JOURNAL OF APPLIED PHYSICS 109, 016107 (2011)

Minority carrier transport in p-ZnO nanowires

Y. Lin,[1] M. Shatkhin,[1] E. Flitsiyan,[1] L. Chernyak,[1,a)] Z. Dashevsky,[2] S. Chu,[3] and J. L. Liu[3]
[1]*Department of Physics, University of Central Florida, Orlando, Florida 32816-2385, USA*
[2]*Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel*
[3]*Department of Electrical Engineering, University of California, Riverside, California 92521, USA*

(Received 11 October 2010; accepted 29 November 2010; published online 7 January 2011)

In this work, we explore the minority carrier diffusion length in zinc oxide nanowires, using the electron beam-induced current technique. Systematic measurements as a function of temperature were performed on p-type, Sb-doped ZnO film, containing a 4 μm thick nanowire layer. The minority carrier diffusion length exhibits a thermally activated increase with the energy of 74 ± 5 meV. Electron beam irradiation also causes the diffusion length increase with the activation energy of 247 ± 10 meV, likely related to $Sb_{Zn}-2V_{Zn}$ acceptor-complex. © *2011 American Institute of Physics*. [doi:10.1063/1.3530732]

Due to their fundamental properties—wide-band gap of 3.37 eV, high breakdown strength, and large exciton binding energy (60 meV)—ZnO has attracted a lot of interest for potential applications in optoelectronic devices.[1–3] Availability of ZnO material in the shape of nanorods (nanowires) presents an additional opportunity for novel solid-state electronics. Diffusion of minority carriers in ZnO is technologically important, as this property defines performance of p-n junctions and other bipolar devices, including photovoltaic ones.[4,5]

We have previously reported electron beam induced current (EBIC) measurements of minority carrier diffusion length, L, in n- and p-type ZnO epitaxial layers, as well as EBIC profiling of ZnO p-n homojunctions.[6–9] It has been found that L can be significantly affected by temperature (both in n- and p-ZnO) and electron injection (in p-type material). In this paper, we report the impact of temperature and electron beam irradiation on minority carrier transport in p-type ZnO nanowires.

The ZnO nanowire layers, studied in this work were grown using a thermal scientific quartz tube furnace system. Zinc source was placed in the center of the quartz tube, while Sb_2O_3 powder was put 5 cm away from the source, which was in sequence 10 cm away from the undoped ZnO film grown on sapphire substrate by plasma assisted molecular beam epitaxy. The furnace was flown continuously by nitrogen while whole system was heated up to 650 °C with a temperature ramp rate of about 30 °C/min. After the desired temperature was reached, an argon/oxygen (1000:5) mixture was introduced into the quartz tube for ZnO nanowire growth during 30 min. Part of the ZnO film and nanowires was covered by Ag contact, as shown in Fig. 1. Electrical transport properties of ZnO nanowires were obtained using Field Effect Transistor (FET) measurements. Standard photolithography techniques were used to define the micro-contacts onto the nanowires. Hole concentration of 4.5×10^{17} to 2.5×10^{18} cm^{-3} was extracted. The carrier mobility was determined to be 0.005 to 0.03 cm^2/(Vs). It should be noted that the mobility value here is actually the low bound limit of the real mobility, since the non-ohmic contacts between the metal and nanowire may bring large series resistance.

In this paper, EBIC technique was employed for minority carrier diffusion length measurements. This technique relies on generation of nonequilibrium carriers in semiconductor under electron beam irradiation with their consequent separation by the built-in field of p-n junction or Schottky barrier. While majority carriers are swept away from the region of built-in field localization, the minority ones are collected due to this field and, therefore, contribute to the electric current, which is, in fact, the EBIC. By measuring the EBIC current dependence on the distance from the p-n junction, the minority carrier diffusion length can be directly extracted from the EBIC line-scan[10] using Eq. (1) (see below). In this work, we measured the minority carrier diffusion length in Sb-doped ZnO nanowire layers under various temperatures. The measurements were carried out on the

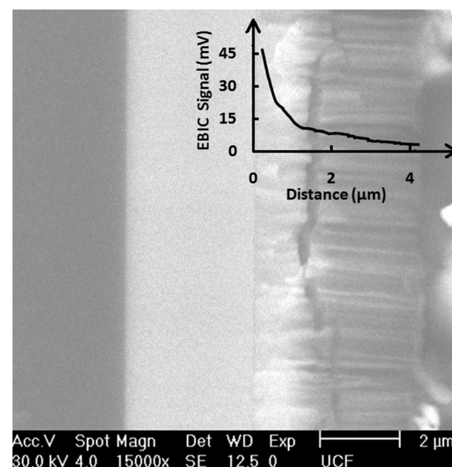

FIG. 1. Secondary electron image of the sample cross-section taken perpendicular to the growth plane. From left to right: sapphire substrate; epitaxial n-ZnO; p-ZnO (nanowire layer); and Ag-epoxy layer (used for a contact). A crack, visible in ZnO nanowire layer, is due to cleavage. A crack-free region was selected for EBIC measurements. Superimposed: exponential decay of EBIC signal vs the beam-to-barrier distance.

a)Electronic mail: chernyak@physics.ucf.edu.

 © 2011 American Institute of Physics

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

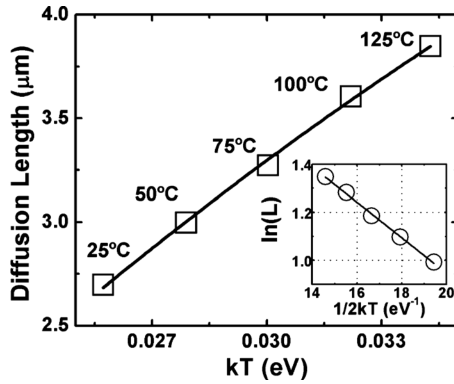

FIG. 2. Dependence of diffusion length on temperature in the nanowire p-ZnO layer. Inset: Arrhenius plot for L vs T dependence resulting in the activation energy of 74 meV.

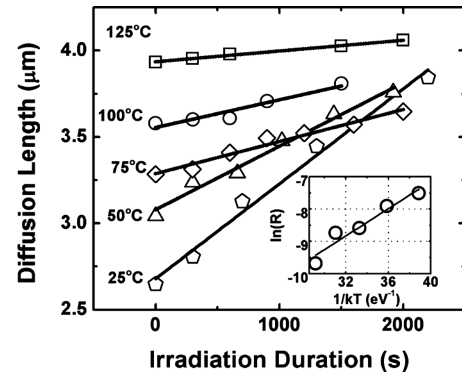

FIG. 3. Linear dependence of the diffusion length on the electron beam irradiation duration under various temperatures. The rates, R, of irradiation-induced increase in L for each temperature is obtained from the slope. Inset: Arrhenius plot for R vs T dependence resulting in the activation energy of 247 meV.

samples cleaved perpendicular to the plane of growth (see Fig. 1), and the EBIC signal was recorded within the nanowire layers, in the direction toward the top sample surface, starting from the interface between the underlying n-ZnO and p-ZnO nanowire films (space-charge region of the p-n junction was thus used for minority and majority carrier separation). In such a way, a diffusion of minority carriers along the nanowires was probed. An average nanowire diameter was found to be around 100 nm.

All experiments were carried out *in situ* in a Philips XL30 scanning electron microscope (SEM) under the accelerating voltage of 30 kV. After the initial 24 s line-scan, EBIC measurement, and extraction of diffusion length, the electron beam irradiation was continued by repeating the line-scan over the same location for up to 2000 s. The sample temperature was adjusted from 25 to 125 °C with 25 °C increment using an external temperature controller (Gatan), with a new area irradiated by electron beam at each temperature.

Before investigating the dependence of L on the duration of electron beam irradiation, it is necessary to first determine the temperature, T, impact on minority carrier diffusion length. The EBIC signal within the nanowire layer, shown in Fig. 1, exhibits an exponential decay versus distance from the p-n junction interface. The Eq. (1) was used to extract L from the EBIC line-scan

$$I = Ad^{\alpha} \exp\left(-\frac{d}{L}\right), \qquad (1)$$

where I is the EBIC signal, A is a constant, d is the beam-to-junction distance, L is the diffusion length. The coefficient α, responsible for recombination mechanism, was taken equal to $-1/2$.[10] By carrying out EBIC measurements at different temperatures and using Eq. (1), the data plot in Fig. 2 was obtained. One can see from Fig. 2 the value of L increasing exponentially with temperature as follows:

$$L = L_0 \exp\left(-\frac{E_A}{2kT}\right), \qquad (2)$$

where L_0 is a scaling factor, k is Boltzmann constant, E_A is the thermal activation energy of 74 ± 5 meV (obtained from the Arrhenius plot in the inset of Fig. 2). The latter parameter likely represents carrier delocalization energy and determines the increase in the diffusion length due to the reduction in recombination efficiency.[6,10]

Continuous irradiation of the sample by the SEM electron beam was also shown to result in an increase in the minority carrier diffusion length. As was previously explained, the irradiation was performed at several temperatures, with the diffusion length showing a linear trend (observed in Fig. 3). This irradiation-induced increase in L suggests a similar origin to that of the thermally induced increase: the nonequilibrium electrons created by the electron beam are trapped by the neutral acceptor levels, and this, in turn, prohibits the path of recombination via these levels, thus reducing the recombination rate and finally leading to longer lifetime of electrons in the conduction band. As excitation proceeds, the concentration of neutral levels goes down and the diffusion length steadily rises (as we have shown in Ref. 6, the increase in L saturates with time, but this is not shown in Fig. 3).

It can also be seen from Fig. 3 that the rate R of the diffusion length increase is reduced with increasing temperature. This occurs when the carriers gain sufficient energy to escape from the trap. Therefore, the increase in the diffusion length caused by trapping is neutralized due to the release of trapped electrons. As the temperature is raised, the energy of electrons increases, which leads to a larger probability of escaping the trap. As a result, the irradiation-induced growth of the diffusion length is weakened. The influence of electron irradiation and temperature on the rate R, as discussed above, can be quantified by the following equation:[11]

$$R = R_0 \exp\left(\frac{E_{\text{injection}}}{kT}\right) \exp\left(-\frac{E_A}{2kT}\right) M, \qquad (3)$$

where R_0 is a scaling factor; k is Boltzmann constant; E_A is the thermal activation energy determined from the above-mentioned temperature-dependent L measurements (~74 meV); $E_{\text{injection}}$ is the activation energy for the electron injection-induced effect. Accounting for rate, R, at various temperatures, which can be obtained from the dependences of L on electron irradiation duration in Fig. 3, $E_{\text{injection}}$ can be calculated from Eq. (3) using a linear fitting of $ln(R)$ versus

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

$1/kT$, as shown in the inset of Fig. 3. We found $E_{injection}$ to be about 247 ± 10 meV. This is in good agreement with the work done by Xiu *et al.*[2] and Limpijumnong *et al.*,[12] which suggests that the level responsible for the increase in L is a $Sb_{Zn}-2V_{Zn}$ acceptor-complex, though this match of results doesn't guarantee the absolute certainty of the statement. It is worth noticing that the dependence of the acceptor activation energy on the concentration of majority carriers has not been put into consideration. Also, when the electron beam hits the sample, the area of effect includes multiple nanowires (up to 20; because of the accelerating voltage of 30 kV), therefore, the result we obtain is, in fact, an average over several nanowires. Other possible native defects, such as, for example, Zn interstitial or Zn vacancy, are not likely to be involved because their energy levels are far too large as compared with the data we have observed.[13] Similarly, the Sb-related defects, such as substitutional defect and single vacancy complex, $Sb_{Zn}-V_{Zn}$, have the reported activation energies of amounts ten times larger than our own results.[12]

In sum, the activation energies for the temperature- and electron irradiation-induced increase in the minority carrier diffusion length were studied in *p*-type, Sb-doped ZnO nanowires. By comparing the values of activation energy, a $Sb_{Zn}-2V_{Zn}$ acceptor-complex is identified as the possible origin for carrier trapping, leading us to believe it is responsible for the observed electron injection effect. It is also worth mentioning that the diffusion length of minority carriers in *p*-type ZnO nanowires is several times larger than that in the epitaxial p-ZnO:Sb layers.[6] This on the one hand indicates a good quality of the nanowire layers, and on the other hand opens up an avenue for a potential use of these layers in bipolar devices.

The authors would like to thank the National Science Foundation (ECCS Grant No. 0900971) and the U.S.-Israel Binational Science Foundation (Grant No. 2008328) for financial support.

[1] F. G. Chen, Z. Z. Ye, W. Z. Xu, B. H. Zhao, L. P. Zhu, and J. G. Lv, J. Cryst. Growth **281**, 458 (2005).
[2] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, J. L. Liu, and W. P. Beyermann, Appl. Phys. Lett. **87**, 152101 (2005).
[3] T. Aoki, Y. Shimizu, A. Miyake, A. Nakamura, Y. Nakanishi, and Y. Hatanaka, Phys. Status Solidi B **229**, 911 (2002).
[4] Y. W. Heo, K. Ip, S. J. Pearton, and D. P. Norton, Phys. Status Solidi A **201**, 1500 (2004).
[5] V. Vaithianathan, B. T. Lee, and S. S. Kim, J. Appl. Phys. **98**, 043519 (2005).
[6] O. Lopatiuk-Tirpak, F. X. Xiu, J. L. Liu, S. Jang, F. Ren, S. J. Pearton, K. Gartsman, Y. Feldman, A. Osinsky, P. Chow, and L. Chernyak, J. Appl. Phys. **100**, 086101 (2006).
[7] L. Chernyak, C. Schwarz, E. Flitsiyan, S. Chu, J. L. Liu, and K. Gartsman, Appl. Phys. Lett. **92**, 102106 (2008).
[8] O. Lopatiuk, L. Chernyak, A. Osinsky, J. Q. Xie, and P. P. Chow, Appl. Phys. Lett. **87**, 162103 (2005).
[9] O. Lopatiuk-Tirpak, L. Chernyak, L. J. Mandalapu, Z. Yang, J. L. Liu, K. Gartsman, Y. Feldman, and Z. Dashevsky, Appl. Phys. Lett. **89**, 142114 (2006).
[10] Y. Lin, E. Flitsyian, L. Chernyak, T. Malinauskas, R. Aleksiejunas, K. Jarasiunas, W. Lim, S. J. Pearton, and K. Gartsman, Appl. Phys. Lett. **95**, 092101 (2009).
[11] O. Lopatiuk, L. Chernyak, A. Osinsky, and J. Q. Xie, Appl. Phys. Lett. **87**, 214110 (2005).
[12] S. Limpijumnong, S. B. Zhang, S. H. Wei, and C. H. Park, Phys. Rev. Lett. **92**, 155504 (2004).
[13] B. Lin, Z. Fu, and Y. Jia, Appl. Phys. Lett. **79**, 943 (2001).

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp