Non-linear $I$-$V$ characteristics of double Schottky barriers and polycrystalline semiconductors

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Abstract

An attempt to determine theoretically the highly non-linear current-voltage ($I-V$) characteristics of polycrystalline semiconductors, such as ZnO-based varistors, is made from the electrical properties of individual grain boundaries under dc bias. The role played by the fluctuations of double Schottky barrier heights at grain interfaces on driving electrical breakdown phenomena of macroscopic samples is pointed out in terms of a binary mixture model. An alternative trial form for the double Schottky barrier height is introduced to reproduce the breakdown voltage as well as the high non-linear coefficient $\alpha$, where $I \propto V^\alpha$.

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A grain boundary in polycrystalline semiconductors (PCS) becomes electrically active as a result of charge trapping by gap states localized in the interface between adjacent grains. Such interface states may be created by the impurities, dislocations or interfacial defects and give rise to the appearance of double Schottky barriers [1]. The electrical conduction through a grain boundary Schottky barrier may be determined by different conducting mechanisms, such as tunneling, field emission, space-charge limit, thermoionic emission, etc., (see, e.g., [2]), depending on the material and preparation. In (commercial) ZnO-based varistors at room temperature, thermoionic emission is believed to be the dominant mechanism for electrical conduction through a (grain-boundary-grain) GBG junction [2, 3, 4, 5].

Nevertheless, a theoretical analysis of the non-linear current-voltage (I-V) characteristics of a macroscopic sample of PCS from the point of view of electrical properties of individual GBG junctions is not trivial. This non-linearity is due to the complex charge and current feedback mechanisms occuring at grain boundaries which lead to a large variety of potential barriers. Thus, the barrier height (and, in correspondence, the breakdown voltage) of a GBG junction differs from one to another as shown by microelectrode measurements [6, 7]. The random nature in size and position of grains is revealed by electron micrograph experiments [2, 3, 6, 7, 8].

The simplest model proposed to characterize ZnO-varistors is due to Levinson and Philipp [9]. In their model all ZnO-GBG junctions are assumed to be identical and regularly arranged in a cubic lattice. To a crude approximation, the I-V characteristics of PCS then became completely determined by the properties of one GBG junction. More recent studies, that included parallel or series GBG structures or used the percolation approximation, have also neglected fluctuations of double Schottky barrier heights [8, 10]. Thus, the question of how the non-linear coefficient $\alpha$, where $I \propto V^\alpha$, and the electrical breakdown voltage of PCS may be affected by the distribution of barrier heights at grain boundaries is still open.

In this work we made the first attempt to determine in simple terms the highly non-linear I-V characteristics of ZnO-based varistors under dc bias by considering the non-linear electric characteristics of single grain boundaries. For that purpose, we use a 3D
effective medium approximation (EMA) \cite{11, 12} for a binary mixture of grain boundary Schottky barriers, having different heights, in conjunction with the thermoionic emission mechanism (TEM) for the carrier transport through grain boundaries. An alternative trial form for the voltage dependence of a single barrier height is also introduced. Herein, we study as a function of barrier probability the variations in the macroscopic (i) non-linear coefficient $\alpha$ and (ii) electric breakdown voltage $V_B$ of a PCS sample featured by the binary mixture.

The quantity $\alpha$ is commonly defined as

$$\alpha(V) = \frac{d(\ln I)}{d(\ln V)} .$$

(1)

For the breakdown voltage $V_B$, however, there are somewhat different definitions. For the present purposes, it is natural to define $V_B$ as the voltage related to the maximum value of $\alpha(V)$, i.e. as the solution of

$$\left(\frac{\partial \alpha}{\partial V}\right)_{V_B} = 0 .$$

(2)

Accordingly, by $\alpha \equiv \alpha(V_B)$ we shall denote the maximum value of the non-linear coefficient.

In the traditional TEM the current that is injected through a potential barrier is

$$I = A^*T^2e^{-\frac{\phi(V)+E_f}{k_BT}}(1-e^{-\frac{eV}{k_BT}}) ,$$

(3)

where $A^*$ is Richardson’s constant, $V$ is voltage drop across a junction, $E_f$ is the Fermi energy in the grain bulk (counted from the bottom of the conducting band), $T$ is the temperature, $e$ is the elementary charge and $\phi$ is the potential barrier height that depends on $V$.

Solving the Poisson equation, within the simplest framework of the double Schottky barrier model (i.e. neglecting effects due to holes and interface processes), such that the interface charge is independent of $V$ and time, $\phi(V)$ is found to be

$$\phi(V) = \phi_o(1 - \frac{eV}{4\phi_o})^2 ; \quad (eV \leq 4\phi_o) ,$$

(4)
where $\phi_o \equiv \phi(V = 0)$ is the potential barrier height at zero applied $V$. The voltage $V_c = \frac{4\phi_o}{e}$, that is related to $\phi(V_c) = 0$, is often interpreted as the critical voltage for electric breakdown in a single GBG junction [1].

Nevertheless, according to definitions (1) and (2) and to the $I$-$V$ characteristics of an individual GBG junction, i.e. Eqs.(3) and (4), the breakdown voltage to a first approximation can be estimated from

$$V_B \approx \frac{2\phi_o}{e},$$

(5)

and, in correspondence, the non-linear coefficient then becomes

$$\alpha \approx \frac{\phi_o}{2k_BT}.$$  

(6)

Thus, the value of $V_B$ given in Eq.(3) is two times less than the above $V_c$ value. The measured breakdown voltages are really about $V_c$ [2, 3, 4]. For a typical value of $\bar{\phi}_o \approx 0.75 \text{ eV}$ at room temperature, Eq.(2) leads to $\alpha \approx 15$, which is not high enough to explain the observed strong non-linearity of $I$-$V$ characteristics of typical ZnO-based varistors ($\alpha \approx 25$ to 50 or more) [9].

In Fig.1 (left-hand side axis) the behaviour of $\phi(V)$ as given by Eq.(4) is compared with measured data normalized to a single junction ($\phi_o = 0.73 \text{ eV}; T = 300 \text{ K}$) [13]. This figure shows the poor agreement obtained with experimental results which have only a slight voltage dependence at small values of applied $V$ and suddenly decrease in the vicinity of the breakdown region. In this figure the principal features of Eq.(3) using Eq.(4) are also depicted for the same set of parameters (right-hand side axis).

We note that at $\frac{eV}{k_BT} < < 1$, i.e. the prebreakdown region, the $I$-$V$ characteristics obtained using (3) and (4) present an ohmic behaviour with activation energy equal to $\phi_o$. Without paying much attention to this ohmic region, the curves in Fig.1 have been drawn to illustrate electrical breakdown phenomena at a GBG junction. In fact, at $V \approx \frac{2\phi_o}{e}$, this figure shows (solid line, right-hand side axis) that the current in the TEM suddenly increases as $V$ increases in accord to Eq.(4). The value of $\alpha$ obtained from the curve $I(V)$ is exactly $\frac{\phi_o}{2k_BT}$ (c.f. Eq.(4)). For $V \geq \frac{4\phi_o}{e}$, it is experimentally found that the current reaches the value limited by the resistance of the ZnO grains. The
$I$-$V$ characteristics are then described by a second ohmic law which is not accounted by Eq.(3).

The above discussion concerns an individual GBG junction only. As mentioned there exists many junctions in PCS which are not (necessarily) identical and have different $\phi_o$’s. So, we determine next by numerical approach the macroscopic $I$-$V$ characteristics of PCS. To achieve this we consider a 3D-EMA for a binary mixture of GBG junctions with non-linear $I$-$V$ characteristics and use the TEM for d.c. conduction through single GBG junctions.

The EMA, originally proposed in Ref.[11], is a self-consistent scheme used to determine the conductivity of inhomogeneous materials (see also [12]). It consists on replacing the random net by a homogeneous lattice, where all lattice bonds have the same conductance $\sum$. Choosing the lattice spacing to be unity, then $\sum$ is also the macroscopic conductivity of the homogeneous material which can be derived self-consistently as discussed in Ref.[11, 12]. However, it is important to mention here that this approach has been initially applied to linear systems with constant bond conductances $\sigma_1, \sigma_2$. Noting that in this work $\sigma_1$ and $\sigma_2$ of GBG junctions depend on the applied voltage $V$, it is straightforward to repeat the EMA procedure to get a system of self-consistent equations for determining the sample conductivity $\sum$ as a function of $V$. In this case, the prediction of the EMA for $\sum$ of a 3D binary distribution of bond conductances is obtained from

\[
p \frac{\sum - \sigma_1(V)}{\sigma_1(V^*) + 2 \sum} + (1 - p) \frac{\sum - \sigma_2(V)}{\sigma_2(V^*) + 2 \sum} = 0 ,
\]

(7)

and

\[
\frac{V_i^*}{V} = \frac{3 \sum + \sigma_i(V_i^*) - \sigma_i(V)}{2 \sum + \sigma_i(V_i^*)} , \quad (i = 1, 2)
\]

(8)

where $p$ is the probability of having bonds with conductance $\sigma_1$.

We represent next the $ZnO$-grains as lattice sites and the $ZnO$-GBG junctions as bonds. Applying Eqs.(3) and (4) to obtain $\sigma_1$ and $\sigma_2$, each of which is derived assuming different values for $\phi_o^{(1)}$ and $\phi_o^{(2)}$, we can then estimate the conductivity of the system as a function of probability $p$ by solving self-consistently Eqs.(7) and (8).
Figure 2 shows our results for the binary mixture conductivity. These are obtained from EMA within the probability range $0.1 < p < 0.9$ by using typical data for ZnO-based varistors, i.e. $\frac{\phi_o^{(1)}}{k_BT} = 9$ and $\frac{\phi_o^{(2)}}{k_BT} = 30$. In the event of an extremely narrow distribution of one type of barrier heights (either $p=0$ or $p=1$), the predictions of the EMA can be shown to be asymptotically correct [12]. To this end we emphasize again that we are dealing with a binary mixture of grain junctions having positive $p < 1$.

From Fig.2 we get interesting results for the sample conductivity over a wide $p$-interval. For $p < 0.3$, the binary mixture conductivity presents a behaviour similar to the case of single GBG junctions with highest double Schottky barriers $\phi_o^{(2)}$ (c.f. Fig.1). On the other hand, when $p > 0.5$, the sample $\Sigma$ is essentially determined by the lowest double Schottky barriers having $\phi_o^{(1)}$. In the intermediate region $0.3 < p < 0.7$, as discussed below, it is worthwhile to mention that there is an asymmetric contribution to the sample electrical properties from each GBG component.

As it is well known, at the EMA percolation threshold value for the component one, i.e. $p_c^{(1)} \approx 1/3$ [12], the binary sample conductivity slightly deviates from a smooth increasing on varying $V$. Similarly, at the percolation threshold value for the second component, i.e. $p_c^{(2)} \approx 1 - \frac{1}{3}$, the sample $\Sigma$ also deviates from a smooth behaviour on increasing $V$. This is due to deficiencies in the EMA which is known to give unaccurate predictions at these particular junction probabilities [12]. Furthermore it must be noted that, for all $p$-values considered, the sample conductivity continues to be an increasing function of applied voltage until –as we shall see next– electric breakdown occurs. For voltages $V > V_B$, $\Sigma$ tends to the grain conductivity which is chosen as unit for conductivities in our calculations.

Having seen from Fig.2 that, to some extent, the EMA is able to reproduce the typical non-linear $I$-$V$ characteristics of ZnO-based varistors, it is then possible to give an estimate of $V_B$ and $\alpha$ for the macroscopic samples. In Figs.3(A) and 3(B) we summarize the $p$-dependences of $V_B$ and $\alpha$ for the binary mixture, respectively. The full lines correspond to different (quality factor) $\chi \equiv \frac{\phi_o^{(2)} - \phi_o^{(1)}}{\phi_o^{(1)}}$ of barrier heights; namely (1) $\chi = 2$, (2) $\chi = 1$ and (3) $\chi = 1/2$, where $\frac{\phi_o^{(1)}}{k_BT} = 10$ is fixed throughout calculations. The three...
curves displayed in each figure are respectively normalized to the electrical breakdown voltage $eV_B^{(1)}/k_B T = 2\phi_o^{(1)}/k_B T = 20$ and to the non-linear coefficient $\alpha^{(1)} = \phi_o^{(1)}/2k_B T = 5$ due to component one. Since we have chosen $\phi_o^{(2)} > \phi_o^{(1)}$, from Eqs. (4) and (5) we then have $V_B^{(2)} > V_B^{(1)}$ and $\alpha^{(2)} > \alpha^{(1)}$. At $p = 0$, the sample $V_B$ and $\alpha$ become identical to those values derived from a junction with barrier height $\phi_o^{(2)}$. At $p \neq 0$, it is clear that the sample $V_B$ and $\alpha$ varies between $V_B^{(2)} \rightarrow V_B^{(1)}$ and $\alpha^{(2)} \rightarrow \alpha^{(1)}$.

As visualized from Figs. 3(A) and 3(B), the sample $V_B(p)$ and $\alpha(p)$ exhibit sharp variations around $p = 1/2$, especially so at $\chi \geq 1$. When $\chi << 1$, a smooth dependence on $p$ of $V_B$ and $\alpha$ is found on decreasing the probability of $\alpha^{(1)}$-component. In the present cases the sample $\alpha$ reaches a maximum value of $\alpha^{(2)} \approx \phi_o^{(2)}/2k_B T$. It is important to note that, when the conductances (or, alternatively, $\phi_o^{(1)}$ and $\phi_o^{(2)}$) of the components of the binary mixture have nearly same probability $p \approx 0.5$, there is an asymmetric contribution of the components to the non-linear coefficient and electric breakdown voltage of the sample. This asymmetry becomes large on increasing $\chi$. These results imply that the components play different roles on driving macroscopic $I$-$V$ characteristics.

The component with barrier height $\phi_o^{(2)}$ becomes important only at $p \leq 0.5$ and dominant for $p < p_c^{(1)}$. On the other hand, for all $p \geq 0.5$, the sample $\alpha$ and $V_B$ are entirely determined by the component with lower barrier height, i.e. $\phi_o^{(1)}$, up to an applied voltage $V$ such that the second barrier conductivity can not be neglected. Simultaneous contributions from both components at higher $V$ determine the behaviour of sample ($I$-$V$) characteristics in the range $p \geq 0.7$. Such asymmetric features of the electrical properties of PCS follow from the monotonic behaviour of the $I$-$V$ curves shown in Fig.2. Moreover, the sample $\alpha$ in Fig.3 is dominated by the potential barriers with average or lower heights. The higher double Schottky barriers do not play considerable role in this case.

In the experiments by Olsson and Dunlop [7], several types of junctions between ZnO grains were distinguished. The various types of junctions characterized by different intergrain structures revealed different $I$-$V$ behaviour. The most frequent interface structures were found to be of ”type A”, i.e. ZnO boundaries containing a thin intergranular amorphous $B_i$-rich film, ”type B”, i.e. boundaries between ZnO grains not
involving any second intergranular phase but containing Bi atoms, and "C type", i.e. ZnO grains separated by an intergranular region containing Bi$_2$O$_3$. Since types A and B exhibited similar $I$-$V$ characteristics, the present theoretical GBG junctions with $\phi_0^{(1)}$ may be related to the "C-type" junctions whereas the GBG junctions with $\phi_0^{(2)}$ to the "B-type" junctions (by neglecting possible differences in the bias dependence for these types of GBG). Further motivation to approximate macroscopic PCS as a binary mixture of grain boundary Schottky barriers is obtained from the experiments by Tao et al. [8]. Our theoretical results in this case may represent the large majority of grain-to-grain junctions characterized from an electrical point of view as "good" junctions and "bad" junctions. As can be seen in Fig.3, our work predicts that for large proportions of "good" GBG, i.e. no less than 70%, the sample non-linear $I$-$V$ characteristics become completely determined by such junctions.

The presence of free electrons in the conduction band, the hole current (created by hot electrons at high enough applied voltages), and interface processes (electron captures, emission and hole-electron recombination at interface states) (see e.g. [3, 4, 14, 15]), might be important to derive a more satisfactory expression for the barrier height $\phi(V)$ than Eq.(4). The new expression should lead to obtain higher values of $V_B$ and $\alpha$ for GBG junctions, and from it, for the ZnO-based varistors too. This complicated problem has been solved numerically for a single GBG junction [3, 15]. Up to now, there is not an analytical expression for $\phi(V)$ which, on the one hand, gives desired results for a single junction problem [10, 17] and, on the other hand, could be basic for studying macroscopic non-linear $I$-$V$ characteristics of ZnO-based varistors as it concerns us here.

As a simple example, let us consider the alternative trial form

$$\phi(V) = \phi_0 e^{\beta_2 \frac{eV}{\phi_0}} (1 - \beta_1 eV) \phi_0^2; \quad (\beta_1 eV \leq \phi_0). \tag{9}$$

It can be seen in Fig.1 by dotted lines (left-hand side axis) that this choice (though not unique) allows us to fit better experimental data [13] than using Eq.(4) from a simple adjustment of two parameters, namely $\beta_1$ and $\beta_2$. Clearly, the first term of an expansion series of the exponential function in Eq.(4) leads to Eq.(4) for low $V$. The following terms in such a series might represent those additional effects that become important at
the high voltage region $\beta_2 eV \approx \phi_o$. Theoretical $I$-$V$ characteristics derived using Eq.(3) for the thermoionic emission current and Eq.(9) for $\phi(V)$ are also illustrated in Fig.1 by dotted lines (right-hand side axis) for completeness.

If we take $\beta_1$ and $\beta_2$ such that, at $\frac{kT}{eV} << 1$, the barrier height becomes weakly dependent on $V$, (i.e. $\frac{\partial \phi}{\partial V} |_{V\to 0} \approx 0$). Then, we immediately obtain $\beta_2 = 2\beta_1$ and Eq.(9) for $\phi(V)$ becomes dependent only on $\beta_1$ which may be chosen to correlate the voltage $V_B (\approx \frac{4\phi_o}{e})$, with a high non-linear coefficient $\alpha$ for the GBG junctions.

In fact, from definitions (1) and (2), for enough high barriers we have

$$V_B \approx \frac{\phi_o}{\sqrt{2\beta_1 e}} ,$$

$$\alpha \approx 32\beta_1^2 (1 - 4\beta_1) e^{8\beta_1} \frac{\phi_o}{k_B T} . \quad (10)$$

For $\beta_1 \approx 0.19$ we get the desired $V_B$ and $\alpha \approx 1.28\frac{\phi_o}{k_B T}$ which is more than twice higher than $\alpha$ from Eq.(3). The coefficient $\alpha$ becomes independent of $\beta_1$, but depends on the zero-voltage barrier height $\phi_o$. If, as before, $\phi_o \approx 0.75 \text{ eV}$ then Eq.(10) gives $\alpha \approx 35$ for a single GBG junction at room temperature. Hence, we feel that Eq.(3) may be a convenient expression to mimic $\phi(V)$ in these systems in the absence of simpler approaches to include effects due to holes and interface processes.

Let us focus again briefly on the EMA. In Figs.3(A) and 3(B) (dotted lines) we plot new values of the sample $V_B(p)$ and $\alpha(p)$ by using Eqs.(3) together with Eq.(9) and $\chi = 0.5$ for a comparison with the solid lines 3. We immediately note that the behaviour of the sample $\alpha$ and $V_B$ is the same than in the previous case by applying Eq.(4). But, even more important, according to relations in Eq.(10) $\alpha$ and $V_B$ reach higher values. The same conclusion can be drawn for different values of $\chi$ (not shown).

To conclude some comments are in order. We have analysed the non-trivial problem of the non-linear $I$-$V$ characteristics of a macroscopic sample of PCS from the point of view of electrical properties of individual GBG junctions. In real percolation systems a network of non-linear elements at breakdown is known to be filamentary. In order to take into account of this effect, a more sophisticated model which includes random fluctuations of (multiple) barrier heights must be considered. In this work we have
restricted ourselves to a simple binary mixture model of PCS (ZnO)-grain interfaces and used the TEM for the carrier transport through the grain boundaries. The use of a binary mixture approach being motivated by the experimental findings of Refs.[7, 8]. In the case of a narrow distribution in fluctuations of barrier heights [6, 20], the $I-V$ characteristics of varistors may became very similar to the single junction data and the simplest model of Levinson and Philipp suffices [9].

We have found that features in the $V$-dependence of $\phi$ and fluctuations of double Schottky barrier heights at (rather than the electrical conduction through) grain boundaries play an essential role to achieving highly, non-linear $I-V$ characteristics of macroscopic PCS samples. For this reason, we have introduced a simple trial form for the voltage dependence of a single barrier height in the absence of simpler approaches to mimic effects due to holes and interface processes. We have assumed that the bias dependence of GBG is the same for both components by considering either Eq.(4) or Eq.(9). As shown in Fig.3, different $\phi(V)$ functions will clearly lead to obtain different results depending on the chosen form. The 3D-EMA for non-linear $I-V$ characteristics of PCS as introduced in this work presents an asymmetric contribution of barrier heights to the sample $\alpha$ and $V_B$ around $p = 0.5$. This asymmetry becoming large on increasing the difference in the barrier height values of the components.

These interesting findings may be useful guidelines to simulation studies of electric breakdown to a network of random potential barriers with non-linear $I-V$ characteristics [18, 19, 21]. In addition, similar EMA calculations may be also extended to 2D systems such as polycrystalline semiconductor films [8]. In the latter, we shall expect analogous results because 2D-EMA equations are equivalent to those in Eqs.(7) and (8) for 3D samples but with a small change of coefficients.
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Figure captions

• **Figure 1**: Double-Schottky barrier height $\phi$ at, and dc current through, a single grain boundary as a function of applied voltage $V$ for $\phi_o = 0.73 \, eV$ at $T = 300 \, K$. Here $I_o = A^* T^2 e^{-\frac{\phi_o}{k_B T}}$. Full lines are obtained from Eqs.(3) and (4) and dotted lines from Eqs.(3) and (9). Squares represent experimental data for $\phi(V)$ [13].

• **Figure 2**: Results for the binary mixture conductivity $\sum$ as a function of applied voltage $V$ for several probabilities $p$ of having bonds with conductance $\sigma_1$. Typical data for ZnO-based varistors are used: $\phi_o^{(1)} = 9$ and $\phi_o^{(2)} = 30$.

• **Figure 3**: (A) Normalized voltage $V_B$ at which electrical breakdown occurs and (B) normalized non-linear coefficient $\alpha$ for a binary mixture as a function of probability $p$ of having component one. In these plots (1) $\chi = 2$, (2) $\chi = 1$ and (3) $\chi = 1/2$. Full lines are obtained using Eqs.(3) and (4). Dotted lines are obtained using Eqs.(3) and (9) with $\chi = 1/2$. 

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