Observation of a large gate-controlled persistent photoconduction in single crystal ZnO at room temperature

Shahnewaz Mondal[a)] and A. K. Raychaudhuri
Department of Materials Science, S. N. Bose National Centre for Basic Sciences, Block-JD, Sector-3, Salt Lake, Kolkata 700 098, India

Gate-controlled enhanced photoconductivity at room temperature is reported in single crystal ZnO using moderate bias and band gap illumination. A substantial part of the enhanced photocurrent is retained over a long time as a persistent photocurrent when the illumination is removed but the gate voltage (applied with a polymer-electrolyte gate) is retained. The current on the removal of illumination shows a stretched exponential decay with time constants more than few hundreds of seconds. An explanation based on change in charge state of oxygen vacancy has been proposed.

ZnO (with wurzite structure) as an UV optoelectronic material has attracted wide attention in recent years due to its wide band gap (~3.37 eV) and a large excitonic binding energy (~60 meV).[1] In addition to the emission near band edge, ZnO also shows defect related emissions in the visible range that has been a topic of considerable research.[2]

In this paper, we report a phenomenon where we observe a gate-controlled large enhancement of the photocurrent and an enhanced persistent photocurrent (on UV illumination) in single crystal ZnO at room temperatures. The gate voltage was applied using polymer-electrolyte gate that makes an electric double layer (EDL) gate. While persistent photoconduction using band gap illumination has been reported in single crystalline as well as nanostructures of ZnO,[3,4] there has been no report where a gate has been used to have a rather large control on the photoconductivity as well as the persistent photoconductivity. Similarly, it has been observed that charge accumulation in excess of 10^{14} cm^{-2} leading to enhancement of electrical conductivity can be achieved in single crystalline ZnO substrates with EDL gate.[5] However, the effect of illumination on such gate induced enhancement of conductivity has not been reported. The present report couples these two effects innovatively and shows that the coupling (of illumination and gate effect) leads to an enhancement of conductivity that is more than the summation of the enhancement by the individual effects. In the following, we discuss the experiment and main observations and propose a likely origin for such an effect.

The EDL-FET (EDL-field effect transistor) devices used in this work [schematic in inset of Fig. 1(a)] were formed on highly resistive bulk ZnO single crystal substrates ($\rho \geq 5 \times 10^3$ Ω-cm at room temperature) grown by the hydrothermal method with oxygen-terminated faces. The crystal used has activation energy ~0.3 eV obtained from resistivity versus temperature curve (not shown). The structural quality of the crystal and orientation were tested by x-ray diffraction. The crystal shows broad visible emission in blue-green [inset of Fig. 1(b)] measured at 10 K using a He-Cd Laser illumination. The EDL gate was fabricated on the substrate using a mixture of polyethylene oxide (PEO) and $LiClO_4$. A platinum (Pt) wire connected to the electrolyte was used to apply the bias. Cr/Au (20 nm/100 nm) contact pads were used as source (s) and drain (d). The electrodes give symmetric nearly linear I_{ds}-V_{ds} curves for the gate bias used here. All electrical and photoresponse characterizations were carried out in a microprobe station with the temperature controlled around 303 K (±0.1 K) with an UV lamp ($\lambda_{peak} \approx 365$ nm).

Figure 1 shows typical dc transfer characteristics [I_{ds}-V_g] of the device in the dark and under UV illumination for a fixed V_{ds}. The I_{ON}/I_{OFF} ratio of the device increased from ~1.6 in the dark to ~2.2 under illumination with similar changes in the transconductance.

An important and noteworthy feature of the observed phenomena is that the enhancement of the I_{ds} under illumination along with a gate applied is more than the summation of the enhancement by the individual effects. The enhancement of I_{ds} due to illumination (for $V_g = 0$ V) is ≈30%. The maximum increase in I_{ds} in the dark due to gate effect is ≈55% with $V_g \sim 9$ V. However, with both illumination and gate voltage ($V_g = 9$ V), the enhancement of $I_{ds} \rightarrow 200\%$.

The enhancement of the device current on illumination is due to its enhancement of the photoconductance. This has

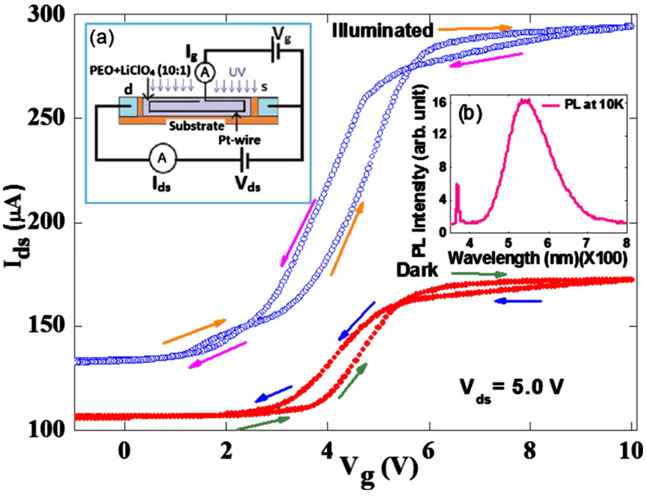

FIG. 1. (Color online) Dependence of the source-drain current (I_{ds}) on the gate voltage with and without illumination. The inset (a) shows the schematic of the EDL gate device used and the inset (b) shows PL of the single crystal used at 10 K.

[a)] Electronic mail: shahnewaz@bose.res.in

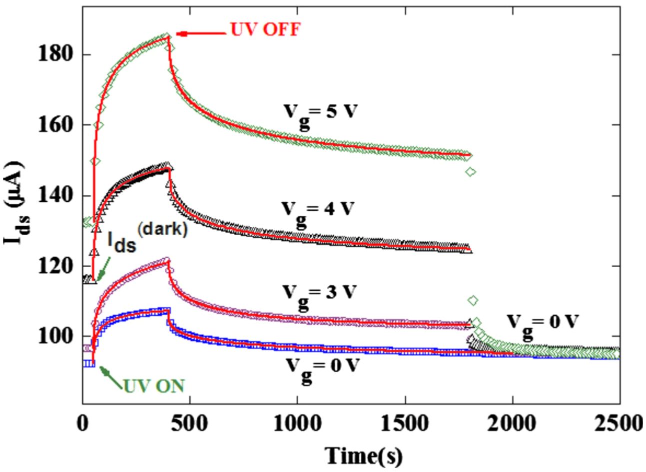

FIG. 2. (Color online) The photocurrent, persistent photocurrent (PPC), and the gate control of the PPC. The photocurrent data with and without illumination have been taken with a series of V_g from 0 to 9 V. Note that the photocurrent is maintained at a high value when V_g is high and the illumination is turned off.

been checked by a direct four-probe measurement of conductance where the conductance showed enhancement of similar magnitude on illumination as that seen in the I_{ds}.

The enhancement of the photocurrent on application of a simultaneous bias can be seen in Fig. 2. For a given V_g, the current increases when the illumination is turned on. The enhancement is also a function of the gate voltage. The rise of the photocurrent on illumination follows the relation

$$I_{ds}(t) = I_{ds}(\mathrm{dark}) + I_{PC}[1 - e^{-(t/\tau_r)^{\beta_r}}], \tag{1}$$

where I_{ds}(dark) is the dark current, I_{PC} is the photocurrent, τ_r is the time constant, and β_r is the stretched exponential. I_{PC} increases substantially as a function of the gate voltage and is shown in Fig. 3. For change of V_g from 0 to 5 V, the photocurrent increases by a factor of more than 3. [The I_{ds}(dark) changes by nearly 50% for the same change in V_g.] The typical time constants $\tau_r \approx 40-60$ s and $\beta_r \approx 0.40-0.45$. Interestingly, the change in sequence (i.e., apply the illumination and then the V_g) leads to nearly the same effect. When the illumination is turned off, the photocurrent relaxes following a stretched exponential relation

$$I_{ds}(t') = I_{ds}^{\infty} + (I_{\max} - I_{ds}^{\infty})e^{-(t'/\tau_d)^{\beta_d}}, \tag{2}$$

where $I_{ds}(t')$ is the device current at a time t' and I_{ds}^{∞} is the limiting drain-source current after a long time after illumination has been turned off. [In Eq. (2), time t' is measured after the illumination is turned off.] $I_{\max}$ is the maximum I_{ds} under illumination. The solid lines through the data are fits to Eq. (2). For $V_g=0$, typical constants for the decay curves τ_d and β_d are around 300 s and 0.34, respectively. The lower value of β_d compared to β_r and substantially larger values for τ_d show that the decay after the illumination is off occurs over a long time. For $V_g=0$, there is a long decay of the photocurrent but the value of the persistent photocurrent I_{PPC} $[\equiv I_{ds}^{\infty} - I_{ds}(\mathrm{dark})] \approx 0$.

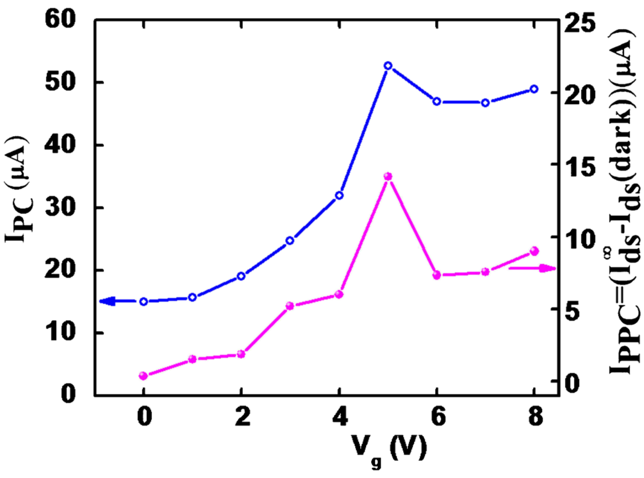

FIG. 3. (Color online) Dependence of the maximum photocurrent I_{PC} and the persistent photocurrent I_{PPC} $[=I^{\infty}_{ds} - I_{ds}(\mathrm{dark})]$ as a function of the gate voltage V_g.

Application of a gate not only enhances the photocurrent I_{PC} as shown before, it also enhances the I_{PPC} as can be seen in Fig. 2. After the illumination is turned off, the gate voltage V_g was kept on for a long time to record the time evolution of the current I_{ds} (t') with no illumination. I_{ds} (t') shows a slow relaxation. For different V_g, the decay curves [Eq. (2)] have $\beta_d \approx 0.33-0.36$ and typical $\tau_d \approx 200-300$ s which show the long tails associated with the relaxation. After some time when the V_g is set to 0 V, I_{ds} immediately goes down and reaches the value for $V_g=0$. Thus, the V_g not only enhances the photocurrent, but a good part of the current is retained when the gate voltage is on but the illumination is turned off. The retention of the large photocurrent even after the illumination is turned off is thus linked to a finite V_g.

I_{PC} as well as I_{PPC} $[\equiv I_{ds}^{\infty} - I_{ds}(\mathrm{dark})]$ show a very clear dependence on the gate voltage as shown in Fig. 3. They both increase as V_g is enhanced until a gate voltage ~ 5 V and then, after a shallow maximum around that voltage, it settles to a constant value. The maximum of ratio I_{PPC}/I_{PC} can be nearly 0.3 occurring for $V_g \sim 5$ V. I_{PC} with a finite gate voltage can be enhanced by a factor of 3.

Though the main purpose of the paper is to report the observed effect, below we provide a plausible explanation. The electronic transport of ZnO is often governed by native defects such as oxygen vacancies or zinc interstitials which act like donors (some times deep donors)[6] and make the material n-type. These defects also give rise to photoluminescence (PL) at the green-blue region when excited by photons of energy more than the band gap.[2,7] The observed phenomena of enhancement of photocurrent and persistent photocurrent can be explained using the likely presence of oxygen vacancy as the native defects and the fact that it can exist in different charge states such as neutral (V_O), singly (V^{+}_{O}), and doubly charged (V^{++}_{O}) states. The control of the filling of these levels in ZnO nanoparticles by control of external parameters and accompanied control of the visible emission from these levels have been established experimentally.[8] The proposed explanation is based on a recent model of persistent photoconductivity of ZnO based on oxygen vacancy.[9] According to this model, the neutral V_O creates a defect localized state in the band gap and does not contribute to the conduction process. On illumination, the neutral defects can get ionized and the charged defect states have higher energy which is in resonance with the conduction band. The electrons promoted to this state can relax to a perturbed host state near the conduction band edge. This process makes the crystal more n-type and conducting. The change in the ionization state also involves change in Zn positions around the oxygen vacancy. For instance, the Zn–Zn nearest neighbor distance ~0.3 nm and the distance for the doubly ionized state becomes ~0.37 nm. The involvement of the lattice relaxation makes the perturbed host state metastable. The reversal from the $V^{++}{}_{O}$ state to the V_O state, when the illumination is turned off, will involve lattice relaxation through a kinetic barrier (~0.2 eV). This leads to a photocurrent relaxation with a long tail of decay and this gives rise to the persistent photocurrent.[9]

We observe substantial enhancement of photocurrent on application of gate along with the illumination. The phenomenon of EDL gate-controlled enhancement of conductivity arises from the enhancement of carrier density in bulk crystals.[5] Though the observation has been made on a bulk crystal, it actually occurs over a small distance scale of the order of few tens of nanometers or even less close to the gate. However, there is no accepted model for the origin of the observed enhancement of the carrier density. We propose that a positive voltage applied at the gate creates negative charge in the conduction band from field induced ionization of the neutral V_O center, which leads to the creation of more charged vacancy. Such ionization has been observed in other semiconductors for applied fields exceeding 10^7 V/cm and has been explained as due to a phonon assisted tunneling process that is enhanced on application of field.[10] In EDL-FET, the field gradient for a given bias occurs almost at few atom levels and thus, even a small bias can produce a high field gradient. When the illumination is accompanied by the gate voltage, even more $V^{++}{}_{O}$ are created leading to a large enhancement of the negative carriers in the conduction band and enhanced photocurrent. The slow relaxation of the photocurrent on the removal of the illumination arises because of potential barrier attached to the relaxation of the charged vacancies to neutral state as stated before. The presence of the applied gate bias helps retain the charge in the ionized state and hinders the process of relaxation even when the illumination is removed and thus enhances the persistent photoconductivity. It is noted that the retention of excess carrier near the ZnO surface, needed for the persistent photoconductivity, can also occur due to band bending at the semiconductor-electrolyte interface that can lead to the accumulation of carriers in the interface region. The removal of the gate will relax these carriers, leading to reduction of the photoconductivity. The above model, though tentative, provides a qualitative understanding of the observed phenomena of gate-controlled enhanced photocurrent on illumination and also the enhancement of the persistent photocurrent. Physical mechanisms other than those stated above can also lead to these effects. For instance, defects such as Li^+ can be present in these semiconductors (due to the growth process) and the electrolyte can electrochemically dope the gate region with Li^+. However, more experimentation is needed to ascertain the exact origin of the observed phenomena.

To conclude, we have observed gate-controlled enhanced photoconductivity and persistent photoconductivity at room temperature in single crystal ZnO using an EDL gate structure. The photocurrent gets enhanced significantly by application of a moderate gate voltage and a substantial part of the enhanced photocurrent is retained over a long time as the persistent photocurrent when the illumination is removed but the applied gate voltage is retained. The observed phenomenon has been explained with a model that is based on change in charge state of the oxygen vacancy, which is accompanied with a structural relaxation.

One of us (S. Mondal) thanks CSIR for a fellowship. The authors want to thank Professor S.K. Ray of IIT, Kharagpur for the PL measurement at low temperatures.

[1] Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).
[2] K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, Appl. Phys. Lett. **68**, 403 (1996).
[3] A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, E. A. Kozhukhova, S. J. Pearton, D. P. Norton, A. Osinsky, and A. Dabiran, J. Electron. Mater. **35**, 663 (2006).
[4] P. Liu, G. She, Z. Liao, Y. Wang, Z. Wang, W. Shi, X. Zhang, S. Lee, and D. Chen, Appl. Phys. Lett. **94**, 063120 (2009).
[5] H. Yuan, H. Shimotani, A. Tsukazaki, A. Ohtomo, M. Kawasaki, and Y. Iwasa, Adv. Funct. Mater. **19**, 1046 (2009).
[6] H. von Wenckstern, S. Weinhold, G. Biehne, R. Pickenhain, H. Schmidt, H. Hochmuth, and M. Grundmann, *Advances in Solid State Physics* (Springer, Berlin, 2005), Vol. 45, p. 263.
[7] A. van Dijken, E. A. Meulenkamp, D. Vanmaekelbergh, and A. Meijerink, J. Lumin. **87–89**, 454 (2000).
[8] M. Ghosh and A. K. Raychaudhuri, Appl. Phys. Lett. **93**, 123113 (2008).
[9] S. Lany and A. Zunger, Phys. Rev. B **72**, 035215 (2005); **81**, 113201 (2010).
[10] S. Makram-Ebeid and M. Lannoo, Phys. Rev. Lett. **48**, 1281 (1982).