AIP | Journal of Applied Physics

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Citation: Journal of Applied Physics **120**, 155103 (2016); doi: 10.1063/1.4965870
View online: http://dx.doi.org/10.1063/1.4965870
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/120/15?ver=pdfcov
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JOURNAL OF APPLIED PHYSICS **120**, 155103 (2016)

Non-ohmic behavior of metal-insulator granular thin films in low-field regime ($e\Delta V \ll k_B T$)

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(Received 9 June 2016; accepted 9 October 2016; published online 18 October 2016)

Non-ohmic behavior is not expected in metal–insulator granular systems in a low-field regime. There is no model to explain this behavior, even though it has been reported in several metal-insulator granular thin films (Fe-Al_2O_3, Co-Al_2O_3, and Ti-SiO_2). In this paper, we show additional experimental results of Fe-SiO_2 granular films and propose an explanation for the electrical properties of all above mentioned systems, based on Mott variable range hopping. The experimental results show that the localization length increases and the electrical resistance decreases with the increase of electrical potential or current. The non-ohmic behavior of the resistance and the increase of the localization length with increasing current are explained by the activation of new pathways for electrons in granular thin films that contain variable grain sizes and/or have different distances between grains. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4965870]

INTRODUCTION

Metal-insulator granular thin films have two regimes of electronic transport: the low-field regime, where the electrical potential energy between grains is much lower than the thermal energy ($e\Delta V \ll k_B T$), and the high-field regime, where this potential energy is equal or higher than the thermal energy.[1]

In the low-field regime, the behavior of the electrical resistance (R) as a function of temperature (T) was described in the literature[2–9] by the general equation

$$R = R_0 \exp\left(\frac{T_0}{T}\right)^{\alpha}, \quad (1)$$

where R_0 and T_0 are constants that depend on the volume fraction of the metal in the insulating matrix and α is an exponent that presents different values depending on the transport mechanism. Even though resistance had been expected to vary with temperature, it should present a linear dependence on voltage at all temperatures. A non-ohmic behavior is not expected in the low-field regime and had not been reported in reviews on metal-insulator granular films.[1–3]

For the study of electrical transport on metal-insulator granular films, one must consider the electrostatic energy of grains. The electrostatic energy is defined as the energy required to put a new electron into a neutral grain and is given by $e^2/2C$, where e is the electron charge and C is the capacitance of grain. In nanometric grains, this energy is considerable, because the capacitance is proportional to the diameter of the (spherical) grain. An electron only is allowed to tunnel into a grain if its thermal energy is equal or higher than this electrostatic energy.[10]

The non-ohmic behavior is expected in the high-field regime ($e\Delta V \gg k_B T$),[1] where it is expressed by

$$R = R_0 \exp\left(\frac{E_0}{E}\right), \quad (2)$$

where E is the applied electrical field, and E_o and R_o are constants. This equation holds in the high-field regime, with E around 10^4 V/cm and temperatures low enough that $e\Delta V \gg k_B T$.

The non-ohmic behavior in the low-field regime includes changes of magnetoresistance[11] as a function of electrical current. Those modifications are possibly interesting for technological applications. Recently, a strong non-ohmic behavior of the Fe-SiO_2 granular film was reported at room temperature.[12]

We have previously reported on effects that occur in several metal-insulator granular thin films in the low-field regime,[12–15] where the non-ohmic behavior was systematically present. In our data, the thermal behavior of the resistance fitted better and over broader temperature ranges when the Mott variable range hopping (Mott-VRH) with $\alpha = 1/4$ was used, as compared to the fitting with $\alpha = 1/2$ that is used for thermally activated hopping (TAH) and Efros and Shklovskii-VRH.[4,5]

In this work, we report on experimental results of electrical properties of a Fe-SiO_2 granular film in the low-field regime, as a function of temperature and applied potential, presenting a model for the mechanisms of this non-ohmic behavior.

EXPERIMENT

The Fe-SiO_2 granular sample was deposited by co-sputtering at room temperature onto glass. Rutherford backscattering spectrometry (RBS) showed that the metal volume fraction (x) was 0.22. Grazing incidence x-ray diffractometry (GIXRD), with an incidence angle of 2° in Seemann-Bohlin geometry of a diffractometer (Shimadzu XRD6000) using Cu-Kα radiation, showed that the iron particles were crystalline α-Fe, with a mean grain size of 8–9 Å, estimated from

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the width of the main diffraction peak using the Scherrer formula.[12] The electrical resistance experiments were carried out using the four-point method with a distance of approximately 2 mm between the electrical contacts. The highest potential applied was 15 V, placing the experiment in the low-field regime. Direct current had been injected parallel to the sample plane. The electrical resistance was measured as a function of temperature from 77 K to 300 K and as a function of the voltage.

RESULTS AND DISCUSSION

The resistance was measured between 80 K and 300 K, and the results are shown in Fig. 1 as a Ln R vs. $1/T^{1/4}$ plot. The straight line in the graph is the fit of the data in the temperature range from 80 K to 300 K with Eq. (1), using $\alpha = 1/4$. The observed behavior was compatible with variable range hopping between metal grains separated by insulating barriers, as it had been observed as well with the Fe-Al_2O_3, Co-Al_2O_3, and Ti-SiO_2 granular thin films.[11–15]

Even though it was originally developed for semiconductors, the Mott-VRH model can be applied to granular systems, because its concepts are stated in a way it is compatible with both. According to Ref. 6, in a semiconductor, the electrical resistance (R_{ij}) of an electron tunneling between a state i and a state j can be written as

$$R_{ij} \propto \exp\left(2\frac{r_{ij}}{\xi} + \frac{\varepsilon_{ij}}{k_B T}\right), \quad (3)$$

where $\varepsilon_{ij} = 1/2\ (|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_i - \varepsilon_j|)$, ε_i and ε_j are the energies of the states i and j, and ε_F is the Fermi energy, r_{ij} is the distance between the two states, $\xi = \hbar/(2m|\varepsilon|)^{1/2}$ is the localization length, m is the effective mass, and the bound particle energy is defined as $\varepsilon < 0$. It can be seen that each of these terms has an equivalent in the granular film. The electronic states used by Mott can very well describe the state of the whole (nanometric) granule, and all other parameters make analogous sense when applied to granular systems. For each electron pathway, the total electrical resistance is the sum of resistances of the individual hoppings. In the Mott-VRH, the resistance is given by Equation (1) with $\alpha = 1/4$.

In the Mott-VRH model, T_0 is related to the localization length ξ via the equation $T_0 = \beta\Delta/N\xi^3$ (β is a numerical factor, N is the number of randomly distributed localized states in a band with energy width Δ, centered at the Fermi level) and $r_{ij} \approx \xi\ (T_0/T)^{1/4}$.

The Coulomb interaction between states is implicitly present in Mott's VRH, because the model takes into account the total energy difference between states, even though it does not mention the interaction between states. The difference between ε_i and ε_j in the Mott model is general and can encompass all Coulomb interactions between localized states. In the case of metal-insulator granular thin films, the ε_{ij} will be the electrostatic energy written as $\varepsilon_{ij} \approx e^2/2C$.

Sheng *et al*. proposed a model for resistivity in granular systems in which the ratio between grain size s and distance d was constant (in restricted volumes), producing a temperature dependence with an exponent $\alpha = 1/2$. We believe that our experimental results fitted better with $\alpha = 1/4$, because the ratio s/d is not constant in our granular, and tunneling could happen between nonnearest neighbors. To clarify the proposed mechanism, we show a granular with variable s/d. In Fig. 2(a), a pathway for electrons is shown following the proposition of tunneling only between nearest neighbors.[1,4] In Fig. 2(b), the electron is allowed to tunnel to other grains, whenever the distance between grains and the energy

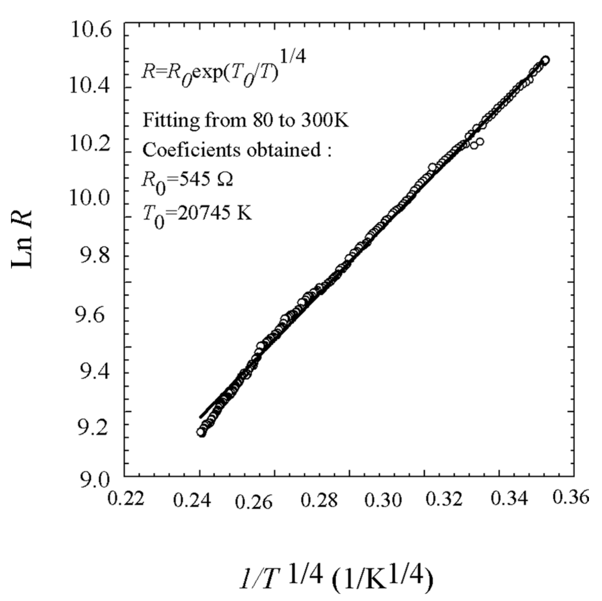

FIG. 1. Ln R vs. $1/T^{1/4}$ curve for Fe-SiO_2. Solid line was obtained fitting the data between 80 and 300 K with Eq. (1) using $\alpha = 1/4$.

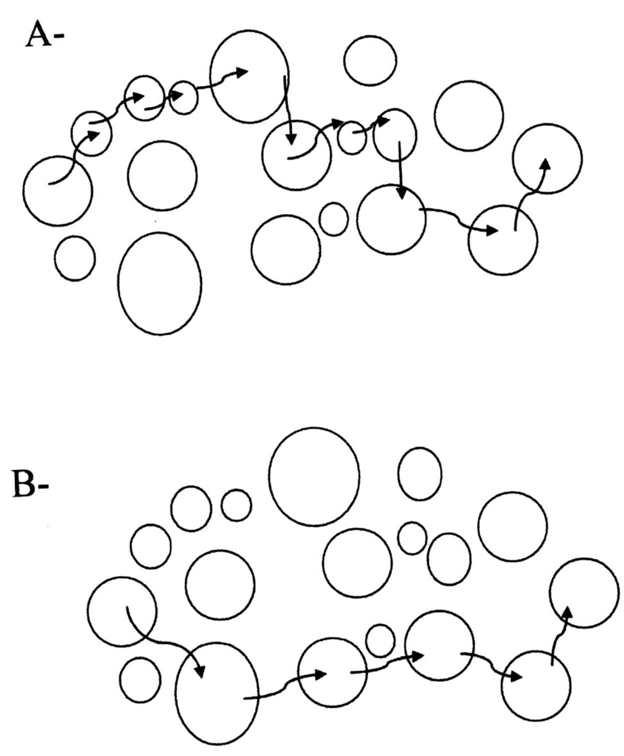

FIG. 2. (a) Model of a granular film with a nonconstant s/d ratio with tunneling between nearest neighbors only and (b) same granular film with tunneling when the distance between grains and the energy difference between states minimize the resistance R_{ij}.

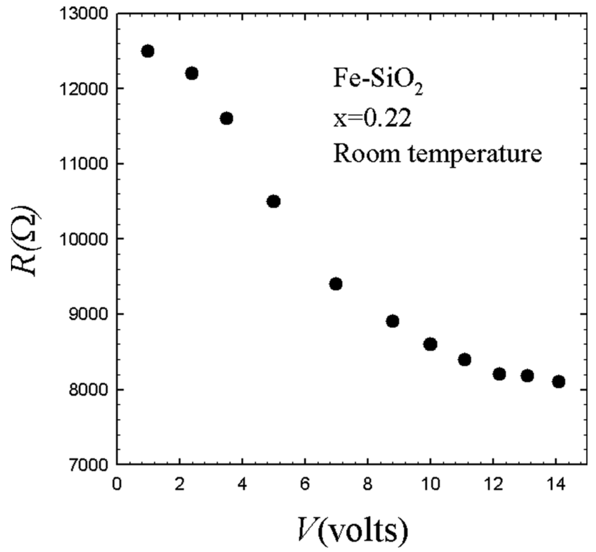

FIG. 3. Resistance behavior at room temperature, shown as R vs. V for the Fe-SiO$_2$ sample.[11]

difference between states are such that they minimize the resistance R_{ij}.

In Fig. 3, the room temperature experimental data of the R vs. V measurements for the Fe-SiO$_2$ granular are shown.

We argue that we observed before that when the current is increased, T_0 decreases.[12–15]

As by Definition $T_0 = \beta\Delta/N\xi^3$, when T_0 decreases, ξ has to increase.

The two most important experimental results:

- The overall resistance R always decreases when the current or potential is increased (Fig. 3);
- The localization length ξ always increases when the current or potential is increased.

The model proposed for the interpretation of the above mentioned results is that additional electrons tunnel on additional new paths between more distant grains; consequently r_{ij} increases; and each new path, being longer, has higher resistance.

The overall resistance R drops because the new paths are turned on in parallel.

The description of the results shown in Fig. 3 is that there is an initial pathway at low voltages, in which the electrical resistance R_1 is the sum of resistances of the individual hoppings (resistances in series). This would be the "most probable" path, with the lowest resistance. When the voltage is increased, additional new paths between more distant grains are activated in parallel.

The new overall resistance can be obtained analogously to an electronic circuit with parallel resistances, given by

$$\frac{1}{R_{Total}} = \frac{1}{R_1} + \frac{1}{R_2}, \tag{4}$$

where R_1 is the resistance of the first path and the other resistances correspond to the additional paths turned on when the potential is increased. It is important to take into account that $R_2 > R_1$.

The total resistance of the parallel circuit is given by Eq. (4) with $R_1 = 12\,500\,\Omega$ and R_2 to $V = 12$ V. When the V = 12 V, $R_2 = 24\,584\,\Omega$ and the sample has a total resistance $R_{\text{Total}} = 8200\,\Omega$.

When $V > 12$ V, there are two paths with the mathematical expression for resistance given by

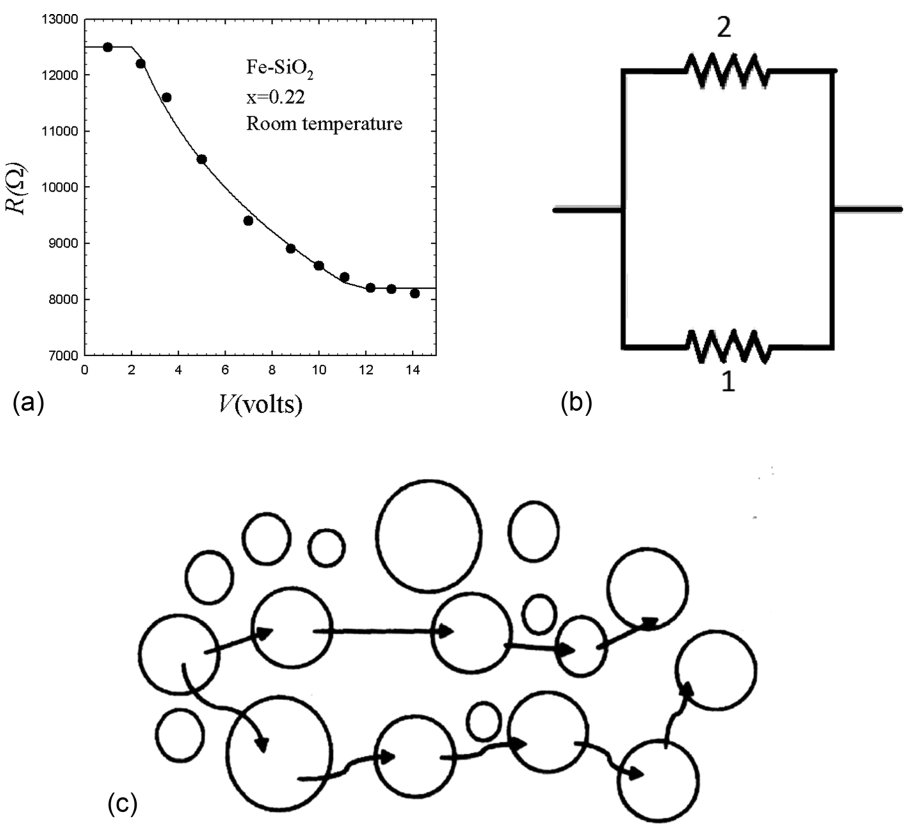

FIG. 4. (a) Experimental resistance values (R vs. V) and fitting curve behavior; (b) electric circuit with new resistances in parallel, considering resistances $R_2 > R_1$; and (c) model of parallel paths between nonnearest neighboring grains only.

$$R_1 = 609 \exp\left(\frac{25\,000}{300}\right)^{1/4} = 12\,500\,\Omega \text{ and}$$
$$R_2 = 2730 \exp\left(\frac{7000}{300}\right)^{1/4} = 24\,584\,\Omega.$$

One can perceive that T_0 of resistance 2 is lower than the T_0 of resistance 1, because the localization length is higher in the new paths and the tunneling happen between more distant grains.

We propose a fit for the behavior of the total resistance between 2 V and 12 V with R_0 and T_0 given by $R_0 = (R_{0i} + G/(T_0^{1/4}))$ and $T_0 = T_{0i}$ (1-F·V^H) in Eq. (1) where $R_{0i} = 1306\ \Omega$ and $T_{0i} = 25\,000$ K. We choose this dependence on R_0 and T_0 because R_0 should increase when V increase and T_0 should decrease when potential increase based on experimental results. The coefficient values are G = 0.602 Ω $K^{1/4}$, F = 0.16 V^{-H}, and H = 0.13.

The interpretation, for $V > 2$ V and $V < 12$ V, is the explanation of formation of R_2. We suppose that small resistances (small paths) are created in parallel between more distant grains in different parts of R_1. For $V > 12$ V, all these small resistances (small paths) are turned on in series. Finally, the R_2 is completely formed in parallel.

For $V < 2$ V, the total resistance is the maximum probability path and is equal to 12 500 Ω and constant. This path is in Fig. 2(b).

For $V > 12$ V, all parallel paths are activated and the total resistance is equal to 8200 Ω and considered constant.

Fitting R as a function V with this model is shown in Fig. 4(a).

In Fig. 4(b), the electric circuit equivalent of resistances is shown; and in Fig. 4(c), the new paths activated in parallel on granular films are shown.

The trend of this behavior in the low field regime was verified as well on Fe-Al_2O_3,[12] Co-Al_2O_3,[13] and Ti-SiO_2[15] systems and the parallel additional paths seem to be plausible for this phenomenon. In all samples, the resistance decreased when the potential increased, an effect that was even stronger at low temperatures.[12–15]

CONCLUSIONS

The studies on metal-insulator granular thin films showed that the non-ohmic behavior in the low-field regime is associated with new electronic paths between more distant grains, which are turned on in parallel and decrease the total resistance of samples, while increasing the localization length.

ACKNOWLEDGMENTS

The authors thank the Brazilian funding agency Capes for financial support.

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