Research Article

Persistent Photoconductivity in ZnO Nanowires in Different Atmospheres

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We investigated the photoconductivity of single ZnO nanowire device as a function of the surrounding atmosphere, considering the comparison between reduced pressure, inert gas environments, and air. We show that after UV excitation the photocurrent persists for hours, in particular in vacuum, nitrogen, and argon. In the presence of oxygen, the photodecay rate is initially fast but then becomes considerably slower, resulting in a long persisting photo-conductivity tail. Our proposed model explains the persistence of the photoconductivity (PPC) in terms of band bending at the surface of the nanowires, which is related to the trapping of electrons from the conduction band.

1. Introduction

The possibility of integration of semiconducting nanowires into electronic devices improved considerably during the last decade, giving rise to a dramatic enhancement of the application range in nanoelectronics and optoelectronics, gas, and biosensing and photodetection [1–3]. Due to the small size of the diameter (around 100 nm), surface related effects can significantly influence the electronic and optical properties of the nanowires. For example, observations of enhanced UV sensitivity of ZnO nanowires compared to corresponding thin films have been reported [4, 5] and attributed to the increased surface-to-volume ratio. For this reason, ZnO has attracted attention as a promising material for fabrication of UV photodetectors based on nanowires. The ease of the growth technique and the intrinsic n-type conductivity properties are further important elements, which make the implementation of ZnO nanowires as a block component for UV photodetector devices convenient.

However, the major drawback for photodetection applications with ZnO is the strong persistence of the photoconductivity (PPC) after UV excitation, which prevents a fast recovery of the dark current. This effect has been observed not only in nanowires [6–8] but also in thin film and bulk

[9, 10]. There are some controversial opinions about the origin of the persistence of the photoconductivity; some authors attributed it to the slow trapping of photoexcited electrons at surface defects [7, 8, 11], whereas others [12–15] assigned the effect to the presence of metastable conductive states related to bulk oxygen vacancies. Some further studies are therefore necessary in order to clarify the possible origin of this effect.

In this study, we present the dependence of the photoconductivity properties of ZnO nanowires on the surrounding atmosphere, considering in particular the effect of reduced pressure and the presence of inert gases like argon and nitrogen in comparison with air.

2. Experimental

The nanowires used were grown by vapor transport on top of Si substrates enabled by the vapor-liquid-solid method, at a pressure of 100 mbar with a growth temperature of 1050°C. Further details of the growth procedure are described elsewhere [16]. The nanowires were on average 20 μm in length and 200 nm in diameter. They were transferred by mechanical imprinting on clean Si substrate with a SiO_2 top layer of 850 nm thickness. Fifteen pairs of electrodes with separation of 5 μm were defined on the substrate by

FIGURE 1: Scanning electron microscopy (SEM) image (a) shows the electrical connection via gold wire bonding between the device electrodes and the chip carrier; in (b) a close up of the single ZnO nanowire bridging the two electrodes is presented.

UV photolithography, and 10 nm of Ti and 100 nm of Au were deposited by e-beam evaporation. The substrate was then glued to a chip carrier and some selected single ZnO nanowire devices were bonded with a $25\ \mu\text{m}$ gold wire to the electrical pads of the carrier. A typical device is showed in Figure 1. The sample was placed in a sealed chamber and connected to a Source-measure Unit (SMU) Keithley (Model 237) by means the electrical measurements were performed.

A UV LED light source with a central emission around 370 nm and an emission intensity of $10\ \text{mW}/\text{cm}^2$ was used to excite the devices. Electrical measurements were performed under vacuum conditions at 10^{-5} mbar, in nitrogen in air or argon atmosphere (at a pressure of 1 atm). Prior to every measurement the sample was kept in the chamber in dark for at least 24 hours, in order to reach a constant value of the dark current.

3. Results and Discussion

The current voltage (I - V) characteristics of a typical device, shown in Figure 2, are quite symmetric for all environment conditions investigated, indicating good ohmic contacts on both sides. Under UV excitation the current increases by some orders of magnitude, in particular under vacuum. The temporal dependence of the photoconduction increase is illustrated in Figure 3 in more detail: the current rises quickly within the first seconds of UV excitation and afterwards at a slower rate. As can be seen in the linear scaled inset of Figure 3, the photocurrent in nitrogen and argon reaches a

FIGURE 2: Current-voltage (I - V) characteristics of a single ZnO NW device in vacuum and two different inert gas atmospheres. The photosensitivity of the nanowires to UV excitation is clearly shown.

saturation value after two hours of illumination, whereas it does not stop to increase under vacuum conditions.

When the LED is switched off, the photocurrent decays extremely slowly, both in vacuum or inert gas atmospheres, decreasing by less than one order of magnitude in 3 hours,

FIGURE 3: Photo-current increase under UV excitation of a single ZnO nanowire device in vacuum and two different inert gas atmospheres plotted in a logarithmic scale. The linear scaled inset clearly shows that for nitrogen and argon the current saturates after 2 hours, but not in vacuum. All measurements were performed at $V_{ds} = 5$ V.

as shown in Figure 4(a). Only when air is introduced into the chamber the decay rate speeds up drastically. Figure 4(b) shows a magnification of the photocurrent decay immediately after letting air into the chamber. It is clearly seen that the initial drop is extremely fast, but afterwards the current decreases much more slowly.

The experimental results suggest that the presence of oxygen molecules in the surrounding atmosphere plays the major role in the photoresponse properties of ZnO nanowires, as nitrogen alone does not have such a significant effect. It is well known that in dark the surface of ZnO is always partially covered by adsorbed oxygen, which tends to bond in particular at surface oxygen vacancies sites [17, 18] and to trap electrons from the conduction band. This process results in the formation of an upward band bending at the surface and a corresponding depletion region [19]. The conductivity of our device in dark is thus determined by the nondepleted core of the nanowire.

As illustrated in Figure 5(a), when the UV light is switched on, the initial band bending separates quickly the photogenerated carriers, sweeping the holes toward the surface and keeping the electrons in the inner part of the nanowires. Due to this separation, the probability of carrier recombination is relatively low and the lifetime of the electrons in the conduction band becomes higher than in the bulk-case within the flat band approximation (around 100 ps) [20]. The photoconductivity rises thus initially extremely fast, as clearly shown in Figure 3. After a few minutes, the current continues to increase, but at slower rate, in particular in argon and nitrogen atmospheres. To interpret this result, we assume that the photogenerated holes localized at the surface can induce desorption of the oxygen from the surface of the nanowire, by recombining with the trapped electrons. As a result of this process the

concentration of electrons previously trapped at the surface reduces and correspondingly the height of the upward band bending lowers, as it is illustrated in Figure 5(b). Since this energy barrier decreases, the probability that electrons from the conduction band can overcome it and reach the surface becomes higher. Therefore, some of them can get trapped again, favoring the process of oxygen re-adsorption. After a while an equilibrium between the desorption and re-adsorption rate will be reached, and the photocurrent saturates. In vacuum the rate of the photocurrent increase remains relatively high, because the desorbed oxygen is continuously pumped away and there is consequently a low probability of readsorption, which is not the case for the nitrogen and argon atmospheres. The measurements in these gas atmospheres are performed under static conditions (and not under continuous gas flow) and therefore the probability of oxygen readsorption according to the proposed mechanism is higher. This is the reason why the saturation of the current is observed in argon and in nitrogen but not under vacuum conditions.

When the UV light is switched off, the current photocurrent starts to decay slowly as a result of the trapping of electrons from the conduction band due to the readsorption of the few oxygen molecules present in the atmospheres investigated. As soon as air is introduced into the chamber, the oxygen concentration in the surrounding of the nanowire increases suddenly, inducing immediately a faster trapping of electrons and a corresponding fast drop of the photocurrent. As a consequence, after a while the height of the band bending rises again, and therefore the probability of further electron trapping lowers, resulting in a decrease of the photodecay rate (as evident in Figure 4(b)).

4. Conclusions

In conclusion, we investigated the effect of different atmospheres on the photoconductivity properties of single ZnO nanowire devices, and we observed that in presence of inert gases (nitrogen and argon) and under reduced pressure the photocurrent tends to persist for a long time after UV excitation. In the presence of oxygen, the photocurrent decay is initially faster but presents anyway a long tail of persistent photoconductivity. Oxygen is supposed to adsorb on the ZnO surface, trapping electrons from the conduction band. This is the main process, which leads to the initial drop of the photo-current. After a while, the accumulation of negative charge at the surface determines an increase of the height of an upward surface band bending, and this prevents a further trapping of electrons from the conduction band. As a result, the photoconductivity of the nanowire tends to persist and only after hours the original value of the dark conductivity is reached. Our results are in agreement with other studies, which attribute the persistence of the photoconductivity to surface properties of the nanowire [7, 8, 11]. Due to the strong dependence of the effect on the presence of atmospheric oxygen, the long decay of the photo-current cannot be induced by bulk defects of ZnO.

FIGURE 4: Photocurrent decay of a single ZnO nanowire device after removing the UV excitation, in vacuum and inert gas atmospheres; (b) shows a magnification of (a), when air is introduced into the chamber. The decay rate increases considerably.

FIGURE 5: (a) The photogenerated electrons and holes in a ZnO nanowire are separated due to the built-in electric field cause by the band bending. The life-time of the pair is thus increased and the photoconductivity rises fast; (b) as the excitation process continues, the energy barrier at the surface lowers and oxygen molecules can reabsorb. This leads to an equilibrium between adsorption and reabsorption and as a consequence the photo-current saturates. In both figures, the color of photogenerated-carriers is blue, whereas other electrons in the conduction band determine the intrinsic n-type conductivity of ZnO and are indicated in black. The green arrows describe the retrapping of electrons and the oxygen reabsorption.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] C. M. Lieber, “Nanoscale science and technology: building a big future from small things,” *MRS Bulletin*, vol. 28, no. 7, pp. 486–491, 2003.
- [2] F. Patolsky, G. Zheng, and C. M. Lieber, “Nanowire-based biosensors,” *Analytical Chemistry*, vol. 78, no. 13, pp. 4260–4269, 2006.
- [3] D. K. Ferry, “Materials science: nanowires in nanoelectronics,” *Science*, vol. 319, no. 5863, pp. 579–580, 2008.

- [4] C. Soci, A. Zhang, B. Xiang et al., “ZnO nanowire UV photodetectors with high internal gain,” *Nano Letters*, vol. 7, no. 4, pp. 1003–1009, 2007.
- [5] J. D. Prades, R. Jimenez-Diaz, F. Hernandez-Ramirez et al., “Toward a systematic understanding of photodetectors based on individual metal oxide nanowires,” *Journal of Physical Chemistry C*, vol. 112, no. 37, pp. 14639–14644, 2008.
- [6] K. Keem, H. Kim, G.-T. Kim et al., “Photocurrent in ZnO nanowires grown from Au electrodes,” *Applied Physics Letters*, vol. 84, no. 22, pp. 4376–4378, 2004.
- [7] J. D. Prades, F. Hernandez-Ramirez, R. Jimenez-Diaz et al., “The effects of electron-hole separation on the photoconductivity of individual metal oxide nanowires,” *Nanotechnology*, vol. 19, no. 46, Article ID 465501, 2008.
- [8] J. Bao, I. Shalish, Z. Su et al., “Photoinduced oxygen release and persistent photoconductivity in ZnO nanowires,” *Nanoscale Research Letters*, vol. 6, no. 1, article 404, 2011.
- [9] R. J. Collins and D. G. Thomas, “Photoconduction and surface effects with zinc oxide crystals,” *Physical Review*, vol. 112, no. 2, pp. 388–395, 1958.
- [10] D. A. Melnick, “Zinc oxide photoconduction, an oxygen adsorption process,” *The Journal of Chemical Physics*, vol. 26, no. 5, pp. 1136–1146, 1957.
- [11] P. Gao, Z. Z. Wang, K. H. Liu et al., “Photoconducting response on bending of individual ZnO nanowires,” *Journal of Materials Chemistry*, vol. 19, no. 7, pp. 1002–1005, 2009.
- [12] Y. Wang, Z. Liao, G. She, L. Mu, D. Chen, and W. Shi, “Optical modulation of persistent photoconductivity in ZnO nanowires,” *Applied Physics Letters*, vol. 98, Article ID 203108, 2011.
- [13] S. Lany and A. Zunger, “Anion vacancies as a source of persistent photoconductivity in II-VI and chalcopyrite semiconductors,” *Physical Review B*, vol. 72, Article ID 035215, 2005.
- [14] S. Hullavarad, N. Hullavarad, D. Look, and B. Claflin, “Persistent photoconductivity studies in nanostructured ZnO UV sensors,” *Nanoscale Research Letters*, vol. 4, no. 12, pp. 1421–1427, 2009.
- [15] A. Jannotti and C. G. van de Walle, “Oxygen vacancies in ZnO,” *Applied Physics Letters*, vol. 87, Article ID 122102, 2005.
- [16] C. Borchers, S. Müller, D. Stichtenoth, D. Schwen, and C. Ronning, “Catalyst-nanostructure interaction in the growth of 1-D ZnO nanostructures,” *Journal of Physical Chemistry B*, vol. 110, no. 4, pp. 1656–1660, 2006.
- [17] W. An, X. Wu, and X. C. Zeng, “Adsorption of O₂, H₂, CO, NH₃, and NO₂ on ZnO nanotube: a density functional theory study,” *Journal of Physical Chemistry C*, vol. 112, no. 15, pp. 5747–5755, 2008.
- [18] J. D. Prades, A. Cirera, J. Ramon Morante, and A. Cornet, “Ab initio insights into the visible luminescent properties of ZnO,” *Thin Solid Films*, vol. 515, no. 24, pp. 8670–8673, 2007.
- [19] C. Y. Chen, J. R. D. Retamal, I. W. Wu et al., “Probing surface band bending of surface-engineered metal oxide nanowires,” *ACS Nano*, vol. 6, no. 11, pp. 9366–9372, 2012.
- [20] J. S. Reparaz, F. Güell, M. R. Wagner, A. Hoffmann, A. Cornet, and J. R. Morante, “Size-dependent recombination dynamics in ZnO nanowires,” *Applied Physics Letters*, vol. 96, Article ID 053105, 2010.