United Nations Educational Scientific and Cultural Organization
and
International Atomic Energy Agency
THE ABDUS SALAM INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ON THE I-V CHARACTERISTIC IN THE NON-LINEAR TENARY MIXTURE MODEL FOR POLYCRYSTALLINE SEMICONDUCTORS

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Abstract

A simple expression for the voltage dependence of grain-boundary potential barrier heights is proposed and the Effective Medium Approximation is extended for calculating the I-V characteristic in tenary mixtures of highly non-linear circuit elements. Numerical calculations are performed for the case of polycrystalline semiconductors, such as ZnO-based varistors, where the thermoionic emission is believed to be the dominant mechanism for the electric conduction across double Schottky barriers at room temperature.

MIRAMARE – TRIESTE
August 2000

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1 Introduction

The transport properties in materials of the polycrystal-like grain boundary (GB) microstructures have attracted increasing interest in last decades due to their very specific electrical behaviours and their great technology applications (polycrystalline Si-devices, ZnO-varistors ...) [1,2]. The double Schottky barrier formulated at the grain boundaries controls electric currents and causes a high nonlinearity for the current-voltage characteristics (*I-V characteristic*)[3-13]. The parameter used to measure a nonlinearity is defined as the power α in the current-voltage relation $I \propto V^{\alpha}$, i.e.

$$\alpha(V) \;=\; d(\log I)/d(\log V). \tag{1}$$

The typical $\alpha(V)$-curve looks like a bell shape interpolating two linear regimes of $\alpha = 1$. The voltage $V = V_B$ relating to the bell top, where $\alpha(V)$ reaches the maximum value, is often called *the breakdown voltage* and could then be determined as the solution of the equation

$$(\partial\alpha(V)/\partial V)|_{V_B} \;=\; 0. \tag{2}$$

Correspondingly, the maximum value of the power α at breakdown, $\alpha \equiv \alpha(V_B) = max[\alpha(V)]$, is in practice named *the non-linear coefficient*. The breakdown voltage V_B and the non-linear coefficient α are the main parameters, characterizing a nonlinearity in electric conduction of materials. Note that the typically observed values of the coefficient α for the varistors based on zinc oxide ceramics (ZnO-varistors), for example, may be as large as 50 or more [3,4,12]. The polycrystal-like materials with such a high nonlinearity should be adopted as the original interest of the present work.

Theoretically, the study of the I-V characteristic for GB materials should consist of two steps: (i)- to calculate I-V characteristics of single GB barrier junctions, and, (ii)- using these single junction I-V characteristics to calculate an overall I-V characteristic of the material.

The current transport across a single Schottky barrier was investigated in great detail in a number of works [3-13] and the physics of the problem is now widely recognized. A very high non-linear I-V characteristic is believed to be caused by the holes created in the forward barrier at high voltages, which inject along the electric field into interface states and recombine the electrons trapped there. Thus, the interface processes (hole-electron recombination, electron capture and emission) should certainly be counted self-consistently in getting a single junction I-V characteristic. Unfortunately, all attempts of including the interface processes unavoidably lead to very complicated numerical calculations even for a single junction problem [4,13]. Hence, they could not be realized in practical procedures of calculating the overall I-V characteristic of systems, containing an enormous number of junctions with different electrical behaviours.

The difficulty in calculating the overall I-V characteristic of polycrystalline semiconductors is mostly related to a randomly inhomogeneous nature of materials. In contrast to the early Levinson-Philipp model of identical and regularly arranged GB junctions [5], the micro-

photographies of varistor ceramics show not only a randomness in grain space positions, but also a large variation in grain sizes [10,11]. Furthermore, the fluctuation of junction barrier heights and, correspondingly, of breakdown voltages, mentioned early, for example, by Einzinger [10], has been systematically and convincingly investigated in different materials [14-18] . ¿From microelectrode measured data by Olsson and Dunlop [15] three most frequent types of junctions between ZnO grains were distinguished. These types of junctions characterized by different intergrain structures reveal very different Schottky barrier heights, and therefore, very different non-linear behaviours. Such a model of ZnO varistors with three kinds of grain boundaries: (1)"good" junctions with a highly non-linear I-V characteristic; (2) "bad" junctions with a low nonlinearity; and (3) low-resistivity ohmic GBs, was recently simulated by Bartkowiak et al.(BMMALM) [18]. However, the Kirchhoff's equations simulations of ref.[18] are only limited to two dimensional systems and to some exclusive parameter values, and, moreover, the expressions for single junction I-V characteristics used in these simulations are very particular that could not be seen as typical for polycrystal-like materials [19].

In the present work the Effective Medium Approximation (EMA) is extended to calculate an overall I-V characteristic of such a nonlinear tenary mixture as that of Olsson and Dunlop [15] and of BMMALM [18]. Concerning the single junction problem, we propose a simple expression for the voltage dependence of the potential barrier height, which, on one side, describes experimental data, and which, on the other side, is suitable for further calculating bulk properties. The work is then formulated in a closed form of self-consistent equations with a few parameters. The numerical results for both two (2D) and three dimentional (3D) cases will be discussed in detail.

2 Single Junctions

Depending on materials, on the temperature, and on applied voltages, the electric current transport through a GB Schottky barrier may be formulated by different conducting mechanisms, such as tunnelling, field emission, space-charge limited current, or thermoionic emission [6-8]. For the materials with such a high nonlinearity as ZnO-varistors at room temperature, however, the thermoionic emission (TIE) is widely believed to be dominant in the pre-breakdown region $V \leq V_B$ [7,9,12,20].

Within the framework of TIE theory the current that is injected through a Schottky barrier is [7-12]:

$$J(V) \;=\; J_0 \;\exp\left(-\Phi(V)/k_BT\right)\left[1-\exp(-eV/k_BT)\right]\,, \tag{3}$$

where the voltage-independent current $J_0 = A^*\,T^2\;\exp\left(-E_F/k_BT\right)$, A^* is the Richardson's constant, E_F is the Fermi level in the grain bulk (counted from the bottom of the conducting band), T is temperature, e is elementary charge, V is the voltage drop across the junction, and Φ is the potential barrier height which depends on V.

In the simplest double Schottky model, when the effects due to holes and interface processes are neglected, the functional form of $\Phi(V)$ could easily be found by solving the one-dimensional Poisson equation $d^2\Phi(x)/dx^2 = \rho(x)/\epsilon$, where $\rho(x)$ is the charge density in the barrier region, ϵ is the grain dielectric constant. In the so called abrupt approximation for the charge density:

$$\rho(x) \;=\; eN_D\{\theta(x+x_l) - \theta(x-x_r)\} - Q_I\delta(x)\;, \tag{4}$$

with N_D being the donor concentration in grains, $\theta(x)$ and $\delta(x)$ - the Heaviside step and the Dirac δ-function, respectively; x_l (x_r) - the length of the left (right) depletion region, Q_I - the density of surface charges, one has got [10,12]:

$$\Phi(V) \;=\; \Phi_0\;(1 \;-\; eV/4\Phi_0)^2, \quad eV \;\leq\; 4\Phi_0\;. \tag{5}$$

Here $\Phi_0 \equiv \Phi(V=0) = Q_I^2/8e\epsilon N_D$ is the barrier height at zero voltage.

The $\Phi(V)$-expression of eq.(5) is very simple and easy to be used for the aim of calculating the bulk I-V characteristics, and since there is no other analytical $\Phi(V)$-expression available for this aim, it was often addressed in literatures [1-12].

However, as can be seen in Fig.1, the $\Phi(V)$-behaviour given by eq.(5) (dashed line) is very far in describing experimental data for ZnO-varistors (solid circles), measured by Mahan et al.[4]. While the measured barrier height is almost unchanged in a large range of applied voltages until $eV/\Phi_0 \approx 3$, the curve of eq.(5) immediately goes down with the slope of $\approx -1/2$ and shows a barrier height $\Phi \approx \Phi_0/2$ at the voltage as low as $eV/\Phi_0 \approx 1$. Such a discrepancy in the $\Phi(V)$-dependence should be manifested in the non-linear feature which is characterized by quantities V_B and α. Substituting eq.(3) with $\Phi(V)$ of eq.(5) directly into eqs.(1), (2) one can, to the first approximation, get [21]:

$$V_B \;\approx\; 2\Phi_0/e; \qquad \alpha \;\approx\; \Phi_0/2k_BT. \tag{6}$$

For the junction with typical barrier height of $\Phi_0 = 0.4\;eV$ at room temperature, this eq.(6) gives a value of the breakdown voltage V_B, which is in about 3 times less than the experimentally observed value [1,4,12] and gives to the non-linear coefficient a value as small as $\alpha \approx 8$ (in comparison with typical experimental values of ≈ 50).

It is important to note that the $\Phi(V)$-expression of eq.(5) is essentially related to the assumption of neglecting the hole effects and the interface processes. A variety in the form of the space distribution of donors as well as an inclusion of the conduction band electrons into the charge density $\rho(x)$ will lead to different values of Φ_0 only, while the functional form of $\Phi(V)$ seems to be still the same as given in eq.(5) (see Appendix).

Recall that although it is perhaps possible to calculate self-consistently the $\Phi(V)$-dependence for an individual GB-junction by taking into account both the hole effects and the interface processes as it was tried to do in Refs.[4,12,13], such complicated numerical calculations unfortunately could not be practically realized in calculating overall I-V characteristics. In this

work, as an alternative way to avoid this unsolved difficulty, we speculatively suggest for $\Phi(V)$ a simple expression as the following:

$$\Phi(V) \;=\; \Phi_0 \;\tanh^{-1}(\beta_1)\;\tanh[\beta_1(1-\frac{eV}{\beta_2\Phi_0})]\;, \qquad eV \leq \beta_2\Phi_0, \tag{7}$$

where β_1 and β_2 are adjusted parameters, which depend on materials. One can think about this $\Phi(V)$-expression of eq.(7) as a solution of some one-dimensional Ginzburg-Landau type equation [22]. It should also be noted that the *tanh*-functions have often appeared in different approximate (empirical) expressions of the I-V characteristics for ZnO-varistors [4,7,23].

Using the $\Phi(V)$-expression of eq.(7), from eqs.(1), (2) and (3) to the first approximation the breakdown voltage could be estimated as

$$eV_B \;\approx\; \beta_2\Phi_0 y \tag{8}$$

and, correspondingly, the non-linear coefficient as

$$\alpha \;\approx\; y(\beta_1/\tanh\beta_1)\{1-\tanh^2[\beta_1(1-y)]\}(\Phi_0/k_BT), \tag{9}$$

with y being the positive solution of the equation

$$2\beta_1 y\tanh[\beta_1(1-y)] \;=\; -1. \tag{10}$$

We would like to note that the temperature dependence of the non-linear coefficient in the form $\alpha(T)\propto T^{-1}$ as is given in eq.(9) was experimentally observed in ZnO-varistors [1,23].

Fig.1 shows the best fit of the $\Phi(V)$-expression of eq.(7) (solid line) to the experimental data from ref.[4] (solid cirles) that gives $\beta_1 = 3.72$ and $\beta_2 = 5.63$. Using these values of β_1 and β_2, from eqs.(8)-(10) we have

$$V_B \;\approx\; 5.9\;\Phi_0/e; \qquad \alpha \;\approx\; 3.8\;\Phi_0/k_BT, \tag{11}$$

which are in about 3 times (for V_B) and 7 times (for α) larger than those of eq.(6), respectively. On the other side, the data of ref.[15] support the idea that the (Φ/Φ_0) versus (eV/Φ_0) curves should follow an universal behaviour, characterizing the material under study, regardless of an individuality of junctions. In other words, the parameters β_1, β_2 could be assumed to be material characters, independent of barrier heights Φ_0. Here, it should also be mentioned that, experimentally, there are different suggestions on the behaviour of V_B in dependence on the barrier height. Analyzing a large number of GB junctions, Einzinger [10] recognized that V_B mainly changes between 2.5 and 4.5 V. Olsson and Dunlop [15], using microelectrode measurements, observed a larger variety of V_B, between 0.4 and 4 V, with two peaks at ≈ 0.9 V (bad) and ≈ 3.3 V (good) for ZnO-varistor samples of $0.50-mol\ \%\ Bi_2O_3$. Greuter and Blatter [13] suggested that the interface minority carriers generated by hot electrons at high field could strongly affect the breakdown voltage V_B. We assume that the present model of eq.(7) should be applied for describing I-V characteristics of such materials as that investigated in ref.[15].

Thus, although the $\Phi(V)$-expression of eq.(7) is purely empirical, it nevertherless describes the observed electric characterirtics for the double Schottky barriers of realistic ZnO-varistors. And furthermore, since this $\Phi(V)$-expression is very simple, it could easily be used as a basis for calculating overall I-V characteristics of inhomogeneous barrier systems. In Fig.2, as an example, the pre-breakdown TIE I-V characteristics of eq.(3) with the $\Phi(V)$ of eq.(7) are plotted (solid lines) for two junctions of $\Phi_0 = 0.1\ eV$ and $0.4\ eV$ at $T = 300\ K$. The corresponding $\alpha(V)$-relations defined in eq.(1) are also plotted there (dashed lines) that give to the non-linear coefficient the values of ≈ 14 and 56 for the junctions of $\Phi_0 = 0.1\ eV$ and $0.4\ eV$, respectively.

3 Effective Medium Approximation

The EMA is a self-consistent schema proposed as an approach to transport properties of inhomogeneous materials, long ago [24]. However, this method only received great interest with its successful applications to the percolation problems [25]. The EMA gives very accurate predictions for the percolation probabilities, for the conductivity and other electric characters of binary mixtures [26,27].

Consider a random electrical network on a hypercubic lattice of dimensionality $d > 1$. The bonds of the lattice are circuit elements with independently random conductivities. To calculate the overall conductivity Σ of such inhomogeneous systems the basic idea of the EMA consists in replacing the random resistance net by a homogeneous lattice, where all the lattice bonds have the same conductance Σ. Choosing the lattice spacing to be unity, then Σ is also the conductivity of the sample and it could be derived self-consistently as discussed by Kirkpatrick [25].

It should be mentioned that the EMA had originally been proposed and is often applied to linear systems with bond conductances independent of the applied voltage. An extension of the EMA to systems of non-linear resistances was suggested in refs.[28,21], but the study [21] was only limited to the binary mixtures. For the tenary mixtures of the BMMALM model [18], in the same way as that in refs.[28,25,21] one can show that the self-consistent EMA equations for the overall conductivity Σ as a function of the applied voltage V have the form

$$\frac{p_0(\Sigma - \sigma_0)}{\sigma_0 + (d-1)\Sigma} + \frac{p_b(\Sigma - \sigma_b(V))}{\sigma_b(V_b^*) + (d-1)\Sigma} + \frac{p_g(\Sigma - \sigma_g(V))}{\sigma_g(V_g^*) + (d-1)\Sigma} \;=\; 0 \tag{12}$$

and

$$V_i^* \;=\; \frac{d\Sigma + \sigma_i(V_i^*) - \sigma_i(V)}{(d-1)\Sigma + \sigma_i(V_i^*)}\ V\ ; \qquad i = b,\ g, \tag{13}$$

where $p_0,\ p_b$ and p_g are the probabilities of having bonds with the ohmic σ_0, the "bad" σ_b, and the "good" σ_g conductance, respectively: $p_0 + p_b + p_g = 1$, $d = 2,\ 3$ is dimensionality. The equation (13) is a consequence of a voltage dependence of the non-linear "bad" (i = b) and "good" (i = g) conductances [28].

The EMA equations (12),(13) are very general for tenary systems with any σ_0 and any functional forms $\sigma_b(V)$ and $\sigma_g(V)$. To solve these equations it is convenient to write eq.(12) in the form:

$$\Sigma^3 + a_1\Sigma^2 + a_2\Sigma + a_3 \;=\; 0 \;, \tag{14}$$

where

$$\begin{aligned}
a_1 &= \{p_0[\sigma_b^* + \sigma_g^* - (d-1)\sigma_0] + p_b[\sigma_g^* + \sigma_0 - (d-1)\sigma_b] \\
&\qquad + p_g[\sigma_0 + \sigma_b^* - (d-1)\sigma_g]\}(d-1)^{-1}, \\
a_2 &= \{p_0[\sigma_b^*\sigma_g^* - (d-1)\sigma_0(\sigma_b^* + \sigma_g^*)] + p_b[\sigma_g^*\sigma_0 - (d-1)\sigma_b(\sigma_g^* + \sigma_0)] \\
&\qquad + p_g[\sigma_0\sigma_b^* - (d-1)\sigma_g(\sigma_0 + \sigma_b^*)]\}(d-1)^{-2}, \\
a_3 &= -(p_0\sigma_0\sigma_b^*\sigma_g^* + p_b\sigma_0\sigma_b\sigma_g^* + p_g\sigma_0\sigma_b^*\sigma_g)(d-1)^{-2}.
\end{aligned} \tag{15}$$

Here, $\sigma_b \equiv \sigma_b(V)$; $\sigma_g \equiv \sigma_g(V)$; $\sigma_b^* \equiv \sigma_b(V_b^*)$; and $\sigma_g^* \equiv \sigma_g(V_g^*)$ are introduced for short.

The equation (14) is a standard cubic equation in Σ with the solutions well-known as the Cardan's formula [29], where the coefficients $a_1,\ a_2,\ a_3$ depend not only on $p_0,\ p_b,\ p_g$, on $\sigma_0,\ \sigma_b,\ \sigma_g$, but also on $\sigma_b^*,\ \sigma_g^*$. The last quantities σ_b^* and σ_g^* should be determined from eq.(13). Hence, for given values of probabilities $p_0,\ p_b,\ p_g$, of the conductance σ_0, and given functional forms of $\sigma_b(V)$ and $\sigma_g(V)$ the equations (14) and (13) could be solved self-consistently to get the conductivity Σ for each value of V, i.e. to get an overall I-V characteristic of the system under study.

4 Numerical Examples and Discussions

To solve EMA equations (14), (13) we need the functional forms of non-linear bond conductances $\sigma_{b,g}(V)$. In the framework of the TIE-model of eq.(3), with $\Phi(V)$ of eq.(7) the single junction conductance normalized by the "grain conductance" of $\Sigma_0 \equiv J_0 e/k_B T$ has the form

$$\sigma(v) \;=\; e^{-\varphi(v)}\ [e^{-v} + \frac{\beta_1}{\beta_2 tanh\ \beta_1}(1 - e^{-v})\ cosh^{-2}\ \beta_1(1 - v/\beta_2\varphi_0)]\ , \tag{16}$$

where $\varphi \equiv \Phi/k_B T$, $v \equiv eV/k_B T$, $\varphi_0 = \varphi(v=0)$. This expression of single junction conductances is valid at applied voltages of $v \le \beta_2\varphi_0$ (see eq.(7)). At higher voltages the resistance of (metal) grains becomes dominant that makes the junction conductance saturated: $\sigma(v) = constant$ at $v \ge \beta_2\varphi_0$.

In the conductance expression of eq.(16) the zero-voltage dimensionless barrier height φ_0 is only the parameter characterizing an individuality of junctions. Denoting $\varphi_0 \equiv \varphi_0^{(b)} = \Phi_0^{(b)}/k_B T$ for "bad" junctions, and $\varphi_0 \equiv \varphi_0^{(g)} = \Phi_0^{(g)}/k_B T$ for "good" junctions, where $\Phi_0^{(b)}$ and $\Phi_0^{(g)}$ are the corresponding zero-voltage barrier heights, the conductances σ_b and σ_g in eq.(15) could then be formulated from eq.(16) as

$$\sigma_b(v) \;=\; \sigma(v, \varphi_0 = \varphi_0^{(b)}); \qquad v \le \beta_2\varphi_0^{(b)}\ ;$$

$$\sigma_g(v) \;=\; \sigma(v, \varphi_0 = \varphi_0^{(g)}); \qquad v \leq \beta_2 \varphi_0^{(g)} \;.$$

At higher voltages ($v \geq \beta_2 \varphi_0^{(b)}$ for "bad" or $\geq \beta_2 \varphi_0^{(g)}$ for "good" junctions) the conductance is independent of v.

Thus, in the present model of tenary mixtures the overall I-V characteristics at a given temperature is entirely determined by 5 material parameters: two from the probabilities p_0, p_b, p_g; the ohmic conductance σ_0, and two zero-voltage barrier heights $\Phi_0^{(b)}$ and $\Phi_0^{(g)}$. By changing one of these parameters, while the others are fixed, the EMA equations (14), (13) may allow one to investigate a large variety of electrical properties of polycrystal-like materials.

In solving eq.(14), it should be noted that due to a nonlinearity of conductances the quantity $(-a_1^2/3 + a_2)$ could change its sign as the voltage v varies. Such a specificity of the problem must be adequately counted in using Cardan's solutions [29].

Experimentally [14-18], the microjunctions referred to as "good" have the non-linear coefficient $\alpha \geq 30$ that corresponds to $\Phi_0^{(g)} \geq 0.25eV$ as resulted from eq.(11) at $T = 300\ K$, while the "bad" microjunctions have much lower nonlinearity, $\alpha \approx 10$, or much lower barrier height, $\Phi_0^{(b)} \approx 0.1eV$. To demonstrate some numerical solutions of EMA equations (13) and (14) with the TIE $\sigma(v)$ of eq.(16) we will use here the set of parameter values: $\Phi_0^{(b)} = 0.1\ eV$; $\Phi_0^{(g)} = 0.4\ eV$; $T = 300\ K$; $\beta_1 = 3.72$, and $\beta_2 = 5.63$ that results in the non-linear coefficient $\alpha_b \approx 14$ and $\alpha_g \approx 56$, and in the breakdown voltage $V_B^{(b)} \approx 0.6\ V$ and $V_B^{(g)} \approx 2.4\ V$ for "bad" and "good" junctions, respectively. These values are close to those used in ref.[18]. The conductance of the ohmic bond is everywhere chosen to be equal to 0.3 (in units of Σ_0). The overall conductivity Σ will then be calculated for different values of probabilities p_b, p_g, and p_0 in the range of voltages $v \leq \beta_2 \varphi_0^{(g)} \approx 90$.

Fig.3 shows the 3D $\Sigma(v)$-characteristics for different values of p_b and p_g, while the probability p_0 is kept to be constant, $p_0 = 0.05$ [18]. The typical feature of all curves is a step-like form with two plateaux at weak voltages $V \leq V_B^{(b)}$ and at $V_B^{(b)} < V < V_B^{(g)}$. The first plateau is related to the fact that at $V \leq V_B^{(b)}$ both $\sigma_b(V)$ and $\sigma_g(V)$ are really ohmic and very small. For all the curves the value of Σ in this plateau is in the order of $\approx 10^{-4}$. At the voltages near to $V_B^{(b)}$ the breakdown of the "bad" junctions creates an abrupt increase of Σ. At higher voltages $V > V_B^{(b)}$, the conductance σ_b, reaching the saturated value of the grain conductance, again becomes independent of applied voltage, while the conductance σ_g is still constant and small. Thus, in the range of voltages $V_B^{(b)} < V < V_B^{(g)}$ all three component conductances seem once more to be ohmic that results in the second plateau in the $\Sigma(v)$-curves. The value of $\Sigma \equiv \Sigma_L$ in this plateau decreases with increasing p_g (p_0 is unchanged), it seems however to be still considerably higher than σ_g (dashed line (g)) even when $p_g = 0.7$ (curve 4).

A rapid rise of Σ at the voltages close to $V_B^{(g)}$ is certainly associated with the breakdown of "good" junctions. Relating the non-linear behaviour of materials to this breakdown, while the general feature of α versus p_g for a given value of p_0 is similar to that shown in Fig.4 of ref.[18], we would here emphasize on the role of the ohmic bonds in decreasing the non-linear coefficient:

the value of $\alpha \approx 40$ for the sample of $p_g = 0.70$ (greater than the 3D bond percolation threshold) with such a small amount of ohmic bonds as $p_0 = 0.05$ (the lowest solid line) is still considerably smaller than that of $\alpha \approx 50$ for the sample of the same p_g, but with $p_0 = 0$ (unshown curve, very close to the lowest dashed line). These results, on the whole, unambiguously imply that the electric conduction properties of considered non-linear tenary mixtures could not be explained within the framework of any current percolation models [26,30].

In Fig.4, the solid lines are the $\Sigma(v)$-characteristics for the 2D case with the same portion of ohmic bonds $p_0 = 0.05$ as for the 3D curves in Fig.3, but with different values of p_g (the values of p_g in the study are chosen in relation to the percolation threshold of corresponding bond problems, which for 2D case is 0.5). Since the feature of $\Sigma(v)$-curves for the 2D case is very similar to that for the 3D case discussed above, Fig.4 is then mainly focused on showing the effect of the third component of ohmic bonds σ_0.

Comparing the pairs of curves (1 and 1′, 2 and 2′, 3 and 3′, 4 and 4′) with the same value of p_g (0.05, 0.25, 0.4, 0.55, respectively), but with different values of p_0 (0.05 for solid lines and 0.15 for dashed lines), in Fig.4, we see that for all cases under study a change of p_0 strongly affects the $\Sigma(v)$-behaviour and, in particular, the value $\Sigma \equiv \Sigma_L$ of the conductivity in the plateau $V_B^{(b)} < V < V_B^{(g)}$. The effects are moreover on different sides, depending on the value of p_g: for small p_g (curves 1 and 2) Σ_L decreases, while for large p_g (curves 3 and 4) it increases as p_0 increases. Such a picture certainly results from the fact that Σ_L should approach the ohmic conductance $\sigma_0 = 0.3$ when the probability p_0 increases. For the case of $p_g = 0.55$, the conductivity Σ_L increases approximately as $(\sigma_0 - \Sigma_L)/\sigma_0 \propto (1 - p_0)$, and the non-linear coefficient decreases about in two times, when p_0 changes from 0.05 to 0.15. Since Σ_L could be explained as a measure of the leaking current the present results thus show an important effect of ohmic bonds on the breakdown quality of materials.

Finally, we would like to emphasize an interesting feature in the voltage-dependence of the non-linear coefficient. From Figs. 3, 4 it is already clear that for all the cases with finite p_0 (both 2D and 3D) in the $\alpha(V)$-dependences they always have two peaks, located at $V \approx V_B^{(b)}$ and $\approx V_B^{(g)}$. The amplitude of these peaks are very sensitive to the change of the ohmic-component portion p_0. A similar double-peaked structure in $\alpha(V)$ was also recognized in the simulation data in ref.[31]. It is undoubtedly caused by randomly distributed GB junctions with ohmic behaviour, and therefore, it is the characteristic feature of the investigated tenary mixture model.

In conclusion, we proposed a simple argument for calculating the I-V characteristic of highly non-linear tenary mixtures that includes (i) an empirical expression for the voltage dependence of GB-potential barrier heights, and (ii) an extension of the EMA to apply to the tenary mixtures of highly non-linear circuit elements. Numerical results performed for polycrystalline semiconductors at room temperature show a strong effect of the ohmic bonds on the breakdown behaviour of materials. In particular, the ohmic bonds increase the leaking current and cause a double-

peaked structure in voltage-dependence of the non-linear coefficient. The model is assumed to be applied for describing pre-breakdown electric properties of the materials as that measured in ref.[15]. It is thus hoped that this work might provide some useful insight into experimental investigations and stimulate further theoretical interest in the problem.

Acknowledgments. One of author (NVL) thanks very much Professor Yu Lu for encouragement and The Abdus Salam International Centre for Theoretical Physics (Trieste, Italy) for kind hospitality.

Appendix

The charge densities of the form (linear)

$$\rho(x) = -Q_I\delta(x) + \begin{cases} eN_D(1 + x/x_l), & \text{if } -x_l \le x < 0 \\ eN_D(1 - x/x_r), & \text{if } 0 < x \le x_r \end{cases}$$

or of the form (parabolic)

$$\rho(x) = -Q_I\delta(x) + \begin{cases} eN_D(x + x_l)^2, & \text{if } -x_l \le x < 0 \\ eN_D(x - x_r)^2, & \text{if } 0 < x \le x_r \end{cases}$$

result in the same expression of eq.(5) for the $\Phi(V)$-relation, but with different values of zero-voltage barrier height: instead of Φ_0 for the abrupt model of eq.(4) it will be $4\Phi_0/3$ and $3\Phi_0/2$ for the linear and parabolic densities mentioned above, respectively.

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Figure Captions

- **Fig. 1**. The normalized barrier height $\Phi(V)/\Phi_0$ as a function of the applied voltage eV/Φ_0: solid circles - experimental data [4]; dashed line - eq.(5); solid line - eq.(7) with $\beta_1 = 3.72$ and $\beta_2 = 5.63$.

- **Fig. 2**. I-V characteristics of eqs.(3), (7) (solid lines, scale at the left) and corresponding non-linear coefficients $\alpha(V)$ of eq.(1) (dashed lines, scale at the right) for single junctions with : $1. - \ \Phi_0 = 0.1\ eV$; $2. - \ \Phi_0 = 0.4\ eV$ $(T = 300K)$.

- **Fig. 3**. The normalized overall conductivities Σ/Σ_0 are plotted as a function of the applied voltage eV/k_BT for 3D system (solid lines). The different curves correspond to different values of p_g: 1.- 0.25; 2.- 0.40; 3.- 0.55; 4.- 0.70 ($p_0 = 0.05$; T = 300 K). Two limit cases of $p_b = 1$ and $p_g = 1$ are also shown (dashed lines (b) and (g), respectively) for a comparison.

- **Fig. 4**. The same as in Fig.3, but for 2D system and with various values of p_g: 1 and 1' - 0.05; 2 and 2' - 0.25; 3 and 3' - 0.4; 4 and 4' - 0.55. Solid lines: $p_0 = 0.05$; Dashed lines: $p_0 = 0.15$. Two curves of the same p_g should be in comparison.