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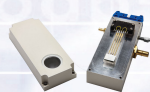
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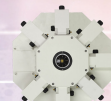
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## Influence of electron injection on the temporal response of ZnO homojunction photodiodes

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The effects of solid-state electron injection on the peak amplitude and decay time of photosignal in a ZnO-based homojunction UV photodiode were studied using temporal photoresponse measurements under femtosecond pulses of 355 nm radiation. The injection of about 50 C of charge, carried out by applying forward bias to the junction, resulted in a nearly twofold increase of the peak photoresponse and a corresponding increase of the decay constant. Both observations are shown to be a consequence of electron trapping. The long-term stability of the induced changes is also discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2764559]

Although ZnO is currently considered a material with great potential for blue and UV electro-optics, there are a number of challenges, particularly that of achieving sufficiently high and reproducible *p*-type doping necessary for homojunction-based devices. Recently, stable *p*-type conductivity with hole concentrations up to  $1 \times 10^{18} \text{ cm}^{-3}$  was demonstrated in ZnO:Sb,<sup>1</sup> allowing to produce a ZnO-based homojunction photodiode with good optical and electrical characteristics.<sup>2</sup> Note that although Sb is a large size-mismatched dopant and therefore is not a likely candidate for a good substitutional acceptor, evidence suggests that the dominant acceptor species in ZnO:Sb is an antimony complex ( $\text{Sb}_{\text{Zn}}-2V_{\text{Zn}}$ ) with a relatively low activation energy of about 160 meV.<sup>3,4</sup>

Small minority carrier diffusion length, common to all direct band gap semiconductors, is another drawback negatively affecting device collection efficiency. Our previous studies have shown that this parameter in ZnO:Sb can be improved by inducing electron trapping [either by irradiation with the electron beam of a scanning electron microscope (SEM) or by solid-state electron injection], which results in the increase of nonequilibrium carrier lifetime.<sup>5</sup> Furthermore, this increase was demonstrated to yield a considerable improvement of spectral photoresponse of a ZnO-based homojunction diode.<sup>6</sup>

On the other hand, carrier trapping on deep levels is often associated with persistent photoconductivity, which is an undesirable characteristic in photodetectors. Temporal photoresponse studies presented in this letter were used to explore the correlation between trapping-induced amplitude increase and the decay time of photoresponse.

ZnO *p-n* junctions were grown by molecular-beam epitaxy as described in Ref. 2. The homojunction was formed by growing an 800 nm ZnO:Sb layer on *p*-Si substrate, followed by a 300 nm ZnO:Ga layer.<sup>6</sup> The SEM micrograph

and schematic of the device are shown in Fig. 1. Sb-doped ZnO layer had a hole concentration, mobility, and resistivity of  $1 \times 10^{16} \text{ cm}^{-3}$ ,  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $6 \text{ } \Omega \text{ cm}$ , respectively, while the Ga-doped layer had an electron concentration, mobility, and resistivity of  $1 \times 10^{18} \text{ cm}^{-3}$ ,  $6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $0.9 \text{ } \Omega \text{ cm}$ , respectively. The Hall effect measurements were carried out on a reference *p*-type sample grown under the same conditions as the *p* layer of the diode, while the Hall data for the *n* layer were obtained directly from the top *n* layer of the diode. It is noted that the mobility for the *p* layer is larger than that for the *n* layer. This is likely due to the contribution from the Si substrate to the Hall mobility of holes measured in *p*-ZnO and, similarly, to the contribution of the *p* layer to the observed Hall mobility of electrons in top *n*-ZnO layer. In addition, two orders of magnitude larger density of ionized donors in *n*-ZnO, as compared to that of ionized acceptors in *p*-ZnO, may cause stronger impurity scattering in the *n* layer.

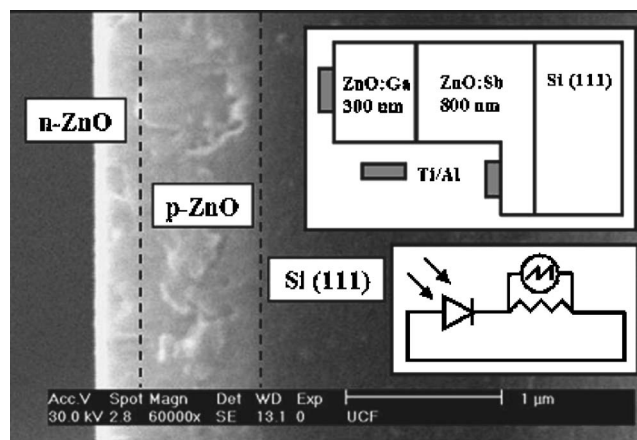


FIG. 1. Scanning electron micrograph of a cross section of a ZnO homojunction diode. The dashed lines indicate the approximate location of the interfaces. Top inset: structure of the investigated device. Bottom inset: schematic of the circuit used in the photoresponse measurements.

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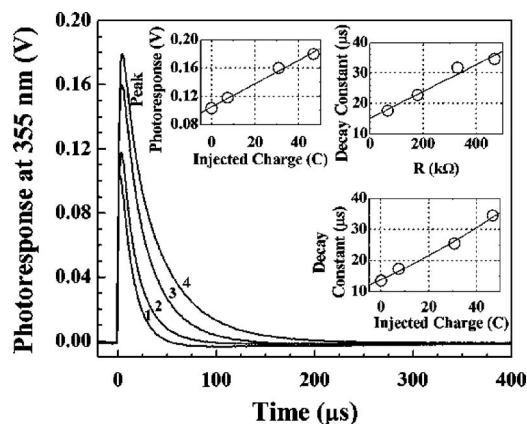


FIG. 2. Temporal photoresponse after several intervals of electron injection: trace 1 corresponds to the preinjection wave form, and traces 2, 3, and 4 to 7.5, 31, and 47 C of the total injected charge. External resistor of about 0.5 M $\Omega$  was used in these measurements. Top left inset: peak amplitude as a function of total injected charge and the linear fit. Top right inset: dependence of the apparent decay constant as a function of external resistance of measuring circuitry. Bottom inset: quadratic increase of the photoresponse decay constant with total injected charge.

Temporal photoresponse of the junction was measured at zero bias. A TOPAS optical parametric generator (Light Conversion), pumped by a Clark-MXR CPA-2010 series laser, was used to generate pulses of 355 nm light with 120 fs temporal width full width at half maximum, a repetition rate of 1 kHz, and average pulse energy density of about 25  $\mu\text{J}/\text{cm}^2$ . The wave form of the photoresponse was recorded by a fast-sampling oscilloscope (Tektronix TDS 680C) with a maximum sampling rate of  $5 \times 10^9$  samples/s. The lower inset of Fig. 1 shows the diagram of the experimental setup. An external resistor (470 k $\Omega$ ) was connected in series with the measured device and in parallel with the oscilloscope. Electron injection into the *p* side of the homojunction was carried out by applying forward bias to the device in 300–600 s increments, resulting in currents from 20 to 40 mA, with total injected charge of about 50 C. Temporal photoresponse was recorded after each injection interval.

Sequential measurements of photoresponse confirmed that its amplitude increases systematically after each electron injection interval, as shown in Fig. 2. A linear dependence of peak photoresponse on total injected charge is shown in the top left inset of Fig. 2. Note that in a lateral-collection device, such as that shown in Fig. 1 (with the cross section of the device being exposed to laser beam excitation), photocurrent is expected to vary linearly with minority carrier diffusion length ( $L$ ).<sup>7</sup> Such dependence is therefore in agreement with earlier studies on a similar device, which demonstrated the increase of  $L$  in direct proportion to the injected charge.<sup>6</sup>

The injection-induced increase of  $L$  likely occurs due to trapping of the nonequilibrium electrons on deep levels that are part of the carrier recombination pathway. As the concentration of filled traps grows with continuous excitation, carrier recombination rate is lowered, leading to the increase of minority electron lifetime in the conduction band and, consequently, diffusion length.<sup>5</sup>

It is also apparent from Fig. 2 that the photoresponse decay time is strongly dependent on the injection level. The exponential nature of the decay is characteristic of trap-

assisted recombination; therefore, it is likely that the slower decay of photosignal at higher injection levels is related to the decrease in the concentration of available recombination centers.

Fitting the data in Fig. 2 to a first-order exponential decay function with a decay time constant  $\tau_d$  allowed to determine the dependence of latter parameter on total injected charge. This dependence is shown in the lower inset of Fig. 2, suggesting a quadratic relation between the nonequilibrium carrier lifetime and injection level (carrier lifetime also is known to decay exponentially<sup>8</sup> and, therefore, is proportional to the decay constant). Since  $L=(D\tau)^{1/2}$  (where  $D$  is the carrier diffusivity and  $\tau$  is the lifetime of photogenerated carriers), the quadratic growth of  $\tau_d$  under electron injection is consistent with the linear increase of the diffusion length [observed earlier by electron beam induced current measurements<sup>5</sup>], as well as with the linear dependence of peak photoresponse on injected charge shown in the upper inset of Fig. 2. Finally, it is insightful to note that the improvement of peak photoresponse by about 180% is accompanied by an increase in the square root of decay time by the same amount (<5% difference), confirming that both observations are different manifestations of the same phenomenon, namely, of the injection-induced increase in nonequilibrium minority carrier (electron) lifetime in the conduction band. In contrast, the rise time of photosignal (on the order of a few microseconds) was found not to be affected by electron injection.

The measured decay time of the photodetector response is determined by the decay constant of the external measuring circuitry and by that of the device itself. For a circuit with a detector (resistance  $r$  and capacitance  $C$ ) in series with an external resistor with resistance  $R$  (see lower inset of Fig. 1), the overall decay constant is  $(R+r)C$ . The intrinsic decay constant of the detector ( $rC$ ) can therefore be estimated by monitoring the apparent decay time as a function of external resistance and extrapolating the obtained dependence to zero (Fig. 2, top right inset). This analysis was applied to the photodetector following the last injection interval (see trace 4 in Fig. 2). While the improvement of photoresponse due to electron injection results in the increase of the overall decay constant to about 35  $\mu\text{s}$  (for the given measurement conditions), the fundamental limit of the device is considerably shorter—about 15  $\mu\text{s}$ . Moreover, since this value is dictated by the series resistance of the device, technological improvements (e.g., lowering the resistance of ohmic contacts by increasing majority carrier concentrations) can yield even better response times.

Partial relaxation of the electron injection-induced changes was observed by measuring the temporal photoresponse of the improved device one week following the injection. The comparison of the preinjection photoresponse with those acquired immediately after and one week following the treatment is shown in Fig. 3. The long-term stability of the improvement is noteworthy, as it has favorable implications for the possible use of electron injection in commercial devices. Furthermore, it is consistent with earlier studies of the kinetics of minority carrier diffusion length in ZnO:Sb under electron irradiation.<sup>5</sup>

In summary, a series of temporal photoresponse measurements demonstrated that the amplitude of the photosignal of a ZnO-based homojunction detector can be significantly improved by solid-state electron injection. This

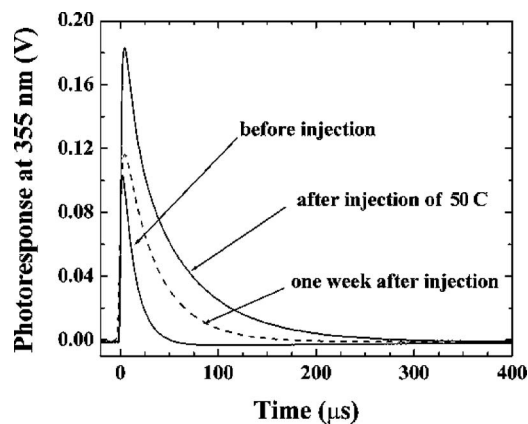


FIG. 3. Temporal photoresponse before, immediately after, and one week following the electron injection.

improvement was correlated with increased carrier lifetime and minority carrier diffusion length and is likely attributed to the charging of deep electron traps. The growth of carrier lifetime was also found to manifest itself through the increased photosignal decay time. Finally, the peak photoresponse of the improved device was shown to persist at the elevated level for at least several days.

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