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# High Temperature Characterization of Electrical Barriers in ZnO Varistors*

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**Abstract.** Two main models have been proposed to describe the potential barriers in ZnO varistors: the surface oxidation and the surface states. It has been difficult to decide which of them better corresponds to the experimental observations. High temperature electrical characterization of these materials is an important tool to understand the formation of the electrical barriers. In this work, using literature data describing ZnO varistor characteristics at high temperature, up to 1153°C, we calculate the energy position of the equilibrium Fermi level at the grain boundary interface, and found that this parameter decreases with the increase of temperature, and for temperatures higher than $\sim$ 700°C it stays close to the ZnO band gap without crossing it. This behavior shows that the interface never presents a p-type character, a starting point to develop the surface states model. On the other hand, 700°C is a temperature too low for the surface oxidation mechanism to be operative. It is then proposed that, during cooling down to $\sim$ 700°C, the interface Fermi level stays close to the middle of the band gap due to the adsorption and subsequent reaction of oxygen with ZnO surfaces/grain boundaries. For lower temperatures, when the interface Fermi level separates from the middle of the band gap, it is proposed that it follows the variation of the bulk Fermi level, which in turn is caused by shallow donors in ZnO. A calculation assuming a reduced electroneutrality condition, gave a donor density of $\sim 3 \times 10^{17}\,cm^{-3}$, which corresponds approximately to the density of carriers in the material for temperatures down to room temperature. This value is in a good agreement with those available in the literature. Knowing both the bulk and the interface Fermi levels, it is then possible to calculate the barrier height at any temperature, and it is observed that it is almost constant from room temperature up to $\sim$ 400°C, with a value of 0.8 eV, and than decreases monotonously up to 1153°C. Taking these values, it is possible to calculate the variation of the low voltage conductivity with temperature, and it is found that, apart from the variation between room temperature and 400°C, with no special significance, the decrease of the barrier height from 400°–1153°C induces an extra change of the conductivity from which a fictitious activation energy of 1.5 eV is obtained. Therefore, these two energies are not related to shallow and deep donors in ZnO grains.

**Keywords:** ZnO, varistors, grain boundaries, space charge boundaries, zinc oxide

## 1. Introduction

The non linear *I-V* electrical characteristic of ZnO varistors is caused by potential barriers at grain boundaries. Two main models have been proposed to describe the occurrence of these barriers: (i) the existence of surface states [1,2]; and (ii) the depletion of oxygen vacancies [3,4]. Depletion of oxygen vacancies is suggested to take place during the cooling of the ceramic samples, after the sintering process, when defects must migrate to the grain boundaries to be there annihilated. This model, called surface oxidation because oxygen vacancies are being annihilated at the grain boundaries, predicts that inside the grains, far away from the grain boundaries,

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donor defects are frozen and the ZnO bulk remains a n-type semiconductor.

We have observed that the barrier height grows during the cooling period [5]. This conclusion was taken by measuring the variation with temperature of the low resistivity region of samples that had been slowly cooled from the sintering temperature to lower temperatures, from where they were quenched to room temperature. This observation, although qualitatively justifiable by the migration of defects, was not supported by theoretical calculations, performed by Mahan [6], showing that the contribution due to the migration of defects to the barrier height (< 0.1 eV) could be neglected for experimentally observed barriers ( ~ 1.0 eV).

Another possibility to test the depletion of defects model [3,4] could be obtained by calculating the carrier concentrations in the bulk of ZnO grains with different grain sizes after the ZnO varistor is cooled to room temperature. For relatively small grain sizes there is a possibility that the major part of the oxygen vacancies migrate to the grain boundaries turning the ZnO grains bulk resistive. On the other end, for large grain sizes, the bulk of the grains will remain conductive. We have tested this possibility and came to the conclusion that the grain size could affect the ZnO bulk resistivity in the way predicted by the surface oxidation model, provided that the main donor defect is the zinc interstitial rather than the oxygen vacancy [7]. However, the calculated contribution to the barrier height due to this mechanism was again too small ( ~ 0.1 eV).

As we reported in [8], the barrier height depends on the bulk Fermi level, $E_{\mathrm{Fgo}}$, at least from room temperature up to 160°C, and since ZnO is a n-type semiconductor, it depends on the donor concentration inside the grains. In the studied temperature range, the interface Fermi level in equilibrium, $E_{\mathrm{Fbo}}$, decreases with the increase in temperature, and the extrapolation of this behavior for temperatures above 160°C lead us to conclude that around 450°C $E_{\mathrm{Fbo}}$ will reach the half-width of the ZnO band gap. From this point to higher temperatures, $E_{\mathrm{Fbo}}$ could either follow the change of the half-width of the band gap with temperature, or cross it down to lower energies. In the first case the system would be better described by the surface oxidation model, because in that case the grain boundary will behave as a nearly stoichiometric material, while in the second one it would be better described by the surface states one, because in this model the grain boundary behaves as a p-type semiconductor [2]. High temperature characterization is therefore a good tool to understand the formation of the barrier heights in these ceramics. ZnO varistors were characterized at high temperatures by Matsuoka [9] and by Philipp and Levinson [10]. To check the applicability of the situation described above, we used the results of the last authors because some other important parameters could be found in other papers by the same authors.

## 2. Calculations

To calculate the equilibrium Fermi level at the interface, $E_{\mathrm{Fbo}}$, at any temperature, we need to fit the low voltage ohmic region of a theoretically calculated *I-V* curve to an experimental one. We used the Double Schottky Barrier model, developed by Greuter and Blatter [11], to generate the theoretical curves, with the same procedure used before [8], and took the experimental curves from the work of Philipp and Levinson [10]. When both curves fit together, one immediately obtains the value of $E_{\mathrm{Fbo}}$ (in what follows, the subscript ''*o*'' will denote equilibrium conditions, i.e., with no applied field).

In generating the theoretical curves, one must firstly calculate the relation between the barrier height, $e\Phi_B$, with the applied voltage per grain boundary, *V*, which, neglecting the small contribution of deep donors, is

$$\Phi_B = \frac{V_C}{4}\left(1 - \frac{V}{V_C}\right)^2 \quad (1)$$

The critical voltage, $V_C$, is related to the accumulated charge at the interface, $Q_i$, and to the concentration of shallow donors in the grains, $N_D$, by

$$V_C = \frac{Q_i^2}{2e\varepsilon\varepsilon_o N_D} \quad (2)$$

where $\varepsilon$ is the relative permittivity of the material, $\varepsilon_O$ the vacuum permittivity, and *e* the electronic charge.

Upon the application of the voltage, the Fermi level at the interface shifts to higher energies, and therefore more surface states are being filled with electrons. This means that the accumulated charge at the interface is increasing due to the electron trapping, and it follows that

$$Q_i = e \int_{\xi_i^n}^{\infty} N_i(E) f_i(E) dE \quad (3)$$

Here, $\xi_i^n$ is a fictitious Fermi level describing the neutral interface, and $N_i(E)$ and $f_i(E)$ are the density of surface states and their probability of occupation, respectively. So, for a given applied voltage $V$, one can obtain $V_C$ through the calculation of $Q_i$. But $e\Phi_B$ also depends on the interface Fermi level, because

$$E_g = E_{\mathrm{Fb}} + e\Phi_B + \varepsilon_\xi \quad (4)$$

where $E_{\mathrm{g}}$ is the band gap of the material and $\varepsilon_\xi$ is the energy of the bulk Fermi level (relative to the conduction band edge). Consequently, any pair of $(\Phi_B, V)$ values must be found in a self-consistent way [11].

Once the $\Phi_B$–$V$ relation is found, the $I$-$V$ curve can be generated by the equation

$$J_{\mathrm{dc}} = A^* T^2 \exp[-(e\Phi_B(V) + \varepsilon_\xi)/\mathrm{kT}] \\ [1 - \exp(-eV/\mathrm{kT})] \quad (5)$$

assuming a thermionic emission mechanism, and omitting the small correction factor of the electron capture probability. In Eq. (5), $J_{\mathrm{dc}}$ is the dc current density, $A^*$ is the Richardson constant, $T$ the absolute temperature, and $k$ the Boltzmann constant. This equation applies to the case when the varistor quality factor, the $\alpha$ value of the empirical equation $I = kV^\alpha$ for the breakdown region, is less than $\alpha < 25$ [12], because for higher $\alpha$ values other mechanisms should be incorporated to describe the electrical behavior, namely the impact ionization [13]. In this work, we are only analyzing the low ohmic resistivity part of the $I$-$V$ curves, i.e., the region where Eq. (5) is observed.

To calculate the equilibrium Fermi level at the interface, we need to know the density of ionised donors near the interface, $N_D$, which can be obtained by $C$-$V$ measurements [14,15]. Philipp and Levinson did not present $C$-$V$ values in their work, and therefore we had to get around this in another way. The equilibrium Fermi level at the interface determines, for a given temperature, the low voltage resistivity of the varistor. This can be seen from Eq. (5) when $V \to 0$, which gives the conductivity (we are assuming that $V$ is the voltage per grain boundary and not the voltage applied to the ceramic sample),

$$\sigma_{\mathrm{dc}} = eATk^{-1} \exp[-(e\Phi_{B0} + \varepsilon_\xi)/kT] \quad (6)$$

and noting that the activation energy for the conduction, $E_A = e\Phi_{B0} + \varepsilon_\xi$, is controlled by $E_{\mathrm{Fbo}}$ (Eq. (4)).

Without applied voltage, the barrier height is given by

$$\Phi_{B0} = \frac{Q_{io}^2}{8e\varepsilon\varepsilon_O N_D} \quad (7)$$

and $\varepsilon_\xi$ is fixed by the bulk chemical defect. Therefore, for a given temperature, the resistivity of the sample reveals the equilibrium Fermi level at the interface through Eq. (6), whatever the relative proportion of $e\Phi_{B0}$ and $\varepsilon_\xi$ in $E_A$. If we know the $\varepsilon_\xi$ value, we can know the $e\Phi_{B0}$ value, and in this case we do not need the value of $N_D$ to calculate the interface Fermi level. In fact, $N_D$ will only affect the $Q_i$ value in Eq. (7), and in the calculations we are pursuing, this is not important.

Fixing $\varepsilon_\xi$ in Eq. (4), we can find a $e\Phi_{B0}$ value that gives the appropriate $E_{\mathrm{Fbo}}$ energy. In Eq. (4) all the parameters change with temperature, and one can not know a priori the $\varepsilon_\xi$ value. However, since it is the resistivity, through $E_{\mathrm{Fbo}}$, that determines the $(e\Phi_{B0} + \varepsilon_\xi)$ pair, $E_{\mathrm{Fbo}}$ can be readily calculated if one uses any reasonable $\varepsilon_\xi$ value for a semiconductor. We must point out that our calculations are done in an iterative way, i.e., we have fixed the $\varepsilon_\xi$ value, calculated the interface Fermi level, and feedback the new $\varepsilon_\xi$ value coming out from the considerations explained later in section 4. In spite of this procedure, the calculation of the $E_{\mathrm{Fbo}}$ value was not affected by the $\varepsilon_\xi$ value, as expected.

To generate the theoretical $I$-$V$ curves, we also need other parameters, namely the mean grain size, $G$. The mean grain size value is taken from other papers of Philipp and Levinson, since the authors worked with the same type of varistors, and is listed in Table 1 together with other important features for ZnO.

## 3. Variation of $E_{\mathrm{Fbo}}$ With Temperature

As pointed before, all the energy values in Eq. (4) are temperature dependent, being particularly important the variation of the band gap, $E_g$, with temperature. Kröger [18], Einzinger [3], and Schwing and Hoffmann [4], used the temperature coefficient $\beta$ in the following equation,

$$E_g = E_{gO} - \beta T \quad (8)$$

equal to $\beta = 10^{-3}$ eV/K. However, Philipp and

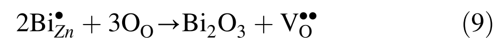
*Table 1.* Material parameters used to generate the theoretical *I-V* curves

| Parameter | Value | Ref. |
|---|---|---|
| Relative permitivity, $\varepsilon$ | 8.5 | 16 |
| Effective mass (kg) | 0.25m$_o$ | 11 |
| Grain size ($\mu$m) | 20 | 17 |
| Richardson constant (Acm$^{-2}$K$^{-2}$) | 30 | |

Levinson [9] obtained a variation of the breakdown voltage, $V_b$, with temperature of $dV_b/dT = \beta' = -2 \times 10^{-4}$ VK$^{-1}$, and this change is correlated to the variation of the ZnO band gap with temperature. In fact, the breakdown region in varistors is empirically described by $I = kV^{\alpha}$, and when $\alpha$ is greater than 25, which is the case here, tunneling of electrons from one grain to the other [4] or the impact ionisation generated by hot electrons near the interface [13], must be taken into consideration when modeling the physical behavior of these materials. In both cases, the potential energy, eV, at the interface must be equal or higher than the energy of the band gap. Therefore, the decreasing of $V_b$ with temperature is caused by the decreasing of the ZnO band gap with temperature, i.e., $\beta' = -2 \times 10^{-4}$ VK$^{-1}$ is equivalent to the change of the ZnO band gap. This value is lower than the proposed one, $\beta = 10^{-3}$ eV/K. Jensen [19] measured the variation of the ZnO band gap by optical methods, up to 300 K, and obtained $E_g = 3.46 - 3.65 \times 10^{-4}$ T. We did use this equation because $\beta$ is close to the value of $\beta'$, and there is always some uncertainty in the determination of the *I-V* curves in the breakdown region, particularly when $\alpha$ is high. Our extrapolation of this equation to temperatures much higher than those where it was obtained is of course questionable, but in view of the good agreement with $\beta'$, one can consider it a good approximation for the present case.

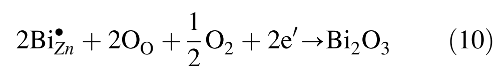
Figure 1 shows the variation of $E_g$, $E_g/2$, and $E_{\mathrm{Fbo}}$, with temperature. It can be observed that $E_{\mathrm{Fbo}}$ decreases with temperature more rapidly up to around 700°C, and then follows the $E_g/2$ curve. The Fermi level at the interface almost reaches the situation where the material behaves stoichiometrically, and never shows a p-type character. This is expected if the surface oxidation mechanism is operating. However, as already pointed out, the diffusion coefficients for the ZnO intrinsic defects are not sufficiently high at temperatures as low as 700°C to promote the annihilation of the defects at the grain boundaries [6,7]. Moreover, there is no observable differences in the *I-V* and *C-V* curves of two samples, both slowly cooled to 650°C and kept at that temperature for 2 h and 60 h, respectively, before quenching to room temperature [5]; if the surface oxidation mechanism was operating at this temperature, the sample with longer heat treatment should show higher resistivity (both samples had the same mean grain size). Therefore, the variation of $E_{\mathrm{Fbo}}$ with temperature, as shown in Fig. 1, must be viewed in a different way. The oxidation of intrinsic or extrinsic donors in the grain boundaries, which keeps the local Fermi level near the middle of the band gap, must be due to species able to operate down to temperatures as low as 700°C. One obvious candidate to promote the oxidation of the donor species is the oxygen molecule itself, adsorbed at the grain boundaries in the form of $O^-_{2(\mathrm{ads})}$. We shall analyse this possibility in what follows, using whatever experimental evidence we can take from the literature to suggest a possible mechanism.

We observed by TEM analysis [20] that, among the dopants normally added to ZnO, only Bi is clearly segregated to the grain boundaries during cooling of the samples, and that this process occurs for temperatures lower than 950°C. Although the solubility in the grain boundaries is higher than that in the bulk material, there is always the possibility that the Bi segregation to the grain boundaries can reach the solubility limit. An exsolution process will than take place. In the case of Bi one can have



$$2\mathrm{Bi}^{\bullet}_{Zn} + 3\mathrm{O_O} \rightarrow \mathrm{Bi_2O_3} + \mathrm{V}^{\bullet\bullet}_{\mathrm{O}} \qquad (9)$$

where we used the Kröger-Vink's notation for bismuth in a normal zinc site, $\mathrm{Bi}^{\bullet}_{Zn}$, and for oxygen vacancy, $V^{\bullet\bullet}_{O}$, both completely ionized. Reaction (9) should be observed in a reducing atmosphere. In air, or in oxidising atmosphere, the reaction of exsolution can be



$$2\mathrm{Bi}^{\bullet}_{Zn} + 2\mathrm{O_O} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{e}' \rightarrow \mathrm{Bi_2O_3} \qquad (10)$$

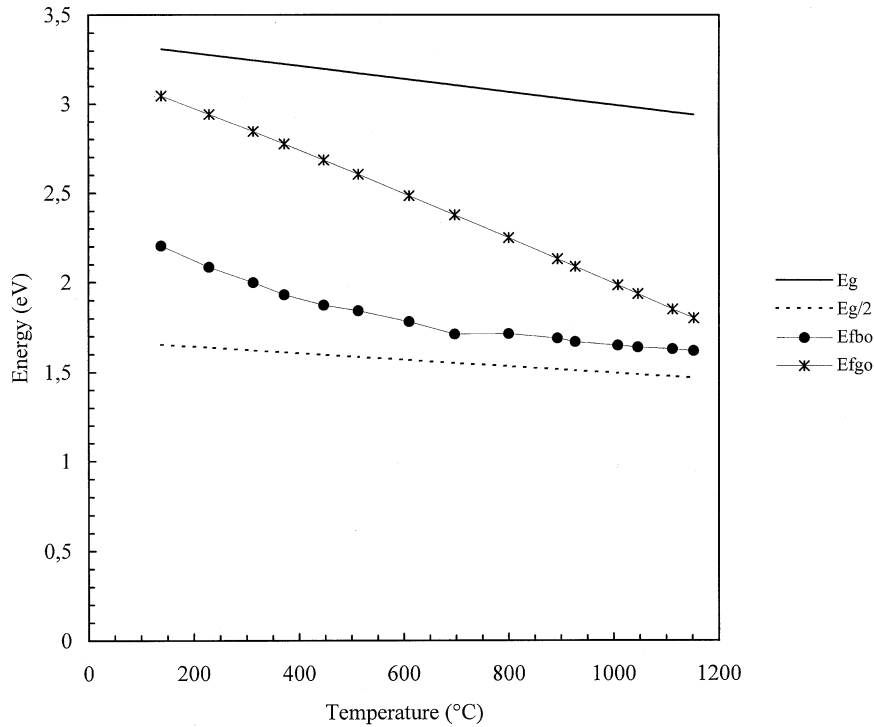
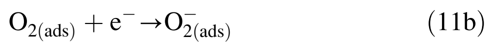


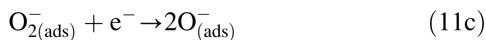

*Fig. 1.* The variation of the energies from room temperature up to 1153°C. The temperature variation of the ZnO band gap, $E_g$, was taken from the data of Jensen [14]. It is also represented the variation of the middle of the band gap, $E_g/2$, to show that the interface Fermi level in equilibrium, $E_{fbo}$, approaches it up to 700°C and stays close to it afterwards. The temperature variation of the bulk Fermi level, $E_{fgo}$, is calculated trough the reduced electroneutrality condition, Eq. 11. Note that the difference between the two Fermi levels is the barrier height energy.

The oxygen molecule could pass through the following reactions:

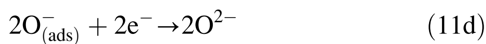
$$O_{2(g)} \rightarrow O_{2(ads)} \quad (11a)$$



$$O_{2(ads)} + e^{-} \rightarrow O^{-}_{2(ads)} \quad (11b)$$



$$O^{-}_{2(ads)} + e^{-} \rightarrow 2O^{-}_{(ads)} \quad (11c)$$



$$2O^{-}_{(ads)} + 2e^{-} \rightarrow 2O^{2-} \quad (11d)$$

and each of them will be more or less completed depending on the temperature. So, in Eq. (10) the reaction product can also be $Bi^{\bullet}_{2}O_2 \cdot \frac{1}{2}O^{-}_{2(ads)}$ if the temperature is low, emphasizing the fact that it is not a complete exsolution process. This means that chemical analysis of fracture surface can either show the presence of $Bi_2O_3$ in its different polymorphs [21], or no second phase at all [22,23]. Greuter and Blatter [11] showed the tight relation between the oxygen coverage of the surface of the grains and the varistor electrical properties in these materials: the higher the oxygen coverage, the higher the resistivity of the low voltage region, i.e., the higher the barrier height. A degradation process gave the minimum of the oxygen coverage [11], and the degradation phenomenon was viewed as caused by the exhaustion of surface states and the release of oxygen [24]. A heat treatment at 500°C in air of the degraded sample, restored the original *I-V* curve [11], i.e., the migration of the oxygen through grain boundaries is observed for temperatures as low as this one.

Accepting that oxygen adsorption is a possible mechanism for the oxidation of the surface of the grains, the intrinsic donor species at the grain boundaries, oxygen vacancies or zinc interstitials, will be annihilated from the sintering temperature down to at least $\sim$ 700°C, and since donors are the major defects contributing to the n-type character of the ZnO conductivity, any decrease of these defects will turn the material a resistive one, or, in other words, ZnO becomes an intrinsic insulator at the grain boundaries. This means that the interface Fermi level

is kept at the middle of the ZnO band gap during the oxidation of the grain boundaries. We are now able to understand the formation of the barrier height in these materials. A last comment should be put on before that, and it is related to the possibility of the exsolution mechanism be observed in reducing atmosphere, as shown by Eq. (9). In this case completely ionized oxygen vacancies will be formed. This is a deep donor defect lying at an energy of $\sim 2.0\,\text{eV}$ from the conduction band edge [4], and its concentration arising from Eq. (9) is low. These two conditions are also enough to keep the interface Fermi level very low in energy, near the middle of the band gap, which means that a material prepared in reducing atmosphere should also show a barrier height at the interface. In fact, we observed [20] that samples sintered and slowly cooled in nitrogen and then quenched at different pre-defined temperatures, have good varistor properties below $\sim 750°\text{C}$; samples quenched from higher temperatures showed ohmic semiconductor characteristics.

## 4. Growth of the Barrier Height, $\Phi_{B0}$

Up to now, we have explained how $E_{\text{Fbo}}$ is kept near the middle of the band gap from high temperatures down to $\sim 700°\text{C}$. Below this temperature, $E_{\text{Fbo}}$ increases in energy with decreasing in temperature (Fig. 1), and it is approaching to the bulk Fermi level, $E_{\text{Fgo}}$ (we don't know yet the exact energy of $E_{\text{Fgo}}$, but it must be near the conduction band since ZnO grains are n-type semiconductors). Due to the oxidation of the surface the material is in a metastable situation; if the oxidation is no longer effective, then the Fermi level at the interface must follow the change of the bulk Fermi level. This is what happens for temperatures below 700°C, and we shall use the temperature change of $E_{\text{Fbo}}$ to compute the change of $E_{\text{Fgo}}$ with temperature.

Considering that the ZnO bulk is a n-type semiconductor, we have the reduced electroneutrality condition

$$n = [D^{\bullet}] + p \tag{12}$$

where $n$ is the electron concentration in the conduction band, $[D^{\bullet}]$ a monoionized donor, and $p$ the concentration of holes in the valence band. All of them are related to the bulk Fermi level, $E_{\text{Fgo}}$, trough

$$n \approx N_C \exp\left[-\left(E_g - E_{\text{Fgo}}\right)/kT\right] \tag{13a}$$

$$p = N_V \exp\left(-E_{\text{Fgo}}/kT\right) \tag{13b}$$

$$[D^{\bullet}] = [D][1 - P(E_D)] \tag{13c}$$

considering the zero of the energy scale in the top of the valence band, $E_V = 0$, and

$$N_C(N_V) = 2\left(\frac{2\pi m_e^*\left(m_h^*\right)kT}{h^2}\right)^{3/2} \tag{13d}$$

$$P(E_{\text{D}}) = \frac{1}{1 + \exp\left[\left(E_D - E_{\text{Fgo}}\right)/kT\right]} \tag{13e}$$

[[D] is the total donor concentration, $E_{\text{D}}$ is the donor level, $m_e^*$ and $m_h^*$ the electron and hole effective mass, respectively, $P(E_{\text{D}})$ is the probability of occupancy of the donor level, and $h$ is the Planck's constant.] For each temperature, Eq. (12) can be solved numerically and give the $E_{\text{Fgo}}$ value. The only parameter that must now be defined is the energy of the donor level, $E_{\text{D}}$, and its change with temperature. Since it is usual to accept that the donor in ZnO is an intrinsic defect, either the oxygen vacancy, ${V_O}^x$, or the zinc interstitial, ${\text{Zn}_i}^x$, with an energy $\varepsilon_D = E_g - E_D = 0.05\,\text{eV}$ at room temperature, we took this value together with its variation with temperature in the same way used by Schwing and Hoffmann [4], to get

$$E_D = 3.409 - 3.60 \times 10^{-4}\,\text{T eV} \tag{14}$$

With this equation and Eq. (8), defining the [D] concentration, Eq. (12) can be solved for any temperature. As mentioned above, we are looking for a temperature variation of $E_{\text{Fgo}}$ equal to the temperature dependence of $E_{\text{Fbo}}$, at least for temperatures below $\sim 400°\text{C}$, since it is below this temperature that the variation of $E_{\text{Fbo}}$ is more pronounced (between 400° and 700°C there is some uncertainty of the effectiveness of the oxidation of the grain boundaries in keeping the Fermi level near the middle of the band gap) (Fig. 1). The best fitting between $E_{\text{Fgo}}$ and $E_{\text{Fbo}}$ for these conditions to be verified is obtained for $[D] = 3 \times 10^{17}\,\text{cm}^{-3}$. Since donors are controlling the concentration of electrons in the conduction band and in this temperature range donors are almost exhausted, then $n \sim [D] \sim 3 \times 10^{17}\,\text{cm}^{-3}$, which is in excellent agreement with the experimental values [25]. The ZnO grain resistivity is then $\rho \sim 20\,\Omega\text{cm}$ (assuming an electron mobility of $\mu_e = 100\,\text{cm}^2/\text{Vs}$). Philipp and

Levinson [10] obtained $\rho \sim 10\,\Omega$cm by *I-V* measurements at high temperatures, $\sim$ 1300°C.

We can now calculate the barrier height, $\Phi_{B0}$, at any temperature, since $\Phi_{B0} = E_{\text{Fgo}} - E_{\text{Fbo}}$. This is plotted in Fig. 2. It can be seen that $\Phi_{B0}$ is almost constant from room temperature up to $\sim$ 400°C, and then decreases with temperature. This behavior is in good agreement with that obtained from the *I-V* curves of quenched samples [5], and explains the variation of the low voltage ohmic conductivity with temperature. For this last point, Philipp and Levinson [10] obtained three activation energies from the plots of $\ln(\sigma) - vs - 1/\text{T}$ : 0.7 eV, from room temperature up to around 400°C; 1.6 eV, from 400°C to around 900°C and 0.8 eV, from 900°C to 1300°C. In the present calculations, taking $\sigma = \sigma_O \exp(-\Phi_{B0}/\text{kT})$ and making the same type of plotting, we obtain 0.8 and 1.5 eV for the first two cases (we didn't calculate the activation energy for higher temperatures because our calculations were limited to 1153°C). This means that these activation energies determined by the conductivity measurements at low applied fields are not related to shallow or deep donors in the ZnO grains, but instead to the change of the barrier height with temperature: up to 400°C, $\Phi_{B0}$ is almost constant, $\sim$ 0.8 eV, but after that it decreases, and because of that, the conductivity increases more than if $\Phi_{B0}$ was constant; consequently, it will show a higher activation energy.

## 5. Further Considerations

We should make some final remarks concerning the above calculations and look for their consequences in ZnO varistor development. We used the Double Schottky Barrier (DSB) model to calculate the energy of the interface Fermi level in equilibrium for different temperatures, using *I-V* data taken from the literature. In this model, it is assumed that the concentrations of the donor species in the material, shallow and deep, are constant throughout the material. This is not strictly true, particularly in the case of Bi ions, since the solubility of the species is higher in the grain boundaries than in the bulk of the material. Any physical/electrical description of the system needs to solve the Poisson equation, and obviously one need to define the charge density, $\rho(x)$,

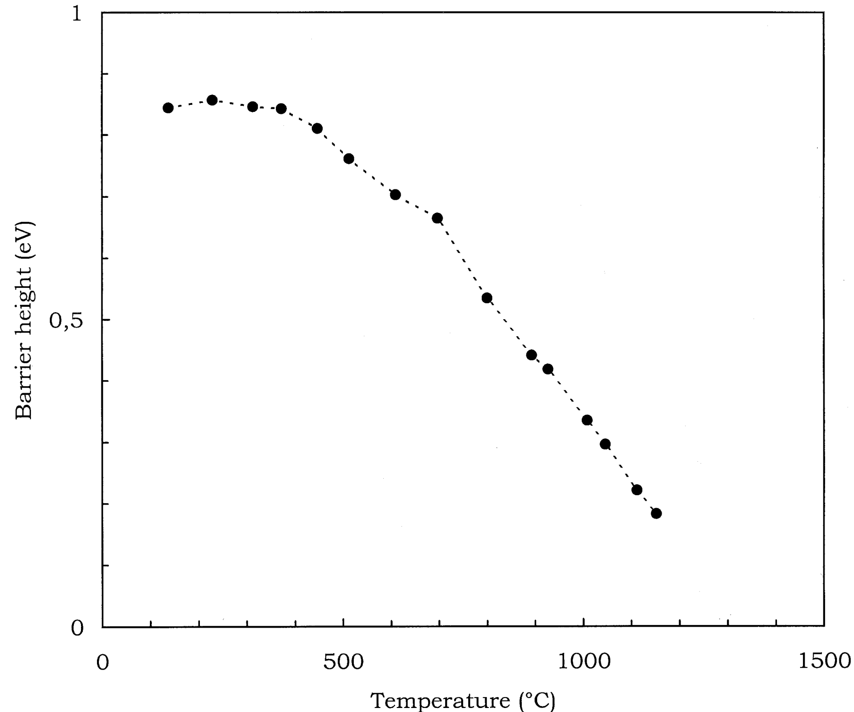



*Fig. 2.* Variation of the barrier height energy with temperature.

for the case under analysis. The definition of a charge density arising from the diffusion of defects to the grain boundary, as is done in the case of the surface oxidation model, will give a potential function, $\Phi(x)$, quite different from the DSB model (Fig. 3). However, whatever the charge density function, the final target is always the derivation of the experimental *I-V* curves, and, since the barrier height is controlled by the Fermi level at the interface and this in turn controls the low voltage resistivity part of the *I-V* curves, any charge density must give the same energy for the Fermi level. We used the DSB model because it gives an easier way to calculate the interface Fermi level. Consequently, our goal was to look for the implications of the variation of this energy with temperature on the proposal of a mechanism for the growth of the barrier height. We shall turn to this point later in this section.

One important item in our calculations is the temperature variation of several parameters, particularly that of the band gap. The other parameter variations were related to this one, or were omitted, like the variation of the ZnO permittivity that enters in Eqs. (2) or (7), or the temperature variation of the surface states. The variation of the permittivity does not interfere with the calculation of the barrier height (the barrier height is calculated from the bulk and interface Fermi levels), and we are not calculating the variation of the surface states. We emphasize again that only the low voltage ohmic region of the *I-V* curves was used in our analyses; for higher voltages and to calculate the distribution of surface states, for example, other parameters should be known a priori, namely the density of ionised donors near the grain boundaries, as already stated.

From the variation of the equilibrium Fermi level at the interface with temperature, we arrived to the conclusion that grain boundaries are being oxidized during cooling, down to $\sim 700°C$, but with a mechanism different from the surface oxidation one. Calculations made by Mahan [6], and also by ourselves [7], showed that the surface oxidation will only contribute to the barrier height growth by not more than 0.1 eV, due to the low diffusion coefficient of the defects at low temperatures. In view of this result, we propose that the oxidation of the grain boundaries is done by ambient oxygen reacting with bismuth, the varistor ''forming'' element. There is always the possibility for oxygen to react with other extrinsic defects, and that such reactions could pursue

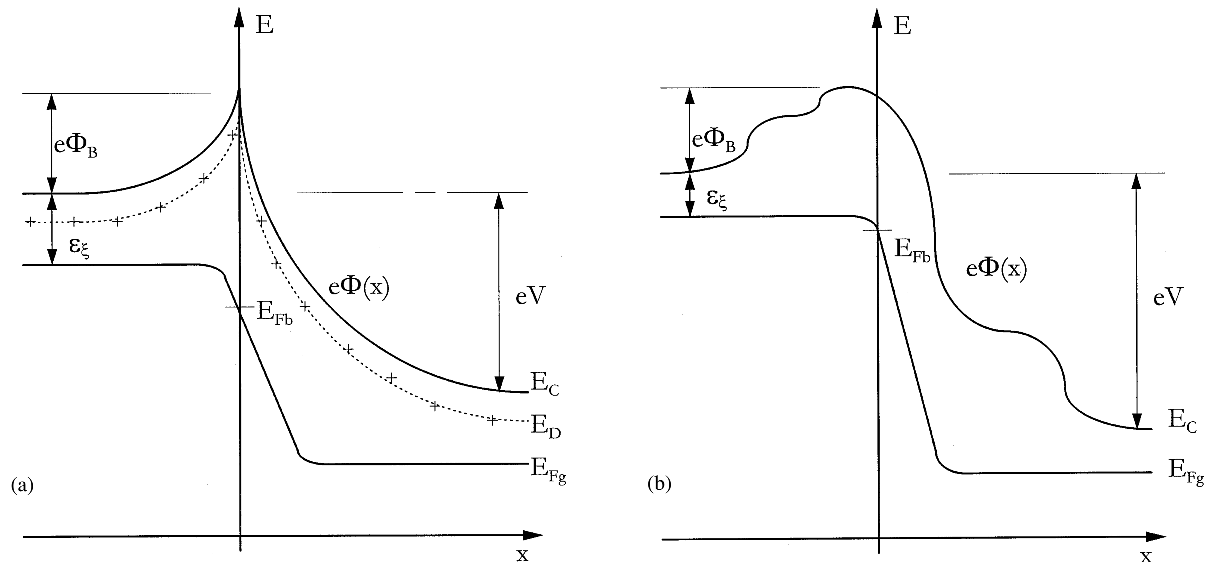



*Fig. 3.* Energy band diagram for the Double Schottky Barrier (DSB) model (a), and for the surface oxidation one (b). In both cases, the diagrams are adapted from [11] and [4], respectively, and only the upper energy part of the diagram is represented. It can be seen that the potential function, $\Phi(x)$, is very dependent on the distribution of the charge density, $\rho(x)$: in (a), uniform distribution of donors is assumed to be present in the bulk of the material and a delta function is assumed for the trapped charge at the interface [11]; in (b) the charge distribution is depending on the cooling conditions, which affect the diffusion coefficient of the chemical defects [4].

to temperatures lower than 700°C. However, the increase of the interface Fermi level below that temperature, is consistent with the change of the bulk Fermi level, meaning that, even if these reactions are present they are less important to the growth of the barrier height.

The present work explains previous experimental results [5] showing that the cooling of ceramic samples must be slow down to around 700°C, in order to allow the grain boundary oxidation, and then can be fast to room temperature since electronic equilibrium is easily attained. At this temperature, the equilibrium Fermi level at the interface reaches its lowest value in energy relative to the bottom of the conduction band, and begins to increase below that temperature following the variation of the bulk Fermi level. Therefore, in order to have a higher barrier, it is important to increase the bulk donor concentration, because in that case the bulk Fermi level will change smoothly with temperature. This can be done either by doping, e.g., by Al doping, or controlling simultaneously the sintering time (to have large grains) and the cooling rate (to avoid a large diffusion of defects to the grain boundaries).

## 6. Conclusions

We calculated the equilibrium Fermi level at the interface, $E_{\mathrm{Fbo}}$, using the Double Schottky Barrier model, in a way described elsewhere [8], in the temperature range of $\sim 100$°C to $\sim 1150$°C, using the *I-V* data from the work of Philipp and Levinson [10] and the variation of the ZnO band gap, $E_g$, given by Jensen [19]. It is observed that $E_{\mathrm{Fbo}}$ never crosses the middle of the ZnO band gap, i.e., the interface never shows a p-type character. Above $\sim 700$°C, $E_{\mathrm{Fbo}}$ is close to $E_{\mathrm{g}}/2$ and this means that the interface must be oxidized because ZnO is a n-type semiconductor after normal processing conditions. Since the surface oxidation mechanism due to the migration of intrinsic defects to the grain boundaries during cooling, is inoperative at low temperatures (700°C), we suggest that the oxidation is being due to the adsorption of oxygen molecules on the surface of the ZnO grains. This adsorption will occur in specific sites connected with the presence of the segregated bismuth ions. For lower temperatures, when this mechanism is also inoperative, $E_{\mathrm{Fbo}}$ follows the temperature change of the bulk Fermi level, $E_{\mathrm{Fgo}}$. With this assumption, it is possible to calculate the $E_{\mathrm{Fgo}}$ values for the different temperatures, and a good fitting is obtained when one considers that the bulk donor concentration is $[D] = 3 \times 10^{17}\,\mathrm{cm}^{-3}$. This result is in good agreement with the experimental values, and the calculation of the barrier height for each temperature gives a temperature dependence also in good agreement with experiments.

On one hand, electrical barriers in ZnO varistors are formed during the cooling period after sintering, but they are not caused by the migration of defects to the grain boundaries, as the surface oxidation model proposes. On the other hand, the pre-existing charge at the interface is not a ZnO intrinsic feature, as it would be if it was originated by the zinc vacancies, which would turn the grain boundaries a p-type material, as the surface states model proposes. The charge at the interface is caused by oxygen adsorption, which can turn the grain boundaries nearly stoichiometric, keeping the interface Fermi level close to the middle of the band gap. This is the main conclusion of the present work; however, it must be emphasized that our conclusion is only related to equilibrium conditions, since the interpretation of the variation of the barrier height with applied voltage, i.e., the varistor properties themselves, is beyond the scope of the present work and will be analyzed in a forthcoming paper.

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