Supporting Information

Section A. The Characterization of GZO

The phase compositions and fine lattice variations of the crystals were characterized using Philip's PANalytical X'Pert Pro x-ray diffraction (XRD) and Rietveld refinement. XRD data were recorded with Cu *Kα* radiation (40 kV, 40 mA) in continuous scanning mode. The 2θ scanning range is from 15° to 85° in step of 0.03° with a collection time of 20 s per step. The crystallinity of (001) oriented GZO crystals is investigated by rocking curve measurement using (002) reflection. The data are collected on a Bruker D8 DISCOVER GADDS microdiffractometer equipped with a VANTEC-2000 area detector. Element components of the crystals are detected by using a Jobin-Yvon Ultima2 inductively coupled plasma (ICP) atomic emission spectrometer (AES) method. Temperature-dependent Hall effect measurements are performed over the temperature range of 77–300 K with a self-assembled apparatus. Hall effect measurements are carried out at a magnetic field of 5000 Gauss and 10 mA direct current using the van der Pauw configuration, and Ohmic contacts are achieved by soldering small indium dots onto the corners of 5 mm× 5 mm×0.5 mm wafer. The optical transmittance spectrum of the 5 mm× 5 mm×0.7 mm wafer is collected using a Perkin-Elmer Lambda-900 ultraviolet-visible-near infrared spectrometer at room temperature. The range of incident light wavelength is 300-1600 nm, and the spectrometer resolution is 1 nm. To test the thermal stability, air annealing of the GZO single crystal is conducted. The crystal is put into a quartz tube, and then annealed at 1100 °C under air atmosphere for 24 h in a furnace. Pure ZnO crystals grown by the same hydrothermal method are taken as control samples for comparison.

Section B. The possible mechanism of the temperature independence of carrier concentration

We propose some physical phenomena that arousing interest to the semiconductor researchers could be further explored in this GZO crystal. For example, people may be curious to the phenomenon that the carrier concentration of GZO shows temperature independence from 77-300 K. In fact, this may be attributed to two possibilities, which still needs intensive study to confirm.

i) It is very possible that the electrons are generated from the main donor with very shallow energy level (<10meV) in this crystal. Thus most of the electrons bound in the shallow donors can still be thermally excited into the conduction band even the temperature is as low as 77 K. In this situation, the GZO crystal could behavior with high carrier concentration at low temperature.

ii) Because of the heavy doping, the GZO crystal might change into degeneracy semiconductor, considering that the carrier concentration is quite close to the Mott critical density N_c (above which the Fermi level enters into the conduction band, $N_c=2.74\times10^{19}$ cm^{-3}, the details can be found in *SI* Section C).[1] It means that the carriers are basically degenerate, so the carrier concentration is independent of temperature.

Section C. The calculation of Mott critical density (*N*c)

The calculation equation for Mott critical density (*N*c) is as follows,

$$Nc = (2\pi 0.25 m_e^* e^2 / \varepsilon_0 h^2)^3 \qquad (1)$$

π pi, π=3.1415926;

m_e^* denotes the electron effective mass. In the case of heavily doped semiconductors, m_e would increases with the increment of carrier concentration, similar with the trend in ZnO:Al films.[2] According to the Pisarkiewicz model,[3] the effective mass for a wide-band-gap semiconductor can be expressed as

$$m_e^* = m_0^* \left[1 + 2C \frac{\hbar^2}{m_0^*} (3\pi n)^{2/3} \right]^{1/2} \qquad (2)$$

where m_0^* is the effective mass at the bottom of the conduction band with the value of 0.28.[4] The value of m_e^* is obtained when substituting equation (1) into equation (2);

e denotes electron charge 1.6×10^{-19} C;

ε_0 denotes the static frequency dielectric constant. The relative dielectric constant is about 8.75. [5]

h denotes Planck constant, $h=6.626\times10^{-34}$ J·s;

Referrences:

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(3) Pisarkiewicz, T.; Zakrzewska, K.; Leja, E. Thin Solid Films **1989,** *174*, 217-223.

(4) Sernelius, B. E.; Berggren, K. F.; Jin, Z. C.; Hamberg, I.; Granqvist, C. G. *Phys. Rev. B* **1988,** *37*, 10244-10248.

(5) Adachi. S. *Handbook on Physical Properties of Semiconductors*; Kluwer Academic Publishers; Boston: 2006.