ZnO tetrapod Schottky photodiodes

Marcus C. Newton, Steven Firth, and Paul A. Warburton

Citation: Applied Physics Letters **89**, 072104 (2006); doi: 10.1063/1.2335949
View online: http://dx.doi.org/10.1063/1.2335949
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/89/7?ver=pdfcov
Published by the AIP Publishing

ZnO tetrapod Schottky photodiodes

Marcus C. Newton[a)]
Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

Steven Firth
Department of Chemistry, University College London, Gordon Street, London WC1H 0AJ, United Kingdom

Paul A. Warburton
Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

(Received 12 April 2006; accepted 25 June 2006; published online 16 August 2006)

The fabrication of an ultraviolet photodiode employing a single ZnO tetrapod nanocrystal is reported. This diode structure is prepared by depositing W and Pt electrodes to form Ohmic and Schottky contacts, respectively. Dark current-voltage measurements show rectifying behavior. The properties of the metal-semiconductor interface are studied with above and below band gap illumination. It is found that with increasing UV excitation the device converts from a rectifying to an Ohmic behavior. This effect is attributed to a flattening of the energy bands due to the migration of photogenerated carriers within the space charge region at the metal-semiconductor interface.
 [DOI: 10.1063/1.2335949]

The use of zinc oxide in UV optoelectronic devices has attracted considerable interest mainly due to its large exciton binding energy of 60 meV and high thermal and chemical stabilities.[1,2] Photodetectors based on the Schottky junction are desirable due to their ability to operate at high switching speeds. Progress in their development is often limited by the difficulty in reproducibly fabricating high quality rectifying contacts to ZnO films.[3–6] There are, however, a number of recent studies addressing the interfacial properties of ZnO.[4,7,8]

More recently reports have been made on Schottky diodes based on ZnO rods that show photoresponse when subject to UV excitation.[9,10] In this letter we report on the fabrication of a diode structure that employs a single ZnO tetrapod nanocrystal. The results of measurements made to the device are also presented.

ZnO tetrapod (ZnO–T) nanocrystals were synthesised using a chemical vapor transport technique as previously reported.[11–13] Here for brevity we summarize the procedure. A mixture of zinc carbonate powder and graphite powder is placed in a crucible at the central region of a quartz tube furnace. A bare Si ⟨100⟩ substrate is mounted in the downstream region of the quartz tube. Nitrogen carrier gas with an oxygen content of 0.5%–5% is then introduced into the quartz tube at a flow rate of 500 SCCM (SCCM denotes cubic centimeter per minute at STP) while the temperature of the furnace is brought up to 900 °C. After a 15 min reaction period a thin white layer of material is visible on the surface of the substrate.

ZnO tetrapods were released from the substrate by sonication in methanol to form a suspension. This solution was subsequently spun onto an oxidized Si substrate prepatterned with Au electrodes. The samples were then treated for 60 min in oxygen plasma at room temperature in order to fully oxygenate any nonstoichiometric surface defects. Metal contacts were made between the Au electrodes and the three arms of a single ZnO–T on the substrate surface with the aid of a Carl Zeiss 1540 XBeam field emission scanning electron microscope (SEM) equipped with a focused ion beam and gas injection system. Ion beam deposited Pt and W were used for the first and remaining two contacts, respectively. Figure 1 shows a scanning electron micrograph of the device. The tetrapod used in the experiments reported here has limbs of equal length 3.0 μm and cross-sectional dimension of 300 nm across the hexagonal facet. Photoresponse measurements were carried out with a 325 nm He–Cd laser (6 mW) and a 514.5 nm Ar ion laser (10 mW) as excitation sources.

Two terminal dark *I-V* measurements were made successively between each pair of contacts (Fig. 2). It can be seen that the W–ZnO–W *I-V* curve shows Ohmic properties while the W–ZnO–Pt curve exhibits rectification. The second W–ZnO–Pt curve closely matches that of the former and is omitted for clarity. When the effective barrier heights at each of the metal-semiconductor interfaces, as predicted by the Schottky-Mott rule, are considered we expect Pt to form

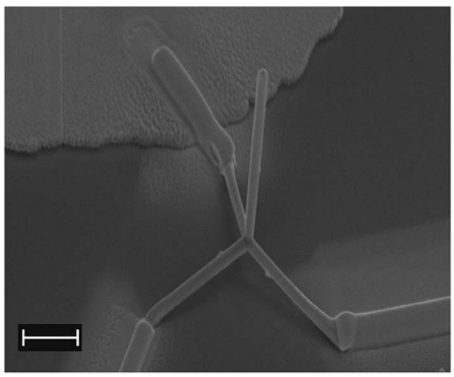

FIG. 1. SEM image of ZnO tetrapod with two W leads and one Pt lead attached (1 μm scale bar).

[a)]Electronic mail: m.newton@ee.ucl.ac.uk

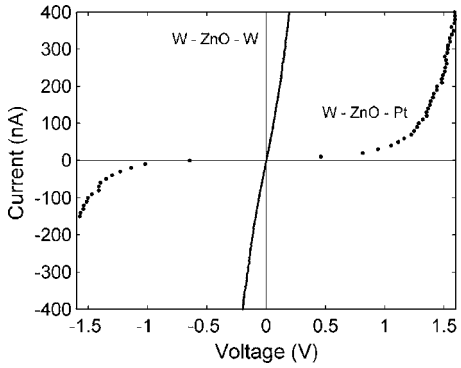

FIG. 2. Room temperature dark *I-V* curves of W–ZnO–W and W–ZnO–Pt junctions.

blocking contacts with a barrier height of ~1.3 eV and W contacts to be Ohmic. Reported barrier heights, however, often deviate quite considerably from this model. Ip *et al.*[14] have observed a barrier height of 0.49 eV for W contacts to ZnO.

The forward bias dark *I-V* data may be fitted to the following equation that describes the thermionic emission of charge over the barrier at the Pt–ZnO interface:

$$J = J_0\left(\exp\left(\frac{e_0 V}{nkT}\right) - 1\right), \tag{1}$$

$$J_0 = A^* T^2 \exp\left(-\frac{e_0 \phi_B}{kT}\right), \tag{2}$$

where $A^* = 4\pi e_0 m^* k^2/h^3$ is the effective Richardson constant, T is the absolute temperature, ϕ_B is the effective barrier height, n is the ideality factor, and $m^* \sim 0.29 m_0$ is the effective electron mass. This fit to the data is shown in Fig. 3 when the junction is strongly forward biased. From the fit a barrier height of 0.43 eV is obtained and is considerably smaller than the previous reports of ~0.89 eV for Pt contact to ZnO films.[5] The ideality factor of 11 that we have obtained is an order of magnitude greater than that of an ideal Schottky diode. It is, however, well known that the presence of defects or contaminants at the metal-semiconductor interface can introduce additional energy states that significantly influence the effective barrier height and ideality factor.[15–17]

Figure 4 shows the *I-V* characteristics measured between Pt and W contacts as a function of UV illumination power density. Increasing the laser power steadily caused the device to vary from rectifying to a more Ohmic behavior. This is further confirmed by the linear increase in current with illumination power density at 1 V in reverse bias as shown in the inset. By assuming that the illumination is uniform over the whole tetrapod we obtain a responsivity of 10.6 A/W. Similar results of Schottky to Ohmic conversion have been reported by Heo *et al.*,[10] and Keem *et al.*[9] for Schottky diodes employing ZnO nanorods. For completeness we performed *I-V* measurements between both W contacts under UV illumination and observed minimal changes in the *I-V* characteristics within the same range of laser powers. Moreover, successive measurements were repeated with an Ar ion 514.5 nm laser at equivalent power densities. No significant deviation from the dark *I-V* curve was observed. The response shown in Fig. 4 therefore cannot be attributed simply to an increase in carrier density in the bulk of the ZnO tetrapod caused by UV photoexcitation. We conclude that the photoresponse of our device is governed by a photoinduced change in the electronic properties of the device at the metal-semiconductor interface.

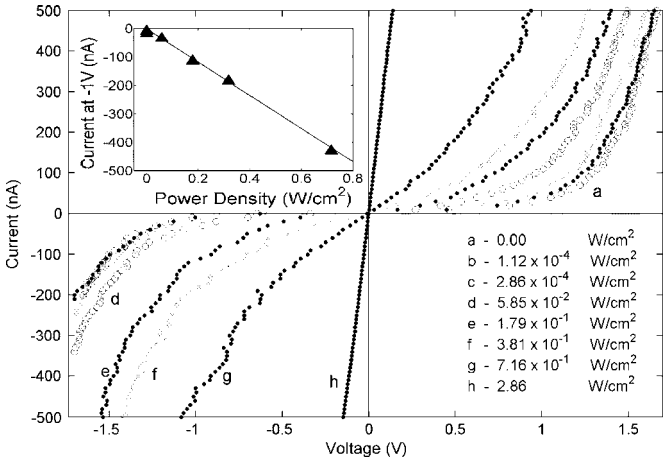

FIG. 4. W–ZnO–Pt current-voltage characteristics under UV illumination.

In Fig. 5 we show the dependence of the effective barrier height at the metal-semiconductor interface on the irradiated power density. Each data point is derived from Fig. 4 using Eq. (1). A rapid reduction in the barrier height is observed as the source is illuminated with increasing laser power density. The effect saturates at high intensity. This saturation arises when the energy bands at the interface have been completely flattened. The resulting barrier height in the flat band condition is therefore understood as the difference in the semiconductor work function and electron affinity, in the absence of

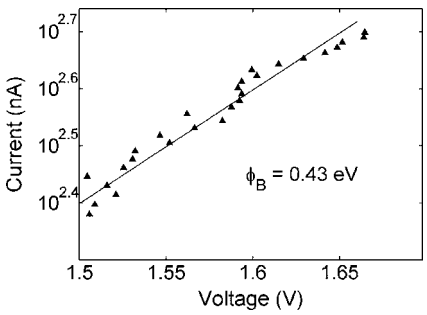

FIG. 3. Dark current-voltage curve of tetrapod diode in forward bias shown with a fit to the data using Eqs. (1) and (2).

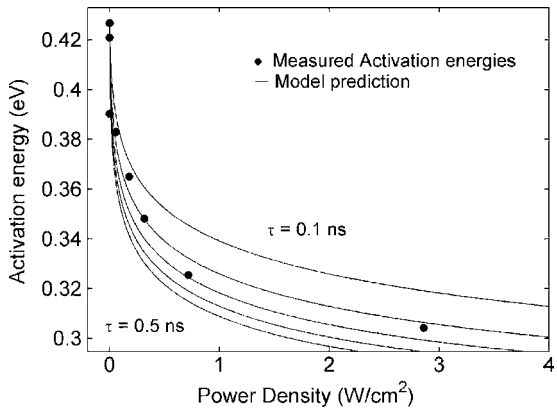

FIG. 5. Activation energy as a function of illumination power density for τ=0.1, 0.2, 0.3, 0.4, and 0.5 ns.

surface states. Using the model outlined below, this is estimated at 0.25 eV.

The illumination induced reduction in barrier height may be understood by considering a simple one-dimensional model describing the distribution of induced charge due to the alignment of energy bands at the metal-semiconductor interface.[16,18] Although a more complete description of semiconductor surface dynamics is made possible through Shockley-Read-Hall statistics this model is found to provide reasonable results.

In this model the fractional increase in electron and hole populations are taken to be spatially constant (flat quasi-Fermi levels approximation), allowing us to define parameters with reference to the thermal carrier concentrations in the bulk. Hence we define normalized photoexcited electron and hole densities,

$$\gamma_n = \frac{n_0 + \Delta n}{n_0}, \tag{3a}$$

$$\gamma_p = \frac{p_0 + \Delta p}{p_0}. \tag{3b}$$

The charge distribution is then given by

$$\rho(z) = e_0\{n_c(1 - \gamma_n \exp(\upsilon)) - p_\upsilon(1 - \gamma_p \exp(-\upsilon))\}, \tag{4}$$

where m is the distance from the metal-semiconductor interface (with $z>0$ in the semiconductor). The density of thermally excited electrons n_c and holes p_υ in the bulk are derived using a conduction and valence band densities of states of 3.7×10^{24} and 3.4×10^{25}, respectively.[19] The normalized potential is given by $\upsilon(z)=e_0\phi(z)/kT$, where $\phi(z)$ is the potential, k is the Boltzmann constant, T is the absolute temperature, and e_0 is the charge on the electron. In the absence of photoillumination Eq. (4) reduces to the standard expression for the charge distribution in the space charge region of a Schottky diode.

Substituting back into the Poisson equation and integrating yields the following space charge distribution at the metal-semiconductor interface:

$$Q_{\mathrm{sc}} = \eta(2\varepsilon_b\varepsilon_0 kT)^{1/2}(n_c\gamma_n(\exp(\upsilon) - 1) - n_c\upsilon + p_\upsilon\gamma_p(\exp(-\upsilon) - 1) + p_\upsilon\upsilon)^{1/2}, \tag{5}$$

$$\eta = \begin{cases} -1, & \upsilon > 0 \\ +1, & \upsilon < 0. \end{cases} \tag{6}$$

Charge neutrality requires that $\Delta n=\Delta p$. The total charge within the space charge region is therefore unaltered by illumination. We may therefore derive the condition for charge neutrality at the surface,

$$p_\upsilon(\exp(-\upsilon_0) - \gamma_p \exp(-\upsilon) - 1 + \gamma_p) - n_c(\gamma_n \exp(\upsilon) - \exp(\upsilon_0) - \gamma_n 1) + (\upsilon - \upsilon_0)(n_c - p_\upsilon) = 0, \tag{7}$$

where υ_0 and υ represent the initial and resulting potentials caused by above band gap illumination at the interface. For a given $\Delta n=\Delta p$ Eq. (7) can be solved self-consistently to obtain $\upsilon(0)$, the normalized potential at the metal-semiconductor interface when illuminated. In order to obtain an estimate of Δn we assume that carriers are uniformly photoexcited in the ZnO up to a depth equal to the photon absorption length d from the surface. Hence Δn is equal to $\tau P/dh\nu$, where P is the irradiated power density, h is Planck's constant, ν is the frequency of the UV photons, and τ is the carrier lifetime. For the 325 nm photons used in this experiment, d is taken as 60 nm.[20]

The results of our model are shown in Fig. 5. The results are plotted for carrier lifetimes τ in the range of 0.1–0.5 ns. In the model the value of the activation energy at zero illumination is a free parameter and is taken as the initial barrier height of 0.43. From the fit to the data we can conclude that band flattening is indeed the photoresponse mechanism in our ZnO nanocrystal Schottky diodes and that the lifetime of excited carriers is in the range of 0.2–0.3 ns, consistent with previous reported measurements on ZnO films.[21,22] For larger power densities (not shown in Fig. 5), the activation energy tends to 0.25 eV, independent of the carrier lifetime. This suggests that the ZnO tetrapod contains deep donors arising from defect states, in agreement with previous measurements carried out for ZnO films.

In conclusion, we have fabricated ZnO tetrapod Schottky UV sensitive photodiodes. We have also shown that the current-voltage characteristics of our device are altered from a rectifying to a more Ohmic behavior under UV illumination. This effect is attributed to a reduction in the Schottky barrier height at the metal-semiconductor interface.

The authors would like to thank Tony Kenyon and Takashi Matsuura for continuing interest with useful discussions and technical input.

[1] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, Nat. Mater. **4**, 42 (2005).
[2] U. Ozgur, Ya Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc, J. Appl. Phys. **98**, 041301 (2005).
[3] Z. L. Wang, X. Y. Kong, Y. Ding, P. Gao, W. L. Hughes, R. Yang, and Y. Zhang, Adv. Funct. Mater. **14**, 943 (2004).
[4] O. Schmidt, P. Kiesel, C. G. Van de Walle, N. M. Johnson, J. Nause, and G. H. Dohler, Jpn. J. Appl. Phys., Part 1 **44**, 7271 (2005).
[5] S. H. Kim, H. K. Kim, and T. Y. Seong, Appl. Phys. Lett. **86**, 112101 (2005).
[6] H. L. Mosbacker, Y. M. Strzhemechny, B. D. White, P. E. Smith, D. C. Look, D. C. Reynolds, C. W. Litton, and L. J. Brillson, Appl. Phys. Lett. **87** 012101 (2005).
[7] Olga Dulub, Ulrike Diebold, and G. Kresse, Phys. Rev. Lett. **90**, 016102 (2003).
[8] W. Monch, Appl. Phys. Lett. **86**, 162101 (2005).
[9] K. Keem, H. Kim, G. T. Kim, J. S. Lee, B. Min, K. Cho, M. Y. Sung, and S. Kim, Appl. Phys. Lett. **84**, 4376 (2004).
[10] Y. W. Heo, L. C. Tien, D. P. Norton, S. J. Pearton, B. S. Kang, F. Ren, and J. R. LaRoche, Appl. Phys. Lett. **85**, 3107 (2004).
[11] M. C. Newton, S. Firth, T. Matsuura, and P. A. Warburton, J. Phys.: Conf. Ser. **26**, 251 (2006).
[12] W. D. Yu, X. M. Li, and X. D. Gao, Chem. Phys. Lett. **390**, 296 (2004).
[13] Z. Chen, Z. W. Shan, M. S. Cao, L. Lu, and S. X. Mao, Nanotechnology **15**, 365 (2004).
[14] K. Ip, B. P. Gila, A. H. Onstine, E. S. Lambers, Y. W. Heo, K. H. Baik, D. P. Norton, S. J. Pearton, S. Kim, J. R. LaRoche, and F. Ren, Appl. Surf. Sci. **236**, 387 (2004).
[15] A. B. McLean, I. M. Dharmadasa, and R. H. Williams, Semicond. Sci. Technol. **1**, 137 (1986).
[16] C. G. B. Garrett and W. H. Brattain, Phys. Rev. **99**, 376 (1955).
[17] W. Monch, *Semiconductor Surfaces and Interfaces* (Springer, Berlin, 2001), p. 67.
[18] D. R. Frankl, Surf. Sci. **3**, 101 (1965).
[19] J. A. Aranovich, D Golmayo, A. L. Fahrenbruch, and R. H. Bube, J. Appl. Phys. **51**, 4260 (1980).
[20] J. F. Muth, R. M. Kolbas, A. K. Sharma, S. Oktyabrsky, and J. Narayan, J. Appl. Phys. **85**, 7884 (1999).
[21] A. Teke, U. Ozgur, S. Dogan, X. Gu, H. Morkoc, B. Nemeth, J. Nause, and H. O. Everitt, Phys. Rev. B **70**, 195207 (2004).
[22] C. K. Sun, S. Z. Sun, K. H. Lin, K. Y. Zhang, H. L. Liu, S. C. Liu, and J. J. Wu, Appl. Phys. Lett. **87**, 023106 (2005).