Stability of p-type conductivity in nitrogen-doped ZnO thin film

Z. Y. Xiao, Y. C. Liu, R. Mu, D. X. Zhao, and J. Y. Zhang

Related Articles

Controlling the resistivity gradient in chemical vapor deposition-deposited aluminum-doped zinc oxide
J. Appl. Phys. 112, 043708 (2012)

Schottky solar cells based on CsSnI3 thin-films
Appl. Phys. Lett. 101, 093901 (2012)

Bipolar resistive switching characteristics of Al-doped zinc tin oxide for nonvolatile memory applications
Appl. Phys. Lett. 101, 052901 (2012)

Experimental observation on the Fermi level shift in polycrystalline Al-doped ZnO films
J. Appl. Phys. 112, 013718 (2012)

Controlling the electrical properties of ZnO films by forming zinc and oxide bridges by a plasma and electron-assisted process
AIP Advances 2, 022167 (2012)

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: http://apl.aip.org/authors

Stability of *p*-type conductivity in nitrogen-doped ZnO thin film

Z. Y. Xiao,[1] Y. C. Liu,[2,a),b)] R. Mu,[3,a),c)] D. X. Zhao,[1] and J. Y. Zhang[1]

[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics, and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China*
[2]*Center for Advanced Optoelectronic Functional Materials Research, Northeast Normal University, Changchun 130024, People's Republic of China*
[3]*Center for Physics and Chemistry of Materials, Fisk University Nashville, Tennessee 37208, USA*

The behavior of *p*-type conductivity in nitrogen-doped ZnO prepared by thermal oxidation of zinc oxynitride thin film was investigated. The sample exhibited a stable *p*-type characteristic in the darkness over a 1 yr period after deposition. However, when the *p*-type sample was irradiated by 2.72 eV photons, it underwent a classic-mixed conductivity transition from *p* type to *n* type. An anomalously thermal equilibrium process was observed. It took 24 h for the persisted *n* type photoconductivity to fade away in the dark and transit back to original *p* type. A local potential fluctuation model was used to explain the transient electrical behavior. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2838330]

ZnO has become a promising candidate for applications in ultraviolet (UV) optoelectronic devices because of its wide band gap and a large exciton binding energy at room temperature.[1] However, the full realization of its optical potential requires the development and the control of *p*-type doping, which has presented to be a real challenge.[2] Two of the major problems, despite of many successes of *p*-type doping reported,[3] are the poor quality of the *p*-type material and the difficulty to maintain a stable *p*-type conductivity.[4–6] Barnes *et al.* have recently noted that *p*-type ZnO films revert to *n* type in time after deposition.[4] Hydrogen-generated donors were suggested to explain the observed electrical behavior. Wang and Zunger have also observed a similar phenomenon and attributed it to a metastable N-on-O substitution, which serves as donors.[5] The development of donor centers seems to be a plausible explanation for the *p*-type conductivity which disappears with time. On the other hand, some reports showed that *p*-type conductivity seems to be unstable and it can even convert to *n*-type conductivity after the exposure to light.[6] This observation can be traced back to persistent photoconductivity (PPC) or noisy Hall-effect measurements.[7] Unfortunately, up to now, the nature of this erratic *p*-type conductive behavior is not well understood and remains to be one of the foremost obstacles hindering device development.

In this paper, the stability of *p*-type conductivity in nitrogen-doped ZnO was studied as a function of time after the film deposition and under photon illumination. The Hall measurements were used to study *p*- to *n*-type transformation processes and back to *p* type with and without photon irradiation.

The samples used in this study were prepared by thermally oxidation of a zinc oxynitride thin film. The zinc oxynitride thin film was fabricated via the plasma enhanced chemical vapor deposition technique. Upon the oxidation, a 500 nm thick nitrogen doped ZnO thin film was obtained on a fused silica substrate. The detailed film growth and structural characterizations have been reported in previous papers.[8] The Hall coefficient measurements were conducted with a Lakeshore's 7707 Hall system in a Van der Pauw configuration. A typical direct current is $\sim$200 nA and a magnetic field strength is 9 kG. Data were collected with positive and negative currents and reversing magnetic fields. The results were averaged in order to reduce various electromagnetic effects. After mounting, the sample was kept in darkness for at least 24 h to minimize any residual PPC effect. Furthermore, the Hall coefficient measurements were repeated many times under similar condition to assure the reliability of the results. Time dependent Hall measurements were conducted to investigate the effect of shelving time under ambient condition after the sample was prepared with confirmed *p*-type conductivity. To clarify the effect of photon illumination on *p*-type behavior, a halogen lamp was used as a white light source. A grating was used to select desired photon energy range. A uniform photon flux was directed onto the sample. Photon energies used for the study were 2.16, 2.51, 2.57, 2.61, 2.67, and 2.72 eV, respectively. A typical exposure time for chosen photon energy was 5 min. The Hall measurements were conducted right after each photon illumination. All Hall measurements were carried out in the dark at room temperature.

Over a span of 18 months of shelving time in the dark, a total of eight Hall measurements were conducted, as depicted in Fig. 1. A *p* type of electrical conductivity was confirmed.

a)Authors to whom correspondence should be addressed.
b)Electronic mail: ycliu@nenu.edu.cn.
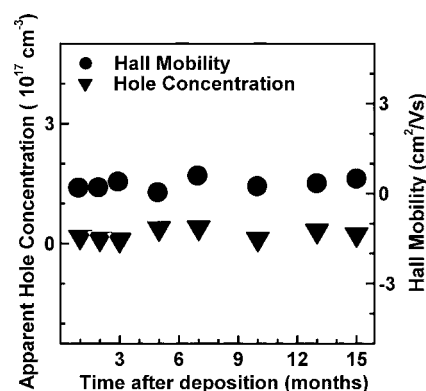c)Electronic mail: rmu@fisk.edu.

FIG. 1. Hall mobility and apparent carrier concentration change as a function of time after film deposition while the sample was kept in the dark.

Measured total carrier (hole) concentration remained the same as $\sim 2.7 \times 10^{16}$ cm^{-3}. Mobility was around 0.3 cm^2/V s at room temperature. The results indicate that the sample is thermally stable and not sensitive to shelving time without photon illumination. The small variation in values for both Hall mobility and hole concentrations may be due to a small Hall voltages as discussed in the literature.[7]

Figure 2 displayed photon energy dependent Hall coefficients and apparent (total) carrier concentrations immediately after photon illumination. The striking observations are as follows: (1) the *p*-type sample is very sensitive to photon irradiation in the energy range of 2.0–2.8 eV; (2) as photon energy increases, the overall *p*-type Hall coefficients and carrier concentrations decrease; and (3) the *p*-type sample converts to *n* type when the illuminating photon energy reaches ~ 2.7 eV through the reverse sign of Hall coefficient. Please note that the apparent (or total) carrier concentration has jumped in two orders of magnitude. This change in conduction types may be explained by the presence of mixed conduction effects. If this is the case, the conductivity and the Hall coefficient take the following form:[9]

$$\sigma = \sigma_p + \sigma_n = e(p\mu_p + n\mu_n), \qquad (1)$$

$$R_H = \frac{R_p \sigma_p^2 + R_n \sigma_n^2}{(\sigma_p + \sigma_n)^2} = \frac{p\mu_p^2 - n\mu_n^2}{e(p\mu_p + n\mu_n)^2}, \qquad (2)$$

where σ σ_p, and σ_n are total, hole, and electron conductivities, respectively. Here, p, n, μ_p, and μ_n are hole and electron carrier concentrations and hole and electron mobilities, respectively. Moreover, R_H, R_p, and R_n are the Hall coefficients for total, hole, and electron, respectively.

Clearly, the Hall coefficient R_H should carry a plus or a minus sign for *p* or *n* type of sample. However, a sign change can happen if the transition processes dominated from impurity to intrinsic ionization. Thus, when the electrical property is examined by the Hall measurements, the type of conductivity can be obtained by the sign of R_H.

From Eq. (2), an increase of $n\mu_n^2$ will contribute to a decrease of R_H. Thus, it results in a decrease in terms of $p\mu_p^2 - n\mu_n^2$. However, so long as $p\mu_p^2 - n\mu_n^2 > 0$, $R_H > 0$, the sample will remain *p* type. Only when the photon energy is up to 2.72 eV, the contribution from the term $n\mu_n^2$ will surpass the term $p\mu_p^2$ and $R_H < 0$. Thus, the sample shows *n*-type behavior. Therefore, it can be argued that the sample exhibits a classic-mixed conduction transition behavior. Further, a long lifetime of the observed *n*-type photoconductivity over 24 h is also rather interesting in the dark. In fact, a similar observation has been reported for *p*-type GaN.[10] Numbers of models have been proposed to explain the origin of PPC in semiconductors. In the macroscopic potential barrier (MPB) model,[11] a spatial separation between photogenerated electrons and holes exists by a built-in electric field from MPB due to band bending at surface and/or interfaces, which can lead to PPC. Based on the deep-level trap centers of large lattice relaxation (LLR) model,[12] the barrier between the photoexcited carriers and the deep impurity centers is believed to be the origin of PPC. In the current experiments, PPC phenomenon was observed at room temperature. That makes both MPB and LLR models unlikely to be the origin of the observed PPC effect since both models should observe PPC phenomenon only at rather low temperature. In the present, *p*-type thin film grown on a fused silica substrate,
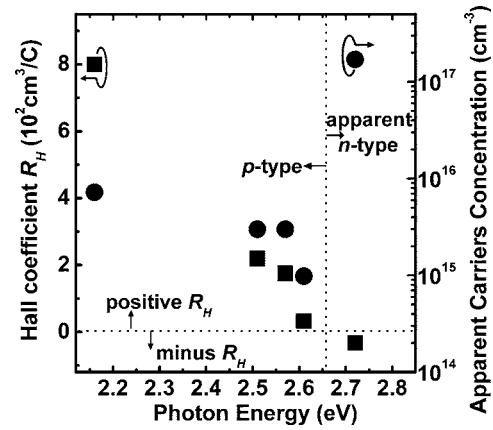

FIG. 2. Hall coefficient and apparent carrier concentration change as a function of illuminating photon energy of the sample. The illumination time at each measurement was 5 min.

x-ray measurement confirmed a polycrystalline structure of the sample. Atomic force microscopy images indicated that the film consists of columnar grains with the sizes of about 60 nm and the surface roughness of ~ 12 nm.[8] Such morphological and structural characteristics imply that a large number of grain boundaries exist in the sample. It is also known that grain boundaries contain high densities of interface defects which induce the variations in potential at the atomic level and hence give rise to localized states. Both theoretical prediction and experimental observation have been demonstrated that a high density of localized states exponentially tailed into the gap.[13] The tailing effects are largely induced by grain boundaries at the a conduction band minimum and a valence band maximum in real space.[14] The energy distribution of band tailing is decided by varying the degree of fluctuation in the sample, which corresponds to the sample quality. With this grain boundary induced local potential fluctuation model, the low potential sites in the conduction band are spatially separated from those in the valence band, which can explain the observed long carrier lifetime. Photoexcited electrons and holes by the illuminating photons below are accumulated near the conduction band minima and the valence band maxima due to the localized states. Once it happens, there are two possible ways to induce *n*-type PPC:[14] (1) thermally activated electrons are able to hop among their adjacent localized sites and (2) these electrons can also percolate through the network of accessible nearby states at conduction band minima. On the other hand, the conductivity originated from the hole transport is less significant due to the heavier mass or low mobility. As the illuminating photon energy increases, more electrons can be excited into the localized states. Therefore, an increase of a nonequilibrium *n*-type conductivity will result via aforementioned two possible pathways. This argument seems to be consistent with the behavior of R_H observed in the current experiments. Because of a large difference in electron and hole mobilities, the *p*-type sample would turn into an apparent *n* type when electron concentration is lower than hole concentration with three to four orders. Such a low threshold value for nonequilibrium electrons is not difficult to meet. In the current experiments, this threshold was achieved after the sample was illuminated by 2.72 eV photons, which leads to the appearance of an apparent *n*-type ZnO thin film.

Figure 3(a) shows a normalized PPC decay curve upon the sample irradiated with 2.72 eV photon flux for 5 min.
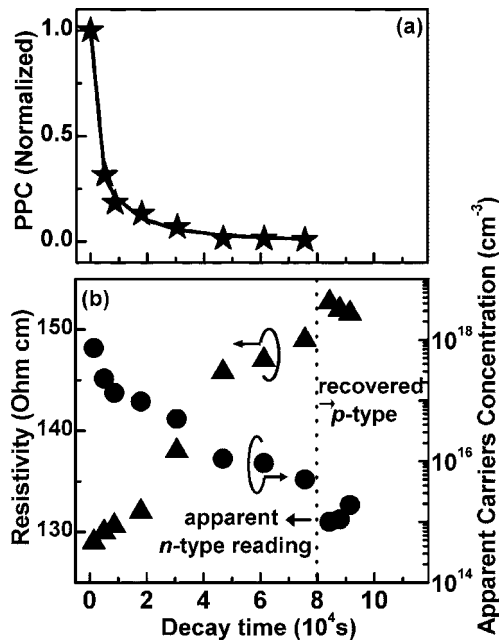
FIG. 3. (a) *n*-type PPC decay as a function of time at room temperature after the *p*-type ZnO thin film was illuminated with 2.72 eV for 5 min. The data were normalized against $t=0$. The solid line represents a model fit with a stretched-exponential function $I_{PPC}(t)=I_{PPC}(0)\exp[-(t/\tau)^{\beta}]$ with $\tau=3.5 \times 10^3$ s and $\beta=0.5$. (b) Time dependent resistivity and apparent carrier concentration measured by a Van der Pauw Hall system.

The best fit to PPC relaxation process can be best described by a stretched-exponential function,

$$I_{PPC}(t) = I_{PPC}(0)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \qquad (3)$$

where τ and β are relaxation time constant and the decay exponent, respectively. The obtained best fit values are $\tau=3.5\times 10^3$ s and $\beta=0.5$. Both τ and β values are consistent with previous report where τ is on the order of 10^3 s and β is around 0.8 for $Zn_{0.3}Cd_{0.7}Se$ at low temperature.[14] A decrease of β value in current fit relative to the previous report may be attributed to a relatively fast decay nature since it is measured at room temperature. It is known that the stretched-exponential function usually describes the relaxation processes of a wide class of disordered system toward equilibrium.[15] In the current system, the decay behavior may suggest that grain boundary induced local potential fluctuation model provides a reasonable interpretation in explaining the origin of the *n*-type PPC. When a relaxation process occurs in the dark, the nonequilibrium *n*-type carriers are gradually recombined through the overlap wavefunctions between electrons and holes in real space and/or assisted by room temperature thermal activation of electrons from the local conduction band minima recombining with the holes located at the maxima of valence band. Similar argument can also be used to account for the increase of the measured resistivity and the decease in the photoinduced electron concentration, as illustrated in Fig. 3(b). Another interesting fact observed in Fig. 3(b) is that the measured time dependent resistivity consists of two separate steps before the sample converted back to *p* type. One occurs before 5×10^4 s and another is between 5×10^4 and 8×10^4 s, respectively. The

sample becomes *p* type again after a long relaxation time of $>8\times 10^4$ s.

The appearance of resistivity change steps should imply a none direct interband recombination between electrons and holes and it seems to further suggest the existence of non-equilibrium *n*-type carrier relaxation processes due to the local potential trap effect.[16] It, therefore, supported the interpretation of local induced potential fluctuation model to explain the observed *n*-type PPC.

It is worthy to point out that, although the relaxation time is very long (27 h), the system will eventually return to its original *p*-type state. In our view, this observation provides a very strong evidence that the prepared film is a truly *p*-type ZnO.[17] However, the relatively poor quality of the *p*-type film is susceptible to mixed conduction effects and difficult to positively confirm the nature of the measured conductivity.

In summary, time dependent *p*-type conductivity in nitrogen-doped ZnO thin film is investigated. A strong persistent *n*-type photoconductivity is observed after the sample was illuminated by 2.72 eV photons. After a long relaxation process in the dark, the original *p*-type state can be recovered. Grain boundaries induced local potential fluctuation model is proposed, which provides qualitative agreement with the observed mixed conduction effects and qualitatively in agreement with all observed data. The experimental finding further suggests that in order to effectively explore the full potential of ZnO materials, it is very important to control the material quality in searching the ways to fabricate *p*-type ZnO material.

[1]T. Makino, Y. Segawa, A. Tsukazaki, A. Ohtomo, and M. Kawasaki, Appl. Phys. Lett. **87**, 022101 (2005).
[2]D. C. Look, B. Claflin, Ya. I. Alivov, and S. J. Park, Phys. Status Solidi A **201**, 2203 (2004).
[3]M. Joseph, H. Tabata, and T. Kawai, Jpn. J. Appl. Phys., Part 2 **38**, L1205 (1999).
[4]T. M. Barnes, K. Olson, and C. A. Wolden, Appl. Phys. Lett. **86**, 112112 (2005).
[5]L. G. Wang and A. Zunger, Phys. Rev. Lett. **90**, 256401 (2003).
[6]B. Claflin, D. C. Look, S. J. Park, and G. Cantwell, J. Cryst. Growth **287**, 16 (2006).
[7]D. C. Look, Semicond. Sci. Technol. **20**, s55 (2005).
[8]Z. Y. Xiao, Y. C. Liu, B. H. Li, J. Y. Zhang, D. X. Zhao, Y. M. Lu, D. Z. Shen, and X. W. Fan, Semicond. Sci. Technol. **22**, 1522 (2006).
[9]D. C. Look, *Electrical Characterization of GaAs Materials and Devices* (Wiley, New York, 1989), Chap. 1.
[10]C. Johnson, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **68**, 1808 (1996).
[11]H. J. Queisser and D. E. Theodorou, Phys. Rev. B **33**, 4027 (1986).
[12]D. V. Lang and R. A. Logan, Phys. Rev. Lett. **39**, 635 (1977).
[13]M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, Phys. Rev. Lett. **22**, 1065 (1969), and references therein.
[14]H. X. Jiang and J. Y. Lin, Phys. Rev. B **40**, 10025 (1989); Phys. Rev. Lett. **64**, 2547 (1990).
[15]R. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).
[16]E. K. Liu, B. S. Zhu, and J. S. Luo, *Semiconductor Physics* (National Defence Industrial, Beijing, China, 1994), Chap. 5.
[17]D. C. Look and B. Claflin, Phys. Status Solidi B **3**, 624 (2004).