 films. In this model, UV illumination in vacuum or inert gas reduces the film, creating oxygen vacancies and dramatically increasing the conductivity, which is restored by exposing the sample to ozone or oxygen plasma.[11]

In this letter, we report the observation of robust PPC in In_2O_3 at room temperature. We found that illuminating a textured polycrystalline In_2O_3 film with a light emitting diode (LED) with a maximum intensity at 365 nm (3.4 eV) produces a large increase in conductance correlated with a corresponding increase in carrier concentration. Most significantly, we find that this high conductance state is stable under ambient conditions for hours or even days and exhibits the relaxation typically associated with glassy systems.

The indium oxide films were prepared by rf sputtering from a 99.99% pure In metal target in high purity oxygen and argon gasses, with partial pressures held at 2×10^{-3} and 1.8×10^{-2} mbar respectively. The fabrication process is described in detail in Ref. 13. The films were deposited onto (0001) single crystal sapphire substrates with a wide band gap, allowing us to measure both the optical reflectance and transmittance of the In_2O_3 samples. The data presented here were collected on 1 μm-thick samples. Using x-ray diffraction (XRD), we find that the spectrum peaks can be fully indexed to In_2O_3 [see Fig. 1(a)], with the polycrystalline samples preferentially oriented along (222) or (400). There is no evidence for secondary phase formation or any significant structural change in the In_2O_3 films upon UV illumination. We also investigated the film structure using high-resolution transmission electron microscopy (HRTEM). A representative HRTEM image is shown in Fig. 1(b), with the two-dimensional HRTEM image taken along the [100]. The lattice displays a clear fourfold symmetry [see the inset in Fig. 1(b)] with a spacing of 2.5 Å corresponding to the (400) *hkl* planes. Occasional defects including edge dislocations can be seen close to grain boundaries as indicated by the arrow.

Hall effect measurements done at $H=\pm4$ T with a variable current from 5 to 100 μA found that the as-prepared In_2O_3 films exhibited *n*-type conduction with a carrier concentration of approximately $n=2\times10^{18}$ cm^{-3}. The typical resistivity of the film at room temperature was ~ 2.5 Ω cm,

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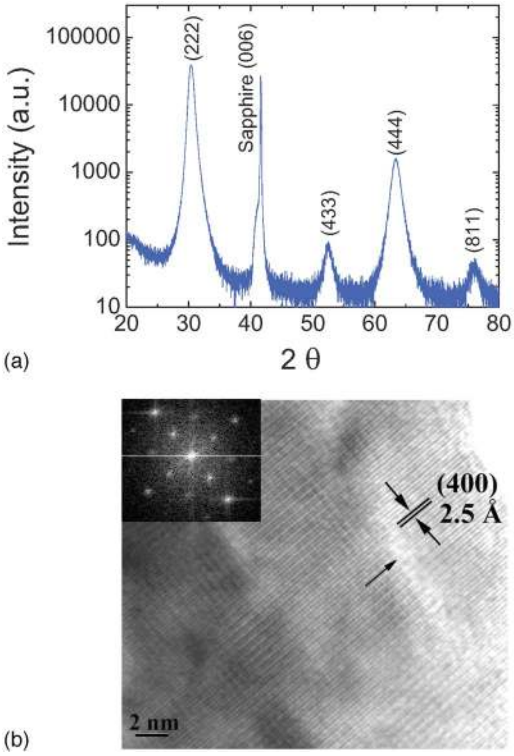

FIG. 1. (Color online) (a) XRD Cu $K\alpha$ diffraction pattern of the In_2O_3 films deposited on the sapphire substrate. (b) HRTEM image of the In_2O_3 film. Although occasional misfit or edge dislocations can be seen, as indicated by an arrow, the quality of the film within a single grain is comparable to the epitaxially grown films. A distance between the (400) planes is 2.5 Å. The TEM samples were prepared by removing a few crystallites from the sapphire substrate and transferring them to the TEM grid. The inset shows the fast Fourier transform of the image indicating the fourfold symmetry of In_2O_3 films.

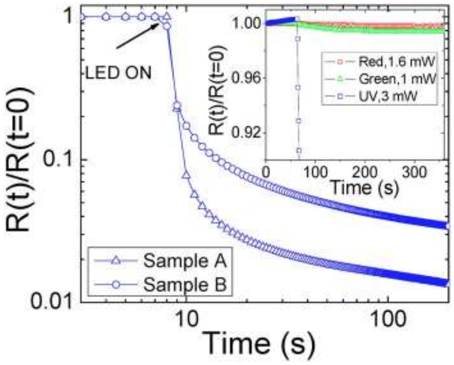

FIG. 2. (Color online) Sharp resistance changes observed upon illumination of an In_2O_3 film with a high intensity ($\sim 225\ \mathrm{mW/cm^2}$) UV LED at 365 nm. The results from several different samples fall approximately within the limits indicated by the two curves from samples A and B. Inset shows the results of exposure of an In_2O_3 film to the red LED, the green LED, and the UV LED. The power of the UV LED in this latter experiment was reduced to ~ 3 mW to match the intensity of the other two LEDs.

with a mobility of $\sim 1\ \mathrm{cm^2/V\ s}$. This mobility is lower than observed in epitaxial In_2O_3 films or single crystals,[14] indicating the presence of additional scattering mechanisms possibly due to vacancies and/or grain boundaries.

We investigated the effects of UV irradiation on the electrical and optical properties of In_2O_3 films by illuminating the samples using a high-power UV LED (Nichia, NCSU033A) having a central wavelength of 365 nm (3.4 eV),[15] with a full width at half maximum of 6 nm. We used a Keithley 6517A electrometer to continuously measure the resistance of an In_2O_3 film before, during, and after UV illumination. Figure 2 shows the change in the sample resistance upon UV illumination (indicated by an arrow) with an intensity of $225\ \mathrm{mW/cm^2}$. The measured resistance drops by approximately two orders of magnitudes within the first 3 min of illumination. We reproducibly observe qualitatively similar behavior in many samples although the magnitude of the resistance change has some sample-to-sample variation as shown in Fig. 2. We tentatively attribute this difference to variations in microstructure among the different films. Illumination with red and green LEDs having wavelengths centered at 626 and 569 nm respectively did not produce any sizable effects. As shown in the inset to Fig. 2, the resistance of In_2O_3 is practically unchanged when illuminated by red or green LEDs but when the same sample is subsequently illuminated by the UV LED (with the intensity reduced to $\sim 1\ \mathrm{mW/cm^2}$ to match the other LEDs), there is a precipitous drop in resistance. We find that increasing the UV LED power increases the rate of the drop in resistance but does not affect its saturation value (not shown here). This allows us to exclude any heating effects. The carrier concentration extracted from Hall effect measurements increased by about an order of magnitude on UV illumination to roughly $n = 2 \times 10^{19}\ \mathrm{cm^{-3}}$, suggesting that the change in resistance can be predominantly attributed to an increase in the number of carriers.

In order to more conclusively establish that UV irradiation modifies the electronic structure of In_2O_3 we conducted UV-visible reflectance and transmittance studies on both as-prepared and UV-illuminated samples. First, we measured the spectra for as-prepared samples using very low intensity to minimize any possible perturbation of the electronic structure and then illuminated the films using the UV LED before measuring the spectra again. The UV-visible reflectance and transmittance data, which we used to extract the absorption coefficient α, were measured using a Perkin–Elmer Lambda 900 spectrometer using a power of less than 10 μW. We plot $(\alpha E)^2$ as a function of energy for both the as-prepared and UV illuminated samples, as shown in Fig. 3. The sharp increase in $(\alpha E)^2$ between 3 and 3.5 eV marks the onset of optical absorption arising from band-gap excitations. We find the band-gap edge increases from 3.2 to 3.31 eV with UV illumination. Assuming that this change comes from the Burstein–Moss shift and using n

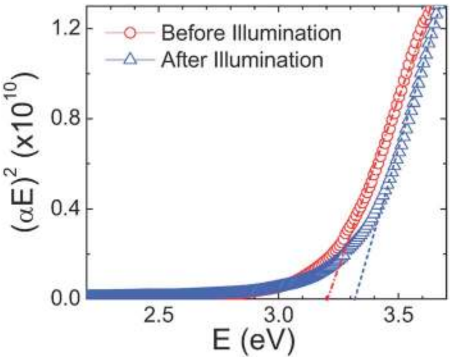

FIG. 3. (Color online) Burnstein–Moss shift determined from the changes in optical absorption in In_2O_3 films before and after irradiation. The dashed lines are a guide to the eye, indicating the optical absorption band edge.

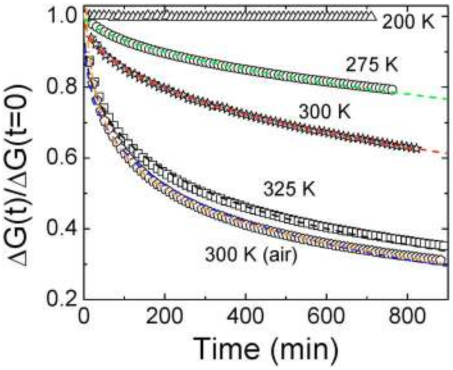

FIG. 4. (Color online) Time decay of the conductance of In_2O_3 film at different temperatures of 200, 275, 300, and 325 K, and in air (at 300 K). The dashed lines show the fit to the stretched exponential. The solid line shows logarithmic relaxation.

$=4\cdot(\Delta E\cdot m^*)^{3/2}10^{21}$, where ΔE is the energy shift in electron volts (0.11 eV) and m^* is the effective mass ($m^*=0.3$),[16] we obtain the carrier concentration $n=2.4\times10^{19}$ cm^{-3}, in good agreement with the results from our Hall measurements on the UV-illuminated films.

The most striking feature of the UV-induced conductivity in In_2O_3 is the long recombination time for these carriers under ambient conditions (exposed to air at room temperature). As shown in Fig. 4, this recombination time is on the order of several hours. To more carefully study the relaxation the UV-induced carrier density, we also illuminated the films at 300 K in a physical property measurement system with negligible oxygen partial pressure and then measured the time dependence of the conductance at various temperatures. The conductance relaxation can be reasonably well described by stretched exponential function $\Delta\sigma/\sigma=\exp[-(t/\tau)^{\beta}]$, with β varying from 0.61 at 275 K to 0.51 at 300 K and to 0.43 at 325 K. The time constant τ being approximately 10 h at room temperature follows Arrhenius behavior with the activation energy of about 0.3 eV. Heating the sample to 325 K increases the relaxation rate, while cooling to 200 K almost completely suppresses the relaxation. Interestingly, the relaxation of the conductance for In_2O_3 in air, as opposed to In_2O_3 under vacuum, can be better described by a logarithmic decay, $\Delta\sigma/\sigma=A-B\ln(t/\tau)$, rather than by a stretched exponential.

We now consider possible mechanisms for this persistent photocurrent in In_2O_3. Previous studies[11] have highlighted the role of oxygen vacancy defects in producing a persistent photocurrent in In_2O_3. Within this framework, we propose that the stretched exponential and logarithmic relaxation we observe, both associated with glassy dynamics, may be related to correlated oxygen motion inside the film. Similar glassy behavior of the electronic properties of hydrogenated amorphous silicon has been attributed to the diffusion of hydrogen, leading to stretched exponential relaxation.[17,19] We note that although electronic glassiness has been observed at helium temperatures in In_2O_3,[18] the effects we are observing at room temperature may have a distinctly different physical origin. Although we are studying crystalline samples, random bond breaking induced by UV illumination could result in the complex energy landscape or hierarchical dynamics[19] to produce such glassy relaxation. The latter model might also explain the different functional forms of the electronic relaxation in air and in oxygen-free helium gas.

In summary, we have observed robust photoconductivity in In_2O_3, which can be initiated by UV irradiation in air and persists for many hours at room temperature. We observe stretch exponential relaxation in oxygen-free environment with a possible transition to logarithmic relaxation in air. Both types of relaxations may be associated with glassy behavior. While systematic studies probing the interplay of persistent photocurrent and film microstructure will be necessary for a more complete understanding of this effect, tuning the oxygen diffusion rate may be crucial for controlling the relaxation. The ability to stabilize a highly conductive phase of In_2O_3 in ambient conditions, without the need of doping it with Sn, has important implications for device applications.

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