High-temperature Schottky diode characteristics of bulk ZnO

2007 J. Phys.: Condens. Matter 19 196206

(http://iopscience.iop.org/0953-8984/19/19/196206)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 196206 (8pp) doi:10.1088/0953-8984/19/19/196206

High-temperature Schottky diode characteristics of bulk ZnO

Emre Gür, S Tüzemen[1], Bayram Kılıç and C Coşkun

Department of Physics, Faculty of Arts and Sciences, Atatürk University, 25240 Erzurum, Turkey

E-mail: stuzemen@atauni.edu.tr

Received 7 February 2007, in final form 22 March 2007
Published 18 April 2007
Online at stacks.iop.org/JPhysCM/19/196206

Abstract

Current–voltage (I–V) measurements of Ag/n-ZnO have been carried out at temperatures of 200–500 K in order to understand the temperature dependence of the diode characteristics. Forward-bias I–V analysis results in a Schottky barrier height of 0.82 eV and an ideality factor of 1.55 at room temperature. The barrier height of 0.74 eV and Richardson constant of 0.248 A K^{-2} cm^{-2} were also calculated from the Richardson plot, which shows nearly linear characteristics in the temperature range 240–440 K. From the nk_bT/q versus k_bT/q graph, where n is ideality factor, k_b the Boltzmann constant, T the temperature and q the electronic charge we deduce that thermionic field emission (TFE) is dominant in the charge transport mechanism. At higher sample temperatures (>440 K), a trap-assisted tunnelling mechanism is proposed due to the existence of a deep donor situated at E_c—0.62 eV with 3.3×10^{-15} cm^2 capture cross section observed by both deep-level transient spectroscopy (DLTS) and $\ln I_0$ versus $1/k_bT$ plots. The ideality factor almost remains constant in the temperature range 240–400 K, which shows the stability of the Schottky contact in this temperature range.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Zinc oxide is a II–VI semiconductor compound, with a wide and direct band gap (3.37 eV at room temperature), which has attracted much attention in the last two decades because of its possible use in ultraviolet and blue-range optoelectronic devices, including lasers. The most important property of ZnO is its high exciton binding energy of about 60 meV [1, 2], which gives the opportunity of use in optoelectronics due to its highly efficient excitonic emission. Besides these valuable optoelectronic properties of ZnO, it has superior electronic parameters such as high breakdown voltage, high thermal conductivity [3], high electron saturation velocity [4] and high radiation tolerance [5], which are better than those of the

[1] Author to whom any correspondence should be addressed.

classical semiconductors, such as Si and GaAs, and is also compatible with the wide band gap semiconductors, like SiC and GaN [6]. These parameters are important for high-temperature, high-power electronics which also require high-quality metal–semiconductor Schottky contacts.

Our knowledge of the Schottky contact characteristics of ZnO is very poor, especially regarding its temperature dependence. However, many metals have been reported for use as a ZnO-based Schottky barrier diode (SBD) such as low reactive ones, Ag [7–9], Au [8, 10], Pd [9, 11], Pt [12, 13], which generally result in a Schottky barrier height (SBH) of about 0.6–0.8 eV and an ideality factor of around 1.5 [7–13]. Also SBDs having better contact parameters have been reported by several authors [14–16]; these are generally formed on oxygen-treated surfaces of ZnO. For example, Coppa *et al* [14] reported that O_2/He plasma-treated Au/ZnO SBDs yield an ideality factor of 1.03 and leakage current of 20 pA. The same ideality factor was also reported by Grossner *et al* [15], with an SBH of 0.83 eV for Pd metallization on the oxygen-terminated (0001) face of ZnO. Recently, Allen *et al* [16] measured the ideality factor to be 1.1 and the SBH to be 0.77 eV for a Ag/ZnO SBD produced on the O-polar surface of ZnO. In addition, Nagata *et al* showed that the O-polar face produces a higher barrier height than that of the Zn-polar face of ZnO for Schottky metal Pt/Ru alloys [17].

Even though the progress in ZnO-based contacts has given hope to future studies, there are not any detailed reports on the high-temperature stability of these contacts in the literature. Grossner *et al* [15] showed that the Pd/ZnO SBD was stable in temperature range 130–340 K. Sheng *et al* [18] declared that the ideality factor of Ag/ZnO varied from 1.37 at 265 K to 1.29 at 340 K. von Wenckstern *et al* [11] measured the temperature dependence of the I–V characteristics of Pd/ZnO SBD between 210 and 300 K and reported an increase in SBH with increasing temperature.

In this study, we fabricated ZnO-based SBDs using Ag and Al metals for the Schottky and ohmic contacts, respectively. Temperature-dependent I–V measurements were conducted in the temperature range 200–500 K. We found that the ideality factor varies between 1.30 and 1.60 and the SBH between 0.88 and 0.68 eV in the temperature range 240–400 K where the diode is reasonably stable. From the nk_bT/q versus k_bT/q graph, we deduce that the thermionic field emission (TFE) is dominant in the charge transport mechanism at sample temperatures above 240 K.

2. Experimental details

The Schottky diode was formed onto bulk ZnO (University Wafers). As an ohmic contact material, purified Al (99.99%) was chosen to obtain a low barrier height by considering the high reactivity of Al atoms with chalcogenides (O atom in ZnO). Ohmic contact was fabricated onto the ZnO face, in a Leybold Heraeus turbo molecular pump, in a high vacuum of 10^{-6} Torr. Subsequent annealing was performed at 573 K for 3 min in a N_2 atmosphere. For the Schottky material, on the other hand, Ag (99.99%) metal was used to form a relatively high barrier height [4, 16, 18]. All the metals and the bulk ZnO before metallization processes were cleaned in an ultrasonic bath for 3 min with organic solvents (trichloroethylene, acetone, methanol) and rinsed with deionized water of 18 MΩ for 3 min in each step. The diode radius was 0.5 mm, resulting in a diode area of 7.86×10^{-3} cm^2. The I–V measurements were carried out using a Keithley 487 picoammeter in 0.01 voltage steps. Temperature-dependent I–V measurements were conducted using a liquid N_2 (LN_2) cryostat equipped with a Lakeshore temperature controller having 0.1 K accuracy. Deep-level transient spectroscopy (DLTS) measurements were made using a Sula Technologies compact system within the temperature range 200–500 K. The Ag/n-ZnO SBD was biased reversely with −1 V together with a 0.8 V positive pulse with 1 ms width and 5 ms period during the DLTS measurements.

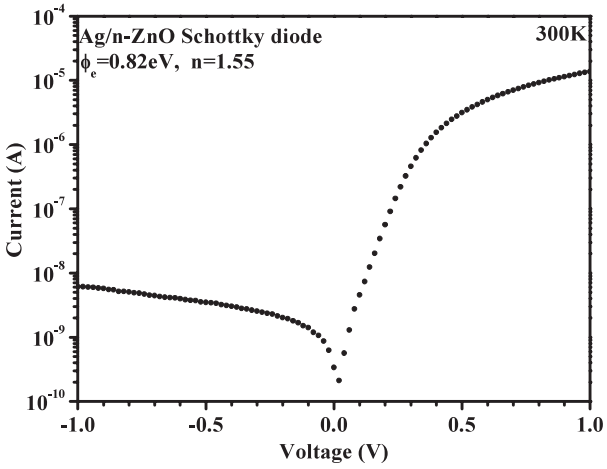

Figure 1. The I–V characteristics of a Ag/n-ZnO SBD at room temperature.

3. Results and discussions

Figure 1 gives the semi-logarithmic I–V characteristics of the Ag/ZnO SBD at room temperature, which shows almost four orders of rectifying behaviour. A leakage current of 6 nA at −1 V and a generation–recombination current of 0.38 nA were obtained. The deviation from linearity above 0.4 V in the semi-logarithmic I–V characteristics is due to the series resistance effect of the structure. Thermionic emission theory shows that the current in a SBD is given by the following equation when higher values of $V > 3kT/q$ [19],

$$I = I_0 \exp(-qV/nkT) \tag{1}$$

and the saturation current

$$I_0 = A^{**}AT^2 \exp(-q\Phi_e/kT), \tag{2}$$

where A is the diode area, A^{**} the effective Richardson constant, T temperature, q electronic charge, k Boltzman constant, V forward bias, n ideality factor, I_0 the saturation current, and Φ_e the effective barrier height. Fitting the forward-bias I–V characteristics between 0.08–0.2 V yields a barrier height of 0.82 eV and an ideality factor of 1.55 at 300 K.

The temperature-dependent I–V characteristics of the Ag/n-ZnO SBD have been given in figure 2(a). The forward-bias characteristics and the turn-on voltage values of the Ag/n-ZnO SBD shift towards the more positive bias region with decreasing temperature. Also, the current values of the SBD increase with increasing temperature for both forward and reverse biases. It is important to obtain an SBD having a low leakage current at high temperatures, at least for capacitance transient measurement reliability. Relatively low leakage currents, 4×10^{-11} A at 200 K and 8×10^{-6} A at 500 K at −1 V, which are thought to be suitable for DLTS measurements [20], were obtained for the Ag/n-ZnO SBD.

The leakage current of the SBDs is wanted to be voltage independent because of the need to have controllable SBH. In the present case, it displays a voltage dependence, as shown in figures 1 and 2, which means that the electric field dependence of the SBH may be a consequence of the barrier lowering effects such as image force lowering [19]. The I–V characteristics of the Ag/n-ZnO device starts to become very bad below 200 K, which may be the outcome of the carrier freeze-out effects, so we cannot obtain the I–V characteristics for lower temperatures. In general, the carrier concentration of ZnO is controlled mainly by a

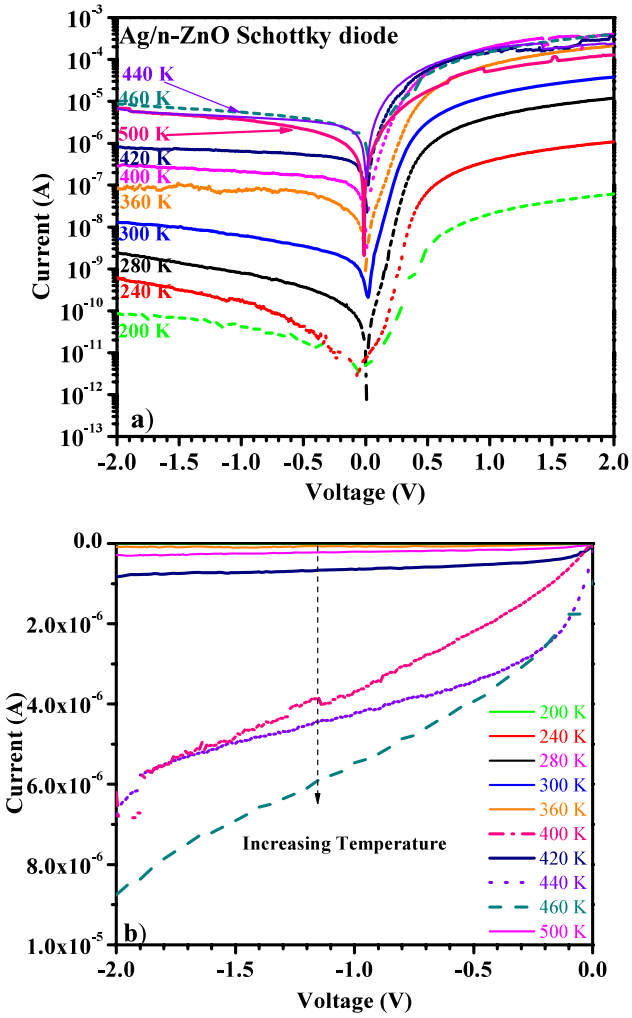

Figure 2. (a) Temperature-dependent semi-logarithmic I–V characteristics of the Ag/n-ZnO SBD. (b) The linear plot of leakage current of the Ag/n-ZnO SBD as a function of temperature.

shallow active donor at about 60 meV below the conduction band [21], which is much deeper than the donors in other semiconductors, so carrier freeze-out may become possible at higher sample temperatures than the usually observed temperature of 100–150 K. A similar effect was observed below 130 K by Grossner *et al* [15]. The linear plot of the leakage current versus voltage shows a sudden increase above 440 K, as shown in figure 2(b), where this is also turning point of the ideality factor to 3.50 from the value of 1.60 (figure 3). Both results show that the SBD properties are very different, and thermionic emission or thermionic field emission processes are replaced by some other kind of transport mechanisms at higher temperatures. This can also be seen as a deviation from linearity in the $\ln I_0/T^2$ versus $1000/T$ plot given in figure 4.

The ideality factor remaining between 1.30 and 1.60 confirms the stability of the SBD in the temperature range 240–400 K. However, it exhibits an increasing trend outside this temperature range. Most of the SBDs in the literature display a decreasing ideality factor while

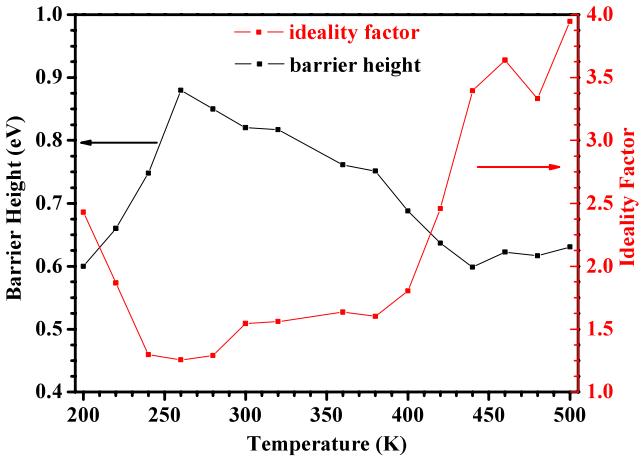

Figure 3. The variation of ideality factor and the SBH as a function temperature for the Ag/n-ZnO SBD.

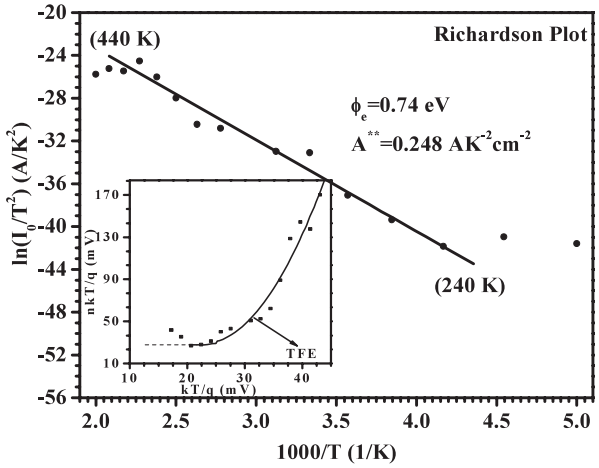

Figure 4. Richardson plot, $\ln(I_0/T^2)$ versus $1000/T$, for the Ag/n-ZnO SBD. The inset shows the q/nk_bT versus q/k_bT variation.

the temperature is increasing. In the present case, at lower temperatures, the temperature trend of the ideality factor fits with variations given in the literature. This variation may be the effect of the so-called T_0 anomaly, which is explained by some authors [22–24]. In order to prove or disprove this assumption, an nk_bT/q versus k_bT/q graph is plotted, as shown in the inset of figure 4. The graph shows that the diode may possibly be obeying the thermionic field emission (TFE) theory according to [22], except for a few data points at low temperatures, which are a result of the increase of n as the temperature decreases.

On the other hand, as discussed by Tung [22], although nk_bT/q versus k_bT/q graphs in the shape shown as the inset of figure 4 are usually attributed to the TFE mechanism, this also gives an indication that some tunnelling mechanisms may also be involved in charge transport at high temperatures when the ideality factor is high. In order to understand the thermally activated current mechanism in the SBD, the saturation current dependence on temperature is

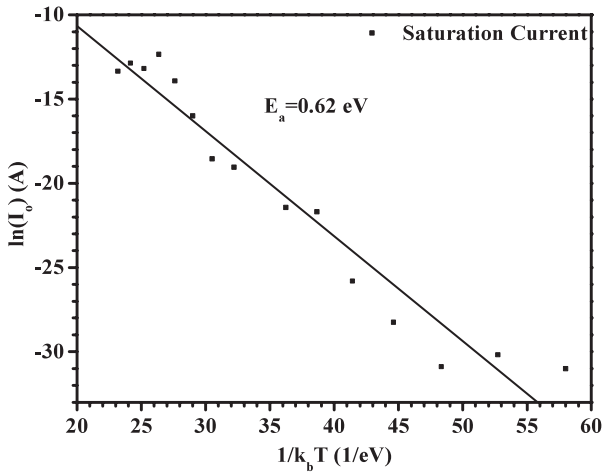

Figure 5. Saturation current versus $1/k_bT$. The linear fit results in a thermal activation energy of 0.62 eV.

generally taken into consideration [25, 26]. The thermal activation energy of such a trap can be found by the slope of the linear fit to this saturation current variation with temperature. If the thermal activation energy value is close to the band gap energy, the current in the SBD will be dominated by interface recombination. If its value is around the mid-gap energy, then the current will be dominated by depletion region recombination [26], as given by

$$I_0 = I_{00} \exp(-E_a/kT) \tag{3}$$

where I_0 is the saturation current, k the Boltzman constant, T temperature and E_a the activation energy of the thermal process. In the present case, we found that the thermal activation energy is 0.62 eV from the slope of figure 5, which is far from the both values mentioned above. We therefore propose that, at high temperatures, a trap-assisted tunnelling mechanism may be dominated by the presence of an electron trap centre with a capture cross section of 3.3×10^{-15} cm^2 located exactly at the same level, the activation energy of which is observed to be around 400 K by DLTS measurements as seen in figure 6.

On the other hand, the SBHs show an increasing trend up to 260 K and then they start to decrease with increasing temperature, which differs interestingly from the literature. The expected trend (SBH increasing with temperature) suddenly returns at temperatures higher than 260 K. This kind of reverse characteristic (SBH decreasing with temperature) of barrier height dependence as a function of temperature is reported by Lu and Mohammad [27] in the literature for metal/n-$Al_xGa_{1-x}N$ SBDs. They have explained this behaviour as a result of the field emission in charge transport. Also, a similar characteristic was reported in [13] for Pt/n-ZnO and [28] for Au/n-GaN diodes. This reverse variation of SBH in the present case can be thought of as a result of the error in calculations. In order to check that this assumption is valid or not, the calculations were repeated. Also some other useful calculation methods for the SBHs can be taken into account, such as those given by Oswald and Dobracka [29] and Ranuarez *et al* [30]. The first is related to the ln I–V curves that have no linear part in the forward direction and the other is related to the device having a low forward voltage region to make appropriate fit. Both calculation methods can be taken into account at temperatures higher than 400 K by considering the decrease in rectification ratio. However, the methods cannot necessarily be applied for the present case, having an almost two orders of magnitude rectification ratio of the

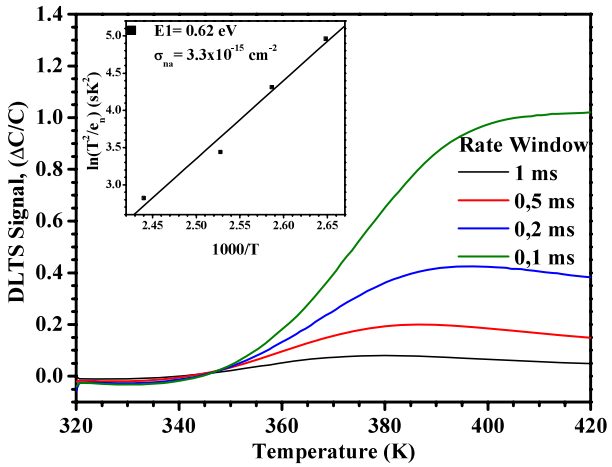

Figure 6. High-temperature DLTS signal for the Ag/n-ZnO SBD. The inset shows the Arrhenius plot, which results in an activation energy of 0.62 eV and capture cross section of 3.3×10^{-15} cm^{-2}.

ln I–V characteristic at 500 K. Therefore, the standard method is used for the device having a similar rectification ratio in the literature [10, 14, 15, 31].

We calculated the SBH to be 0.74 eV and the Richardson constant, A^{**}, to be 0.248 A K^{-2} cm^{-2} from the linear fit in the ln I_0/T^2 versus $1000/T$ plot, as shown in figure 4. This deviation in A^{**} from the theoretical value (32 A K^{-2} cm^{-2}) is a general case for most of the SBDs given in the literature for very different materials. For instance, for an Al/p-Si SBD the Richardson constant, A^{**}, is reported to be six orders of magnitude lower than the theoretical value [32]. A similar result was reported by Pattabi *et al* [25] for a Au/n-CdTe SBD. In the case of ZnO SBDs, A^{**} is found to be 0.15 by Sheng *et al* [18], 61.2 by Ip *et al* [13], and very low value is obtained by Wenckstern *et al* [11]. This deviation in A^{**} is generally explained by barrier inhomogeneity of the contact, which means that it consists of the high and low barrier areas at the interface mainly due to the formation of different oxide layer thicknesses between the metal and semiconductor [11, 32, 33].

4. Conclusion

In conclusion, because of its high-strength bond structure, ZnO is a promising candidate for possible use in high-power electronic devices such as Schottky diodes. We showed the high-temperature I–V characteristics of the Ag/n-ZnO SBD and we proposed some models in which dominant charge transport mechanisms are defined, considering the ideality factor, SBH and reverse-bias variations as functions of temperature. The Richardson plot deviates from linearity at high (>440 K) and low (<240 K) temperatures, which indicates that thermionic emission is not the case for the current transport mechanism. The deviation at low temperatures may be due to the carrier freeze-out effect. At high temperatures the thermionic emission is replaced by a tunnelling mechanism which is probably stimulated by a deep donor level situated at E_c—0.62 eV with a capture cross section of 3.3×10^{-15} cm^2 observed by both DLTS and saturation current as a function of temperature. The high ideality factor and high reverse current values also confirm this tunnelling assumption. Also, the SBD is very stable between 240 and 400 K because of having a relatively low and stable ideality factor around 1.30–1.60.

Acknowledgment

This work was carried out as a part of the Atatürk University Research Fund project (PN: 2004/43).

References

[1] Liang W Y and Yoffe A D 1968 *Phys. Rev. Lett.* **20** 59
[2] Tüzemen S, Gür E, Yıldırım T, Xiong G and Williams R T 2006 *J. Appl. Phys.* **100** 103513
[3] Florescu D I, Mourokh L G, Pollak F H, Look D C, Cantwell G and Li X 2002 *J. Appl. Phys.* **91** 890
[4] Albrecht J D, Ruden P P, Limpijumnong S, Lambrecht W R L and Brennan K F 1999 *J. Appl. Phys.* **86** 6864
[5] Coskun C, Look D C, Farlow G C and Sizelove J R 2004 *Semicond. Sci. Technol.* **19** 752
[6] Morkoç H, Strite S, Gao G B, Lin M E, Sverdlov B and Burns M 1994 *J. Appl. Phys.* **76** 1363
[7] Liang S, Sheng H, Liu Y, Huo Z, Lui Y and Shen H 2001 *J. Cryst. Growth* **225** 110
[8] Polyakov A Y, Smirnov N B, Kozhukhova E A, Vdovin V I, Ip K, Heo Y W, Norton D P and Pearton S J 2003 *Appl. Phys. Lett.* **83** 1575
[9] von Wenckstern H, Kaidashev E M, Lorenz M, Hochmuth H, Biehne G, Lenzner J, Gottschalch V, Pickenkain R and Grundmann M 2004 *Appl. Phys. Lett.* **84** 79
[10] Yuan G, Ye Z, Zhu L, Huang J, Qian Q and Zhao B 2004 *J. Cryst. Growth* **268** 169
[11] von Wenckstern H, Biehne G, Rahman R A, Kaidashev E M, Hochmuth H, Lorenz M and Grundmann M 2006 *Appl. Phys. Lett.* **88** 092102
[12] Ip K, Gila B P, Onstine H, Lambers E S, Heo Y W, Baik K H, Norton D P, Pearton S J, Kim S, LaRoche J R and Ren F 2004 *Appl. Phys. Lett.* **84** 5133
[13] Ip K, Heo Y W, Baik K H, Norton D P, Pearton S J, Kim S, LaRoche J R and Ren F 2004 *Appl. Phys. Lett.* **84** 2835
[14] Coppa B J, Davis R F and Nemanich R J 2003 *Appl. Phys. Lett.* **82** 400
[15] Grossner U, Gabrielsen S, Borseth T M, Grillenberger J, Kuznetsov A Y and Svensson B G 2004 *Appl. Phys. Lett.* **85** 259
[16] Allen M W, Alkaisi M M and Durbin S M 2006 *Appl. Phys. Lett.* **89** 103520
[17] Nagata T, Ahmet P, Yoo Y Z, Yamada K, Tsutsui K, Wada Y and Chikyov T 2006 *Appl. Surf. Sci.* **252** 2503
[18] Sheng H, Muthukumar S, Emanetoğlu N W and Lu Y 2002 *Appl. Phys. Lett.* **80** 2132
[19] Rhoderick E H and Williams R H 1988 *Metal Semiconductor Contacts* 2nd edn (Oxford: Oxford University Press)
[20] Blood P and Orton J W 1992 *The Electrical Characteristics of Semiconductors: Majority Carriers and Electron States* (New York: Academic)
[21] Look D C, Coşkun C, Claflin B and Farlow G C 2003 *Physica* B **340–342** 32
[22] Tung R T 1992 *Phys. Rev.* B **45** 13509
[23] Sullivan J P, Tung R T, Pinto M R and Graham R 1991 *J. Appl. Phys.* **70** 7403
[24] Kiziroglou M E, Zhukov A A, Li X, Gonzalez D C, de Groot P A J, Bartlett P N and de Groot C H 2006 *Solid State Commun.* **140** 508
[25] Pattabi M, Krishnan S, Ganesh and Mathew X 2007 *Sol. Energy* **81** 111
[26] Bayhan H and Erçelebi Ç 1997 *Semicond. Sci. Technol.* **12** 600
[27] Lu C and Mohammad S N 2006 *Appl. Phys. Lett.* **89** 162111
[28] Wang H-T *et al* 2006 *Appl. Phys. Lett.* **89** 122106
[29] Oswald J and Dobrocka E 1996 *Semicond. Sci. Technol.* **11** 1198
[30] Ranuarez J C, Sanchez Garcia F J and Ortiz-Conde A 1999 *Solid State Electron.* **43** 2129
[31] Mosbacker H L, Strzhemechny Y M, White B D, Smith P E, Look D C, Reynolds D C, Litton C W and Brillson L J 2005 *Appl. Phys. Lett.* **87** 012102
[32] Dökme İ, Altindal Ş and Bülbül M M 2006 *Appl. Surf. Sci.* **252** 7749
[33] Gümüş A, Türüt A and Yalçın N 2002 *J. Appl. Phys.* **91** 245