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Influence of electron injection on the photoresponse of ZnO homojunction diodes

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Forward bias electron injection into the *p* side of a *p*-*n* homojunction was shown to result in an improved response of the ZnO photodiodes. Injection of about 25 C of charge yielded a nearly 2.5-fold increase of photocurrent at 350 nm. This improvement was correlated with the increase of the diffusion length of minority electrons in *p*-type ZnO:Sb as determined by electron beam induced current measurements. It is suggested that the increase of the diffusion length is related to the carrier trapping on nonionized acceptor levels. © *2006 American Institute of Physics*.
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ZnO has long been described as a superb candidate for blue and UV optoelectronic devices. In practice, however, there are many challenges that must be overcome before the potential of this semiconductor is fully realized and the reliability of ZnO-based devices reaches sufficient levels for use in commercial applications. Vigorous research efforts are currently being applied to find a method of doping that would consistently yield stable *p*-type conductivity in ZnO.

Advances in *p*-type doping pave the way to the development of all-ZnO-based bipolar devices. Several methods of fabricating ZnO homojunctions have been described in literature.[1–4] While all-ZnO-based devices are in principle superior to those employing heterojunctions, mostly because of the absence of interface-related defects, the majority of the homojunction devices reported so far have been plagued by poor performance characteristics, such as high leakage currents, low breakdown voltages, or poor rectifying behavior.

Recently, some of the authors of this work reported a reliable *p*-type doping method using Sb,[5] which allowed to produce ZnO homojunctions with good electrical and optical properties.[6] While this finding indicates that ZnO technology is maturing rapidly and commercial-quality devices are likely to be available in the near future, the performance of these devices remains fundamentally limited by the transport properties of the minority carriers. Due to the direct band gap of ZnO semiconductor, its minority carrier diffusion length is generally several orders of magnitude lower than that in indirect band gap materials such as silicon or germanium. This has negative implications on the performance of bipolar devices, such as *p*-*n* junction photodetectors, since diffusion length determines their quantum efficiency.[7]

Earlier, we demonstrated that irradiation of ZnO by low energy electron beam of a scanning electron microscope (SEM) results in a marked increase of minority carrier diffusion length.[8,9] In this letter, we report that similar increase may be attained not only by electron irradiation of the material but also by solid-state electron injection into the *p* side of a ZnO *p*-*n* homojunction under forward bias. More importantly, we demonstrate that the increase of minority electron diffusion length results in a significant improvement of *p*-*n* junction's response to UV radiation in the near-band-edge (NBE) region, thus illustrating the practical application of the electron injection effect.

ZnO *p*-*n* junctions were grown by molecular-beam epitaxy according to the procedure described in Ref. 6. A ZnO:Sb layer was grown on *p*-Si substrate (resistivity $\sim 20\ \Omega$ cm) and was followed by a ZnO:Ga layer to form the *p*-*n* junction. Sb-doped ZnO layer had a hole concentration, mobility, and resistivity of 1×10^{16} cm^{-3}, 10 cm^2 V^{-1} s^{-1}, and 6 Ω cm, respectively, while the Ga-doped layer had an electron concentration, mobility, and resistivity of 1×10^{18} cm^{-3}, 6 cm^2 V^{-1} s^{-1}, and 0.9 Ω cm, respectively. The schematic of the device is shown in the inset of Fig. 1.

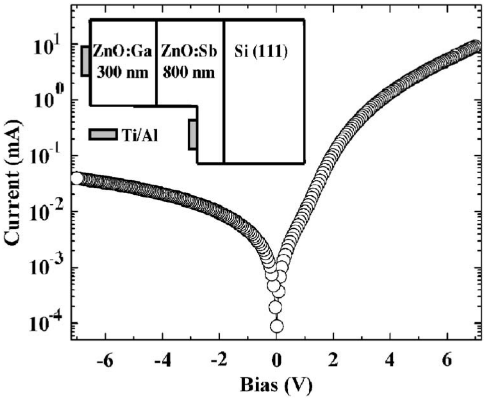

FIG. 1. Dark *I*-*V* curve of a ZnO:Ga/ZnO:Sb homojunction. Absolute value of current is plotted. Inset: Cross-sectional view of the diode. Shaded rectangles represent Ti/Al contacts.

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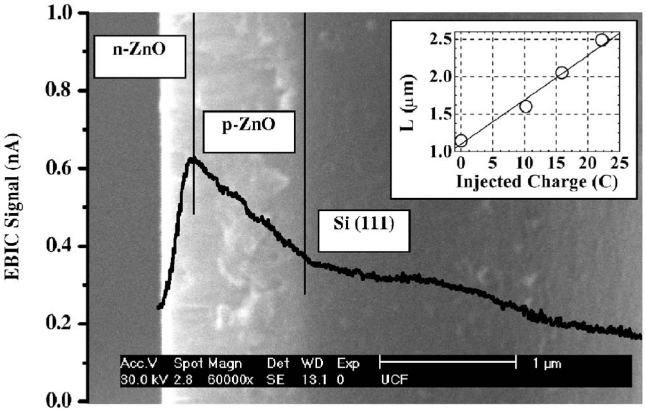

FIG. 2. SEM micrograph showing the cross section of the device. Superimposed is the EBIC line scan, where the peak indicates the position of the *p-n* junction. The scale for the magnitude of the EBIC signal is shown on the left of the micrograph. Inset: Increase of the electron diffusion length in *p*-ZnO:Sb layer as a function of injected charge (open circles) and the linear fit.

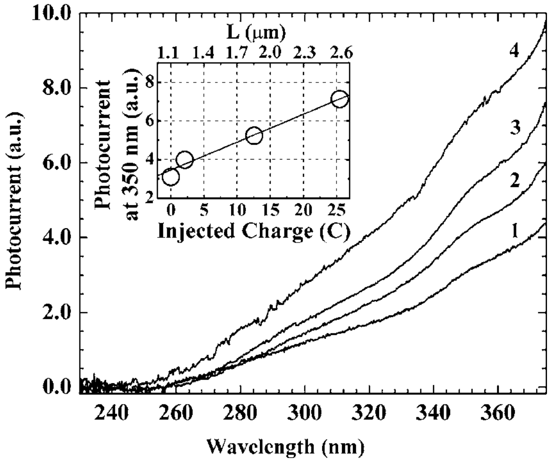

FIG. 3. Photocurrent spectra of a ZnO homojunction photodiode after different injection intervals. Spectrum 1 corresponds to the preinjection state, spectrum 2 to 2.1 C injected, spectrum 3 to 12.6 C injected, and spectrum 4 to 25.5 C injected. Inset: Photocurrent at 350 nm as a function of injected charge (open circles) and the linear fit. The values of *L* are calculated based on the fit of the data in the inset of Fig. 2.

All experiments were carried out at room temperature. Solid-state electron injection into ZnO:Sb was achieved by applying forward bias (~5–10 V) to the *p-n* junction using a Hewlett-Packard 4145A semiconductor parameter analyzer. Forward bias resulted in currents ranging from 7 to 48 mA applied for the duration of about 1500 s, in 300 or 600 s increments, with total injected charge of approximately 25 C. The typical *I-V* curve is shown in Fig. 1. Note that electron injection did not contribute to device degradation as indicated by leakage current measurements. We also note that up to 480 mW dissipated around the forward-biased *p-n* junction caused no significant overheating (less than 15 °C) due to high thermal conductivity of both ZnO and Si substrate ($\sim 1\ \mathrm{W\,cm^{-1}\,K^{-1}}$) and since during the bias application the sample was in contact with a large aluminum sample stage.

Minority carrier diffusion length *L* was determined on *p-n* junction structures, cleaved perpendicular to the growth plane (see Fig. 2), using electron beam induced current (EBIC) method.[8] EBIC measurements and forward bias electron injection were carried out *in situ* in a Philips XL30 SEM using vacuum feedthrough connectors incorporated in the microscope chamber. Accelerating voltage of 30 kV was used, corresponding to electron penetration depth of ~1.5 μm. Following initial determination of *L* from EBIC line-scan measurement, additional measurements of diffusion length were performed after each interval of forward bias electron injection. To avoid influence of electron irradiation on diffusion length,[8,9] electron beam was turned off while external bias was applied. Note that although under EBIC line-scan measurement the sample is subjected to a small amount of electron irradiation, the duration of the scan (~12 s) is negligible compared to the about 1000 s necessary to induce a significant increase of *L* at room temperature (see Refs. 8 and 9).

Spectral photoresponse measurements were carried out at zero bias. To illuminate the *p* side of the *p-n* junction, the measurements were carried out on the cleaved structures (as was the case for EBIC; see Fig. 2). The photoresponse was induced by the light from a Xe lamp that was spectrally resolved with a Jobin-Yvon Triax 320 monochromator. Photocurrent was measured using a Stanford Research Systems SR570 amplifier and a Keithley 2000 multimeter in the voltmeter mode. Specially written LABVIEW-based software was used to record the spectral photoresponse data.

Figure 2 shows the cross-sectional view of the device with EBIC line scan superimposed on the secondary electron (SE) micrograph. The maximum in the induced current signal reveals the physical location of the *p-n* junction. While the interface between Si substrate and *p*-ZnO is easily found due to SE contrast, the location of the junction between *p*-ZnO and *n*-ZnO can only be discerned via the EBIC signal.

EBIC measurements performed periodically after each electron injection interval demonstrated that the diffusion length of minority electrons in *p*-ZnO is significantly increased due to the application of the forward bias to the junction. The inset of Fig. 2 illustrates that the value of *L* is increased by roughly a factor of 2.5 after the injection of about 23 C. As was mentioned above, we observed a similar increase in other ZnO samples after irradiation by the electron beam of the SEM. The effect of electron irradiation on the diffusion length was attributed to the trapping of nonequilibrium electrons on the neutral acceptor levels. As the recombination of the nonequilibrium electron-hole pairs generally involves the levels of neutral acceptors located deep in the band gap, trapping of electrons on these levels inhibits recombination and leads to an increase of carrier lifetime and, consequently, carrier diffusion length.[8,9] Since the presence of Sb has been shown to induce acceptor levels in the band gap far from the valence band edge,[5] it is likely that applying forward bias has similar effects: electrons injected into *p*-ZnO become trapped on the Sb-related levels, preventing the recombination through these levels and thus resulting in the increase of *L*.

Figure 3 displays a series of photocurrent spectra taken after several intervals of electron injection. The photoresponse appears at about 250 nm and increases steadily throughout the UV region. There is a shoulder near 350 nm, corresponding to the effective band gap of ZnO (~3.54 eV),[6] after which the increase becomes less steep around the actual band gap energy (3.39 eV or 365 nm). An increase of the photoresponse beyond 365 nm into the visible region (ideally the response from the device should end there) is mainly due to the collection of photogenerated carriers in the Si substrate.[6]

In the side-illuminated (lateral-collection) configuration shown in Fig. 2, absorption of light and the carrier collection occur in mutually perpendicular planes, such that only the lateral (perpendicular to the direction of excitation) component of the carrier diffusion contributes to the photocurrent. In this configuration, the collection efficiency is improved with increasing diffusion length, because more carriers are able to reach the space-charge region, where they are swept by the built-in field, thus contributing to photocurrent.

For lateral-collection devices, the photocurrent is known to vary linearly with L.[10] The inset of Fig. 3 shows the dependence of the NBE photocurrent on injected charge. The upper scale of the inset gives the values of the diffusion length calculated based on the fit of the data in Fig. 2 in order to demonstrate the linear relationship between the photocurrent and diffusion length. Although EBIC measurements were conducted on a diode different from that used for photocurrent experiments, the inset of Fig. 3 shows that the injection of about 25 C of charge results in an approximately 2.5-fold increase of both L (see inset of Fig. 2) and the photocurrent, in agreement with Ref. 10.

The stability of the injection-induced change was monitored at room temperature over a period of several days, during which the diffusion length of electrons in p-ZnO persisted at the same elevated level as at the end of the last injection interval. Additional experiments are under way to understand the dynamics and mechanism of L relaxation after electron injection. Note that the diffusion length of minority holes in n-type ZnO (which was determined to be on the order of several hundred nanometers) was not affected by forward bias application. This further supports the idea that a significant concentration of acceptor levels is necessary to achieve the increase of L, and therefore is consistent with earlier observations that electron irradiation has no effect on L in undoped ZnO with intrinsic n-type conductivity.[8]

In summary, electron injection into the p side of a ZnO p-n junction via forward bias application results in a marked improvement of response for the photodiodes without degradation of their rectifying characteristics. This improvement was shown to be caused by the increase of the diffusion length of minority electrons. It is suggested that this phenomenon is related to the presence of nonionized acceptor levels, as no increase of diffusion length in n-ZnO was observed.

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