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Electron beam induced current profiling of ZnO *p-n* homojunctions

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Variable temperature electron beam induced current technique was employed for the profiling of ZnO *p-n* homojunctions and the extraction of minority electron diffusion length values in the Sb-doped *p*-type ZnO region. A thermally induced increase for diffusion length of minority electrons was determined to have an activation energy of ~ 145 meV. The latter parameter likely represents carrier delocalization energy and determines the increase of the diffusion length due to the reduction in recombination efficiency. © 2008 American Institute of Physics. [DOI: 10.1063/1.2896613]

Until recently, *p*-type doping of ZnO has been a major challenge for the implementation of bipolar devices. Light emitting diodes (LEDs) with ZnO active region have been successfully demonstrated, however, utilizing *p*-AlGaIn,¹ *p*-SiC,² *p*-diamond,³ as well as *p*-AlGaIn/*p*-GaIn heterostructure^{4,5} for hole emitters. Due to chemical and crystallographic differences between ZnO and AlGaIn (SiC or diamond), the formation of defects at the heterointerface can negatively impact optical and electrical properties. Therefore, devices formed from the heterostructures are expected to be inferior to all ZnO-based devices.

With *p*-type doping of ZnO becoming robust, it is very likely that minority carrier (bipolar) devices such as LEDs, laser diodes, and transparent *p-n* junctions can be achieved in the near future.^{6–8} In such devices, a diffusion length of minority carriers is one of the critical parameters defining their performance as it is closely related to their carrier lifetime (hence, radiative recombination intensity—LED's figure of merit) and charge collection efficiency (crucial for *p-n* junction photovoltaic detectors).⁹ Since, due to its wide band gap (3.3 eV at room temperature), ZnO-based devices show promise for applications at high temperatures, the impact of latter parameter on minority carrier transport is of primary importance. In this paper, we present results of variable temperature electron beam induced current (EBIC) measurements of minority electron diffusion length (*L*) in the *p*-type region of ZnO *p-n* homojunction and propose a possible mechanism for *L* increase with temperature.

ZnO *p-n* junctions were grown by molecular-beam epitaxy, as described in Ref. 10. The homojunction was formed by growing a 425 nm *n*-type ZnO:Ga layer on highly resistive (200 Ω cm) *p*-Si substrate, followed by a 425 nm *p*-type ZnO:Sb layer. Device structures were processed using standard photolithography techniques,⁸ and its device schematic is shown in Fig. 1(a). Au/NiO and Au/Ti Ohmic contacts were formed on *p*-ZnO and *n*-ZnO, respectively. Hall effect measurements showed that Ga-doped ZnO layer had an electron concentration, mobility, and resistivity of 2.8×10^{19} cm⁻³, 8.7 cm² V⁻¹ s⁻¹, 0.02 Ω cm, respectively. The Hall effect measurements were carried out on a *n*-type layer after the top *p* layer [see Fig. 1(a)] was etched off. Therefore,

surface roughness due to etching and Si-substrate effect may impact the obtained values of carrier concentration and carrier mobility in *n*-ZnO. In addition, very large density of ionized donors in *n*-ZnO may cause stronger impurity scattering in the *n* layer and, as a result, lower carrier mobility. Electrical properties of *p*-ZnO cannot be reliably obtained by Hall effect measurements due to the impact from *n*-ZnO layer underneath. Nevertheless, the *p*-type behavior of Sb-doped ZnO was confirmed from diode characteristics. Figure 1(b) shows a typical current-voltage (*I-V*) curve of ZnO *p-n* junction diode in semilogarithmic scale. From Fig. 1(b), the turn-on voltage has been determined to be more than 3.4 V. It should be noted that although *n*⁺-*n*⁻ junctions may also exhibit rectifying characteristics, their turn-on voltage would be normally less than 1.7 V assuming good Ohmic contacts. Thus, it is confirmed that the diode under test is a *p-n* rather than a *n*⁺-*n*⁻ junction.

Minority carrier diffusion length measurements were conducted on the structures which were cleaved perpendicular to the growth plane (cf. Figs. 1 and 2) *in situ* in Philips XL30 scanning electron microscope under a 30 kV electron beam accelerating voltage using the EBIC method. EBIC signal line scans were recorded using homemade software, Stanford Research System low noise current amplifier and a Keithley 2000 digital multimeter, employed as digitizer. Detailed description of the EBIC technique can be found elsewhere¹¹ (and references therein). Note that due to an “in-

FIG. 1. (a) Architecture of ZnO *p-n* homojunction. Metal thickness for contact layers are as follows: Au/NiO, 300/30 nm; Au/Ti, 150/30 nm. ZnO *p*- and *n*-epitaxial layers are 425 nm thick each. Si substrate (shown not to scale) is *p* type with resistivity of ~ 200 Ω cm. (b) *I-V* curve for ZnO *p-n* junction at room temperature.

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FIG. 2. Secondary electron image of device structure cleaved perpendicular to the growth plane and the superimposed EBIC line scan. The image in this figure is rotated 90° counterclockwise relative to the Fig. 1(a).

finite" sample depth in the direction perpendicular to the plain of view (cf. Figs. 1 and 2), a relatively large ($\sim 1.5 \mu\text{m}$) electron range (penetration depth) in ZnO under the above-referenced accelerating voltage does not affect the accuracy of the measurements. For temperature-dependent EBIC measurements, the sample temperature was varied *in situ* from 25 to 125 °C using a specially designed hot stage and an external temperature controller (Gatan). At each temperature, the EBIC measurements were conducted at seven to ten different locations and the mean and standard deviation values for minority carrier diffusion length were calculated from the EBIC line scan (see Fig. 2). While the EBIC signal in *p*-ZnO layer exhibits an exponential decay to the left from the *p*-*n* junction interface, the electron beam induced current in the *n*-ZnO layer increases with scanning electron microscopy electron beam moving to the right of the *p*-*n* junction toward Si substrate (ideally the EBIC signal should decay to zero at *n*-ZnO/Si interface). The latter increase is related to the additional nonequilibrium electron collection from the substrate. Although the Ohmic contacts to *p*- and *n*-ZnO layers are used for EBIC measurements, the electrons from Si substrate, due to their very long diffusion length ($\sim 100 \mu\text{m}$), are swept by the built-in field of the space charge region at *n*-ZnO/Si interface (this region is predominantly located in the highly resistive Si substrate) and are collected at the contact to *n*-ZnO layer, thus, contributing to the EBIC signal and making determination of minority carrier diffusion length in *n*-ZnO impossible under the present configuration. On the contrary, a pronounced exponential decay of the EBIC signal in *p*-ZnO layer allows extraction of minority carrier diffusion length from the EBIC line scan.¹¹

Figure 3 shows the dependence of mean value for electron diffusion length in *p*-ZnO layer on temperature. As it can be seen, the value of L increases exponentially as the temperature is raised. This behavior is common to many semiconductors^{11,12} and is modeled by the following relationship:

$$L = L_0 \exp\left(-\frac{\Delta E_{A,T}}{2kT}\right), \quad (1)$$

where L_0 is a scaling factor, k is Boltzmann constant, and $\Delta E_{A,T}$ is the thermal activation energy. The latter parameter likely represents carrier delocalization energy and determines

FIG. 3. Diffusion length (mean values) of minority electrons as a function of temperature (open circles) and the fit with Eq. (1) (solid line). Standard deviations of mean L values range from 4 to 8 nm for the measurement temperatures. Inset: Arrhenius plot of the same data yielding activation energy of 145 ± 10 meV.

the increase of the diffusion length due to the reduction in recombination efficiency.¹³ Earlier cathodoluminescence studies on ZnO:Sb epitaxial layers had shown that the recombination route of nonequilibrium carriers involves transitions to a deep, neutral acceptor level (e, A^0).¹³ An increase in the temperature of the sample leads to a higher ionization fraction of the acceptors, reducing the concentration of A^0 and thus inhibiting the recombination rate. Lower recombination rate translates directly to greater lifetime of minority electrons in the conduction band (cf. Ref. 13) and, consequently, to greater diffusion length, since $L = (D\tau)^{1/2}$, with D being the diffusivity of the carriers. From the Arrhenius plot shown in the inset of Fig. 3, the value of $\Delta E_{A,T}$ was determined to be 145 ± 10 meV and is in reasonable agreement with the activation energy of temperature-induced lifetime increase obtained by us in Ref. 13 from the temperature-dependent cathodoluminescence measurements. The latter increase was attributed to a $\text{Sb}_{\text{Zn}}-2V_{\text{Zn}}$ complex, theoretically predicted by Limpijumrong *et al.*¹⁴ to have the activation energy of about 160 meV. It should be also noted that the involvement of other Sb-related defects is highly unlikely. The substitutional defect (Sb_{O}) as well as the single-vacancy complex ($\text{Sb}_{\text{Zn}}-V_{\text{Zn}}$) are predicted to have ionization energies about an order of magnitude greater than those obtained experimentally, while other defects can also be ruled out based on their electrical behavior and/or high formation energies.¹⁴

In summary, temperature-dependent EBIC measurements allowed us to estimate the activation energy for the thermally induced increase of the minority carrier diffusion length in *p*-type, Sb-doped ZnO epitaxial layer within a ZnO *p*-*n* homojunction. Based on the value of the activation energy, the phenomenon is suggested to occur due to thermal ionization of Sb-related acceptor level, which is likely a $\text{Sb}_{\text{Zn}}-2V_{\text{Zn}}$ complex.

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