VOLT-AMPERE CHARACTERISTIC OF THE DOUBLE SCHOTTKY BARRIER

A.I. Ivon

Oles Honchar Dnipro National University, Dnipro, Ukraine
**e-mail: aii_vel93@i.ua*

The volt-ampere characteristic (I-V characteristic) of the double Schottky barrier located in the contact region of ZnO grains of zinc oxide based varistor ceramics is calculated using the mechanism of the above-barrier electron emission. I-V characteristic is symmetric to the polarity of the voltage U. At U > $2k_BT/e$ (k_B is the Boltzmann constant, T is the absolute temperature, e is electron charge) the electric current is saturated. The contact of ZnO grains with a double Schottky barrier behaves like an electrical circuit consisting of two oppositely connected Schottky diodes. A small maximum possible decrease in the height of the double Schottky barrier in an electric field ~ $0.7k_BT \approx 0.018$ eV does not allow explaining the high nonlinearity of I – V characteristic of varistor materials by the above-barrier electron emission. The most probable cause of nonlinearity is the tunnel emission of electrons and impact ionization.

Keywords: double Schottky barrier, volt-ampere characteristic, varistor ceramics.

Received11.06.2021; Received in revised form 15.07.2021; Accepted 15.08.2021

1. Introduction

Zinc oxide based ceramic materials with small additions of oxides of cobalt, bismuth, antimony and some others, have found wide application in the production of varistors due to the high nonlinearity of the volt-ampere characteristic (I-V characteristic). Currently, zinc oxide based varistors are the main components used to protect electronic circuits and electrical equipment from overvoltage [1].

The cause for the high nonlinearity of I-V characteristic of varistor materials is the Schottky energy barriers in the grain contact area [2]. The contact regions of grains with a Schottky barrier are depleted in charge carriers and have a high resistance $10^{12} – 10^{13}$ times higher than the bulk resistance of grain. Therefore, in the range of current density from 10^{-13} to 1 A cm^{-2}, the electrical conductivity of varistor ceramics is completely controlled by Schottky barriers. Schottky barriers in the near-surface layer of two adjacent grains form a double Schottky barrier. The volt-ampere characteristic of such barrier determines the I-V characteristic of varistor ceramics.

There are three mechanisms of nonlinear electrical conductivity that are commonly used to explain the high nonlinearity of the volt-ampere characteristic of varistor ceramics. In [3], the nonlinearity of the I-V characteristic is associated with a decrease in the height of intergranular energy barriers in an electric field and, as a consequence, with a sharp increase in current of the above-barrier electron emission. In [4], taking into account the weak effect of temperature on the part of the I-V characteristic with high nonlinearity, it is assumed that the nonlinearity mechanism is due to the tunnel emission of electrons. In [5], to explain the nonlinear properties of varistor ceramics, a mechanism of impact ionization in the contact region of zinc oxide grains, where a double Schottky barrier is located, was proposed.

In this work, in order to clarify whether a decrease in the height of intergranular barriers in an electric field can explain the high nonlinearity of the volt-ampere characteristic of varistor ceramics, the volt-ampere characteristic of the double Schottky barrier is calculated using model of the above-barrier electron emission.

2. Model of the above-barrier electron emission for volt-ampere characteristic of double Schottky barrier

The cause for the formation of energy barriers is the physical adsorption of oxygen atoms on the surface of ZnO grains [2]. Electrically neutral oxygen atoms at adsorption capture free electrons from the conduction band of zinc oxide. As a consequence, a near-surface bending of the energy bands arises, leading to the formation of double Schottky energy barrier in the contact region of ZnO grains.

Fig. 1 shows the energy diagram for the contact of ZnO grains in the absence of external voltage.

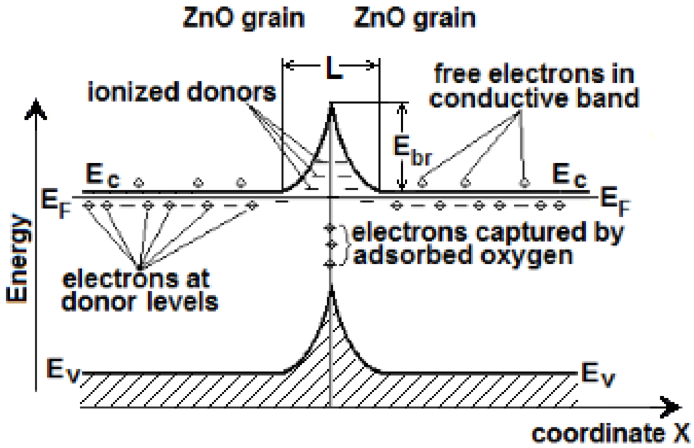


Fig. 1. Energy diagram for the contact of grains in ZnO based ceramics. E_V and E_C are the energies corresponding to the top of valence band and to the bottom of conductivity band, respectively. E_F is the Fermi level. L is the thickness of the layer depleted in charge carriers; E_{br} is the height of double Schottky barrier

The band gap of zinc oxide $\Delta E_g = E_C - E_V$ is about 3.2 eV [6]. The high electrical conductivity of ZnO grains ~ 0.5 Ohm^{-1} cm^{-1} [7], is associated with a high concentration of donors $N_d \approx 10^{18}$ cm^{-3} [8], which usually are the defects in crystal lattice of ZnO. Oxygen atoms adsorbed on the grain surface form deep surface levels with a concentration of N_t. Electrons captured on these levels from the conduction band of zinc oxide charge the surface negatively, and a carrier-depleted layer with positively charged ionized donors forms in the near-surface region of the grains. The thickness of this layer L (Fig. 1) found from the condition of electrical neutrality is defined as $L = N_t/N_d$.

Solving the Poisson equation allows finding the height of the barrier E_{br}:

$$E_{br} = \frac{e^2 N_t^2}{2\varepsilon_{ZnO}\varepsilon_0 N_d} \qquad (1)$$

The calculation of volt-ampere characteristic of a double Schottky barrier presented below assumes that the transfer of electrons through the barrier occurs as a result of their above-barrier thermal emission and the mean free path of electron λ exceeds the barrier width $\lambda > L = N_t/N_d$. The contribution of a thin layer between ZnO grains is not taken into account. Let us assume that at $x = 0$ the potential $\varphi(0) = 0$. In this case at $x = 0$ the electron energy relative to the bottom of the conduction band is equal to E_{br} and does not depend on the voltage U_{br} applied to the barrier. The change in the energy of electrons in an external electric field takes place only outside of the coordinate $x = 0$.

Fig. 2 shows the energy diagram for the contact between ZnO grains in the presence of voltage U_{br} applied to the double Schottky barrier.

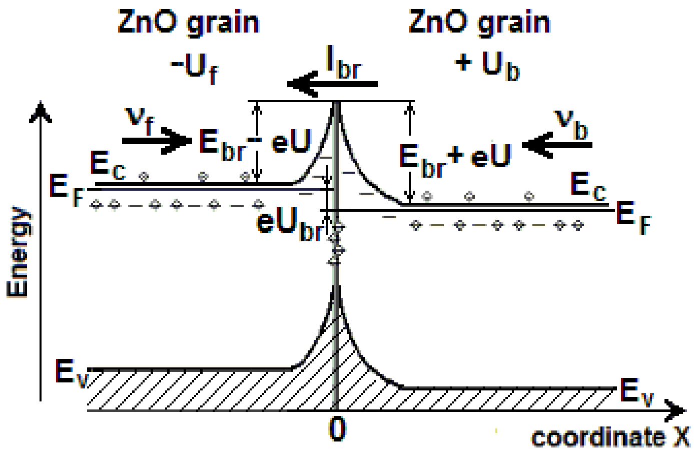


Fig. 2. Energy diagram for the ZnO grains contact in zinc oxide based ceramics, when the voltage $U_{br} = U_f + U_b$ is applied to the energy barrier

The positive potential $+U_b$ applied to ZnO grain shown in Fig. 2 on the right, decreases the energy of electrons in the conduction band of grain on value $-eU_b$. As a result, the bottom of this band E_C shifts downward. For free electrons, which move from the depth of grain to it surface for overcome the barrier is needed the energy of $E_{br} + eU_b$ (U_b is the voltage drop in the part of barrier to the right of grains contact (Fig. 2)). Therefore, the Schottky barrier at a positive potential is biased in the reverse direction.

The negative potential $-U_f$ applied to the grain shown in Fig. 2 on the left, increases the energy of electrons in conduction band on the value $+eU_f$. As a result, the bottom of this zone moves upwards. For electrons that move from the depth of grain to it surface the energy is needed of $E_{br} - eU_f$ for overcome the barrier (U_f is the voltage drop in the part of the energy barrier to the left of the grains contact (Fig. 2)). Therefore, the Schottky barrier at negative potential is biased in forward direction.

The voltage drop U_{br} across the double Schottky barrier is equal to the sum of the voltages on its parts shifted in the forward and reverse directions $U_{br} = U_f + U_b$. Almost all the voltage U applied to the contact of grains falls on the energy barrier. It is allows accepting that $U_{br} = U$. Electrons in the volume of ZnO grain perform only thermal motion, the average velocity of which is V_T. The drift velocity of electrons in the bulk of ZnO grain can be taken equal zero.

The electric current of the above-barrier electron emission is determined by the difference between oppositely directed heat fluxes of electrons on both sides of the grains contact. In the grain volume, electrons move with the thermal velocity V_T. Taking into account the uniform distribution of angles to the X axis for V_T vector, it can be shown that the modulus of the heat flux of electrons ν in any direction parallel to the X axis is determined by the expression:

$$\nu = \frac{1}{4} n V_T \,, \tag{2}$$

where n is the concentration of free electrons in the grain volume.

If in the conduction band the electron gas is nondegenerate, then the increment in the density of free electrons *dn* with energies in the range from *W* to *W* + *dW* is defined as

$$dn = \frac{N_c}{k_Б T}\exp\left(-\frac{W-E_F}{k_Б T}\right)dW\,. \qquad (3)$$

where N_c is the density of states in conduction band, k_B is the Boltzmann constant, *T* is the absolute temperature.

Of the all electrons moving to the contact of grains from the side of the negative potential $-U_f$ (Fig. 2), only those of them that have energy equal to or greater than $E_C + E_{br} - eU_f$ will overcome the energy barrier. Therefore, taking into account (2), the flux of electrons v_f (Fig. 2) which overcame the part of double Schottky barrier displaced in the forward direction is determined by the expression:

$$\begin{aligned} v_f &= \frac{N_c V_T}{4k_Б T}\int\limits_{E_c+E_{br}-eU_f}^{\infty}\exp\left(-\frac{W-E_F}{k_Б T}\right)dW = \\ &= \frac{1}{4}V_T N_c \exp\left(-\frac{E_c+E_{br}-E_F-eU_f}{k_Б T}\right) \end{aligned} \qquad (4)$$

Taking into account that the concentration of free electrons in the depth of grain is $n = N_c exp(-(E_C - E_F)/(k_Б T))$, the equation (4) can be represented as:

$$v_f = \frac{1}{4}nV_T \exp\left(-\frac{E_{br}-eU_f}{k_Б T}\right). \qquad (5)$$

Similarly, for the electron flow v_b (Fig. 2) which overcame the inversely shifted part of the double Schottky barrier we obtain:

$$v_b = \frac{1}{4}nV_T \exp\left(-\frac{E_{br}+eU_b}{k_Б T}\right). \qquad (6)$$

Thus, in a state of dynamic equilibrium, the electric current density J_{br} through the double Schottky barrier is determined as

$$J_{br} = -e(v_b - v_f) = \frac{1}{4}enV_T \exp\left(-\frac{E_{br}}{k_Б T}\right)\left(\exp\left(\frac{eU_f}{k_Б T}\right) - \exp\left(-\frac{eU_b}{k_Б T}\right)\right) \qquad (7)$$

Taking in account, $U = U_{br} = U_f + U_b$, $V_T = \sqrt{\dfrac{3k_Б T}{m}}$ (*m* is the effective mass of electron) for I-V characteristic of double Schottky barrier we obtain:

$$J = J_S \exp\left(\frac{eU_f}{k_Б T}\right)\left(1 - \exp\left(-\frac{eU}{k_Б T}\right)\right), \tag{8}$$

where the electric current density J_S is determined as

$$J_S = \frac{1}{4} en \sqrt{\frac{3k_Б T}{m}} \exp\left(-\frac{E_{br}}{k_Б T}\right). \tag{9}$$

The principle of detailed equilibrium allows finding the relationship between the voltages U_b and U_f. According to this principle, any voltage applied to the double Schottky barrier does not change the sum of the electron fluxes that cross the barrier in both directions. This is due to the fact that in the state of thermodynamic equilibrium, the number of electrons with energy $E_C + E_{br}$, capable for overcoming the energy barrier remains unchanged, since it is assumed that at $x = 0$ the potential $\varphi(0) = 0$ and therefore the electron energy $W(0) = E_C + E_{br}$ is independent of the voltage U applied to the barrier. The voltage U simply redistributes the electron fluxes ν_f and ν_b. In this case, the equality $\nu_f(0) + \nu_b(0) = \nu_f(U_f) + \nu_b(U_b)$ takes place. From this equality, taking into account expressions (5) and (6) can be obtained the equation that establishes the connection between the voltages U_b and U_f:

$$2 = \exp\left(\frac{eU_f}{k_Б T}\right) + \exp\left(-\frac{eU_b}{k_Б T}\right). \tag{10}$$

Thus, taking into account the equations (10) and $U = U_f + U_b$, the expression (8) for the volt-ampere characteristic can be presented in the form:

$$J = 2J_S \frac{1 - \exp\left(-\dfrac{eU}{k_Б T}\right)}{1 + \exp\left(-\dfrac{eU}{k_Б T}\right)}. \tag{11}$$

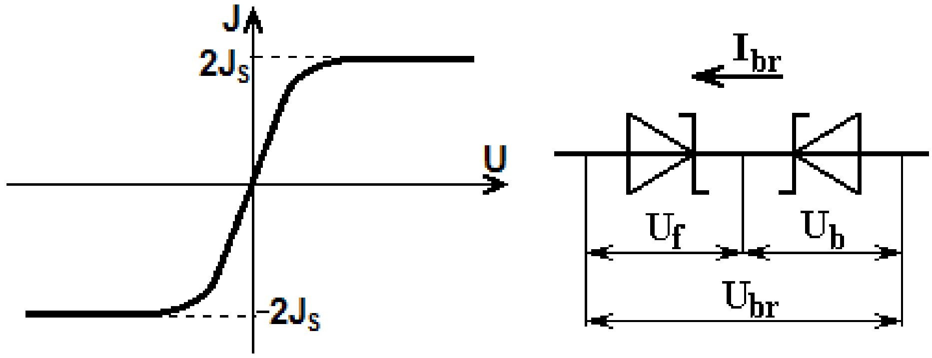
3. Results and discussion

In the model of above-barrier emission of electrons, volt-ampere characteristic of double Schottky barrier, according to (11), has the form shown in Fig. 3a. This characteristic is symmetrical for both polarities of the voltage U.

As can be seen, the model of nonlinearity based on mechanism of the above-barrier emission of electrons does not allow explaining the high nonlinearity of volt-ampere characteristic in varistor materials. As follows from (11), at a voltage $U > 2k_BT/e$, the saturation of the electric current density J takes place, at the level $J = 2J_S$. This is due to the fact that practically all the voltage U applied to the energy barrier falls on its part biased in the reverse direction. The contact of two grains with a double Schottky barrier behaves like electric circuit consisting of two Schottky diodes connected oppositely each other (Fig. 3b). In this circuit, for any polarity of the voltage, one of the diodes is closed always (turned on in the reverse direction) Therefore, its high resistance, which increases with increasing of voltage U due to the expansion of the Schottky barrier, limits the circuit current on the current density level $2J_S$.

At low voltage U, when $k_BT/e >> U$, in the expression (11) the exponentials can be decomposed in a series, limiting ourselves to two expansion terms and this expression can be presented as

$$J = J_S \frac{eU}{k_Б T}. \qquad (12)$$



a **б**

Fig. 3. Volt-ampere characteristic of a double Schottky barrier in the case of above-barrier electron emission (a) and an equivalent circuit with two Schottky diodes, simulating the I-V characteristic (б)

It can be seen from the equation (12) that Ohm's law is fulfilled in weak electric fields. The double Schottky barrier behaves like a linear resistor. Taking into account the barrier thickness L and expression (9), it is possible to estimate the resistivity ρ_{br} of the contact regions of zinc oxide grains, where such barrier is located:

$$\rho_{br} = \frac{4}{e^2 nL}\sqrt{\frac{k_Б mT}{3}} \exp\left(\frac{E_{br}}{k_Б T}\right). \qquad (13)$$

As can be seen, the temperature dependence of ρ_{br} has the activation character. The activation energy is equal to the barrier height E_{br}. Activation energy E_{br} according to the data of measurement in the Ohm's law region of temperature dependence for electrical conductivity of ZnO based ceramics is near 0.7 eV [9]. Let us estimate the value of ρ_{br} at 300 K, assuming that the effective mass m coincides with the electron mass $9.1{\cdot}10^{-31}$ *kg*, the barrier thickness L is ~ 10^{-7} m and the electron concentration n in conduction band of the grains is ~ $N_d \approx 10^{21}$ m^{-3}. Calculation by the formula (13) gives value ρ_{br} ~ $3.4{\cdot}10^{10}$ Ohm cm = $3.4{\cdot}10^{13}$ Ohm cm. This value it is in good agreement in order of magnitude with the resistivity of ZnO based varistor ceramics in the Ohm's law area [9].

Let us find the maximum change in the height of double Schottky barrier in the case of above-barrier electron emission. It follows from (11), when $U \to \infty$ the current density through the double Schottky barrier is $J = 2J_S$. In this case, the part of double Schottky barrier displaced in the reverse direction does not pass electrons and the electron flow through this part is equal to zero. The voltage U_{fmax} applied to the part of energy barrier displaced in the forward direction provides a current density equal to $2J_S$. In this case at $U_b \to \infty$ the equation (10) gives the value of U_{fmax}

$$U_{f\max} = \frac{k_Б T}{e} \ln 2 \approx \frac{0{,}7 k_Б T}{e}, \qquad (14)$$

and the maximum decrease in the height of the double Schottky barrier ΔE_{brmax} is $\Delta E_{br\max} = e\ U_{f\max} \approx 0{,}7 k_Б T \approx 0{,}018$ эВ.

Thus, a small value of ΔE_{brmax} shows that the high nonlinearity of volt-ampere characteristics of ZnO based ceramics cannot be explained by a decrease in the height of intergranular energy barriers under the action of electric field. The volt-ampere characteristic of the double Schottky barrier is largely influenced by its part displaced in the reverse direction by the electric field. It should be expected that the mechanism of nonlinearity of varistor ceramics should be similar to the mechanisms of nonlinearity of I-V characteristic for semiconductor Zener diodes. These mechanisms are associated with tunnel emission and impact ionization [4, 5].

A feature of such nonlinearity mechanisms is that they take place at voltages close to the value of $\Delta E_g/e$ and are characterized by a sharp dependence of current on voltage (here $\Delta E_g = E_C - E_V$ is width of the band-gap). Since the width of the band-gap for zinc oxide $\Delta E_g \sim 3.2$ eV should be expected appearance of the tunnel emission of electrons and the impact ionization in reversely biased part of energy barrier at the voltages of about 3 V. This is confirmed by the data presented in [10] about volt-ampere characteristics for the individual contacts of grains in ZnO based varistor ceramics.

4. Conclusions

The volt-ampere characteristic of double Schottky energy barrier is calculated on the base of model of above-barrier electron emission. I-V characteristic is symmetric to the polarity of voltage U. Saturation of the electric current takes place at the voltage $U > 2k_BT/e$. The contact of ZnO grains with a double Schottky barrier in ZnO based ceramics behaves like an electric circuit consisting of two Schottky diodes connected oppositely. The small maximum possible decrease in the height of the double Schottky barrier in an electric field $\sim 0.7 k_B T \sim 0.018$ eV does not allow explaining the high nonlinearity of the volt-ampere characteristic of varistor materials by the above-barrier electron emission. The most probable reason for this nonlinearity is tunnel emission of electrons and impact ionization.

References

1. **Gupta T.K.** Application of zinc oxide varistors // Journal of the American Ceramic Society. – 1990. – Vol. 73, No. 7. – P. 1817-1840.

2. **Clarke D.R.** Varistor ceramics // Journal of the American Ceramic Society. – 1999. – Vol. 82, No. 3. – P. 485-502.

3. **Glot A.B.** A model of non-Ohmic conduction in ZnO varistors // Journal of Materials Science: Materials of Electronics. – 2006. – Vol. 17, No. 9. – P. 755-765.

4. **Eda R.** Conduction mechanism of non ‐ Ohmic zinc oxide ceramics // Journal of Applied Physics. – 1978. – Vol. 49, No. 5. – P. 2964-2972.

5. **Pike G.E.** Electroluminescence in ZnO varistors: Evidence for hole contributions to the breakdown mechanism / G.E. Pike, S. R. Kurtz, P.L. Gourley, Y.R. Philipp and L.M. Levinson // Journal of Applied Physics. – 1985. – Vol. 57, No. 12. – P. 5512-5518.

6. **Srikant V.** On the optical band gap of zinc oxide / V. Srikant and D.R. Clarke // Journal of Applied Physics. – 1998. – Vol. 83, No. 10. – P. 5447-5451.

7. **Ivon A.I.** Parameters of ZnO grains in ZnO-based ceramics // Inorganic Materials. – 2000. – Vol. 36, No. 10. – P. 1074-1077.

8. **Mukae K.** Capacitance-vs-voltage characteristics of ZnO varistors / K. Mukae, K. Tsuda, I. Nagasava // Journal of Applied Physics. – 1979. – Vol. 50, No. 6. – P. 4475-4476.

9. **Ivon A.I.** Grain resistivity in zinc oxide and tin dioxide varistor ceramics / A.I. Ivon, A.B. Glot, R.I. Lavrov, Zhen-Ya Lu. // Journal of Alloys and Compounds. – 2014, – Vol. 616. – P. 372 – 377.

10. **Olsson E.** Characteristics of individual interfacial barriers in a ZnO varistor material. / E. Olsson, G. L. Dunlop // Journal of Applied Physics. – 1989. – Vol. 66, No. 8. – P. 3666–3675.