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Electrical Properties of Anisotype ZnO/ZnSe Heterojunctions

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The p-ZnO/n-ZnSe heterojunction was prepared by the photothermal oxidation of ZnSe substrate. Current–voltage characteristics are measured and discussed. The potential barrier height is equal to 3 eV at 300 K and its anomalous temperature coefficient reported here is due to the high defects concentration ($\approx 10^{14}$ cm^{-2}) on the interface. It is established that forward current in p–n junction is limited by the recombination processes in the space charge region, carriers tunneling and above the barrier emission. The reverse current is determined by tunneling processes at low bias and avalanche effect at high bias.

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1. Introduction

The wide band gap zinc compounds (ZnSe, ZnO, ZnS) are the most challenging materials for fabrication of large gap electronic active elements with rectifying barrier. Obtaining the p–n homo- and heterojunction structures is complicated by the unipolar conductivity type dominating in these materials [1]. To overcome this drawback a number of technologies can be used (MBE, metal organic chemical vapor deposition (MOCVD), ion implantation), but all of them need complex and expensive facilities and a suppression of radiation defects by additional annealing. Recently, a new method has been proposed, which is the ZnO:N thin films deposition using the radical-beam generating epitaxy method for p-ZnO/n-ZnSe anisotropic heterojuction formation [2]. In this work we report on the photothermal oxidation method applied to the mentioned heterojunction fabrication and the studies of its electric properties.

2. Experimental

Base ZnSe crystals were grown from melt under inert gas pressure and were doped with Al during the growth. At room temperature the obtained material had relatively low electrical conductivity, which was further reduced to 10^{-1} Ω^{-1} cm^{-1} value after the thermal treatment of the crystal in the saturated zinc vapors. Substrates ($4\times4\times1$ mm^3) prepared from the crystals were subsequently mechanically and chemically polished.

The ZnO heterofilm was formed on one side of the substrates by means of photothermal oxidation method. The process took place in an open resistive furnace. UV irradiation through transparent quartz tube walls of furnace, using mercury lamp, caused a photoactivation of oxygen molecules. The substrate temperature could have varied within the temperature range 400–600 °C, the annealing time was 1 h. A differential reflection spectrum R'_ω analysis confirmed a formation of the new semiconducting film on the illuminated substrate's side due to the thermal treatment [3]. A peak in the R'_ω signal was observed at the photon energy of $h\nu = 3.3$ eV, which was well correlated with the zinc oxide band gap energy E_g at 300 K [4]. In addition, the illuminated substrate's side changed its conductivity type from n to p after the annealing, which was confirmed by thermal electromotive force measurements.

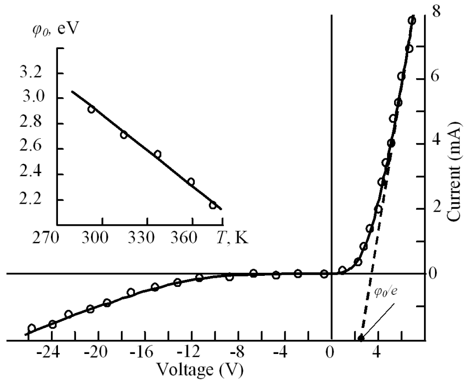

Fig. 1. The p-ZnO/n-ZnSe anisotropic heterojunction current–voltage characteristic at 300 K. The inset shows the potential barrier's thermal dependence. Experimental results are denoted with open points. Solid lines serve as a guide to the eye, dashed line is an extrapolation of experimental results.

Ohmic contacts were deposited on the structure using appropriate components — In on n-ZnSe and Ni on p-ZnO. The current–voltage characteristic measurements were performed by conventional methods. The heterojuction had sharply defined diode characteristics with the rectification factor not less than 10^3 at 300 K and at 4 V (Fig. 1).

3. Results and discussion

The investigation of the I–V characteristics showed the linear dependence of the barrier height ϕ_0 in temperature range of 290–370 K (see the inset in Fig. 1). The characteristic β_ϕ coefficient was found to be equal to 9×10^{-3} eV/K, which is more than ten times larger than the coefficient for ZnSe and ZnO [1]. In our opinion this results from the high concentration of defects at the ZnO/ZnSe interface which is due to the lattice mismatch of both crystals. Concentration of mismatch dislocation is usually estimated as $N_s \sim x^{-2}$ in the first approximation, and the distance x between the dislocations is given by the following equation:

$$x = a_1 a_2/(a_1 - a_2). \tag{1}$$

Using the known values $a_1 = 5.405$ Å (ZnSe) and $a_2 = 3.24$ Å (ZnO), the values for x and N_s are found to be equal to 8 Å and 1.6×10^{14} cm^{-2}, respectively. The high concentration of interface defects has to play a role of charge carrier's traps or recombination centers, affecting the electric current transport mechanism.

The electric current I, in general, consists of three components: generation-recombination in the space charge region I_{gr}, tunneling I_t and overbarrier emission I_d [5]. The initial part of forward bias current–voltage characteristics (Fig. 2) is described by the following equation [6]:

$$I_{gr} = I_{gr}^0 \left[\exp(eV/nkT) - 1\right], \tag{2}$$

where I_{gr}^0 is the cut-off current at $V = 0$, and n is the ideality factor. The ideality factor n is larger than 2 and depends on temperature T. This indicates the presence of recombination and trapping centers. The role of the trapping centers increases with decreasing temperature. The ideality factor reduces n from 3.5 to 2 at temperature changing from 290 K to 373 K.

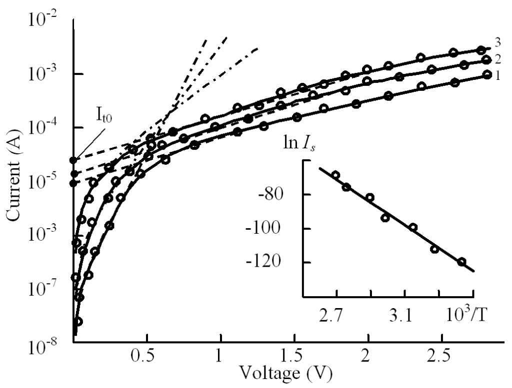

Fig. 2. The forward bias current–voltage characteristic curves at different temperatures: 1 — 292 K, 2 — 336 K, 3 — 373 K. Dashed curves are theoretic and described by Eq. (3), dash dot curves are theoretic and described by Eq. (2). The inset shows the saturated current's dependence on temperature.

Under forward bias > 0.4 V the $I(V)$ dependence becomes slower and well matches the Neuman equation for the tunneling current [5]:

$$I_t = I_{t0} \exp(\alpha V + \beta T), \tag{3}$$

where the parameters α and β do not depend on V and T, respectively, and their experimental values are equal to 1.65 V^{-1} and 1.3×10^{-2} K^{-1}.

Further, the voltage increase causes the potential barrier height's decrease. When the voltage value V approaches ϕ_0/e, the overbarrier current becomes dominating. Under such conditions the current–voltage characteristic curve is well described by the following equation [7]:

$$I_d = I_s \exp\left(\frac{eV - IR_0}{kT}\right), \tag{4}$$

where R_0 — heterojunction serial resistance, I_s — saturation current. R_0 value can be easily determined from the direct current–voltage characteristic branch within its linear region (Fig. 1). Since the saturation current is equal to $I_s \approx \exp(-\varphi_0/kT)$, the barrier's height evaluation at 0 K is possible from the $I_s(T)$ dependence (the inset in Fig. 2). The value obtained is equal to 5.75 eV, which is significantly higher than the E_g for the heterojunction's wider band gap component (ZnO). This can be understood taking into account the anomalously high coefficient of the potential barrier's height dependence on temperature. The substitution of the experimental parameter β_ϕ (the inset in Fig. 1) into equation $\varphi_0(T) = \varphi_0(0) - \beta_\varphi T$ gives real ϕ_0 values within the investigated temperature range.

The initial values of the reverse current–voltage characteristic are given by the well known equation for the abrupt heterojunction tunnelling current [5]:

$$I_{rev} = a_0 \exp\left(-b_0/\sqrt{\varphi_0 - eV}\right). \tag{5}$$

Here a_0 is determined by the filling probability of the energy levels the tunneling is from, b_0 — the logarithmic current change rate versus voltage. The current–voltage characteristics deviation from the dependence (5) at high reverse biases $V > 24$ V is due to the carriers avalanche multiplication caused by impact ionization. This is seen from the positive temperature coefficient of the breakdown voltage change and also the experimentally observed photocurrent multiplication.

4. Conclusion

The p-ZnO/n-ZnSe heterojunction prepared by the photothermal oxidation of ZnSe substrate was studied. I–V curve was measured and discussed. The potential barrier height was equal to 3 eV at 300 K (but $\phi_0(0) = 5.75$ eV) and its anomalous thermal dependence coefficient ($\beta_\phi = 9 \times 10^{-3}$ eV/K) is due to the high defect concentration ($\approx 10^{14}$ cm^{-2}) at the interface. Forward current is limited by the recombination processes in the space charge region, carriers tunneling and above the barrier emission. The reverse current is determined by tunneling processes at low bias and avalanche effect at high bias.

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