Towards the Universal Transport Properties of Metal/Insulator Granular Thin Films in the Low-Field Regime with Increasing Bias Potential or Current

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***Abstract*-Three granular systems ($Fe-Al_2O_3$, $Co-Al_2O_3$, and $Ti-SiO_2$) had their electrical properties analyzed in the low-field regime ($e\Delta V<<k_BT$). Even though the metals and the insulators were different, a systematic non-ohmic behavior was observed in all systems when bias or injected current were varied. The temperature dependence on the resistance was best described with the Mott variable range hopping model. It is suggested that the behavior of the electrical resistance and the electronic localization length are associated with the activation of new electronic paths between more distant grains. As these new paths configure resistances in parallel, total resistance is reduced. In the low-field regime, the resistance drop and the change in localization length seem to be universal to metal/insulator granular thin films.**

Keywords*- *Electrical Properties; Metal/Insulator Granular Film; Variable Range Hopping

I. INTRODUCTION

The structural, electrical, and magnetic properties of composites that consist of nanometric metallic grains embedded in an insulating matrix, known as metal/insulator granular films, have been investigated for almost forty years by many research groups, as was reviewed by several authors [1, 2, 3].

It has been shown that in these systems, the electrical conductivity occurs due to electrons tunneling between grains [1]. 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, and the high-field regime, where this potential energy is equal to 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) is described in literature [3, 4] by the general Eq. (1):

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

Here R_0 and T_0andare constants that depend on the metal volume fraction, and α is a coefficient that depends on the mechanism of the transport process. Several mechanisms have been proposed for the electrical transport in metal/insulator granular films.

Thermally activated hopping (TAH) has a α coefficient of ½ and was proposed by Sheng et al. [4]. This model accepts that the ratio between distance of grains (s) and size of grains (d) is constant and that the tunneling occurs between nearest neighbors only. It has been used in different types of metal/insulator granular [4, 5, 6].

Variable range hopping (VRH) is presented with two distinct propositions that use different coefficients. Efros and Shkklovskii [7] propose α=1/2, this was used on the metal/semiconductor granular [8], while the VRH model of Mott [9] uses a coefficient of ¼. The latter model was developed for amorphous semiconductors, where the hopping occurs as tunneling of electrons between localized states, the paths are the most probably tunneling lanes, and the density of charge carriers does not depend on the temperature. The Mott-variable range hopping was used on arsenic-ion implanted into semiconductor GaAs [10].

The model proposed by Mott can be used for metal/insulator granular as well, since the concepts used in the model are sufficiently general to allow the application to other physical systems, where localized electronic states are available at certain distances throughout the medium.

Our group has previously reported effects that occur in $Fe-Al_2O_3$ [11, 12] and $Co-Al_2O_3$ [13] granular thin films in the low field regime. In those samples, ferromagnetic granules were dispersed in an alumina matrix, and it was observed that the thermal behavior of the resistance fitted better and over a broader temperature range when the Mott-VRH with α=1/4 was used, as compared to the fitting with α=1/2 (TAH). Additionally, it was observed that the electrical resistance decreased with increasing current (or potential) for $Fe-Al_2O_3$ [12] and $Co-Al_2O_3$ [13] samples.

In this work, it was reported the results obtained with a granular composed of a non-magnetic metal in a different insulator ($Ti-SiO_2$). When the electrical resistances (*R*) and localization lengths (ξ) of $Fe-Al_2O_3$, $Co-Al_2O_3$ were compared to those obtained in the $Ti-SiO_2$ granular films, the behavior of all systems was found to be analogous. The modification of *R* and ξ occurred in all samples, regardless of the metal (Fe, Co, or Ti) and the insulator (Al_2O_3 or SiO_2) utilized. It is suggested an interpretation for the change in the electrical properties in the low field regime and propose that these modifications are universal in metal/insulator granular thin films, regardless of the type of metal or insulator.

The novelty of this paper is the report of consistent non-ohmic effects in the low-field regime in various granular systems. Many research groups report on magneto transport and electrical properties in metal/insulator granular [14-19], but the systematic analysis of the modifications of electrical properties with the change of bias/current is not common [11-13].

II. SAMPLE CHARACTERIZATION AND ELECTRICAL MEASUREMENT METHODS

Three granular systems ($Ti-SiO_2$, $Fe-Al_2O_3$, and $Co-Al_2O_3$) with different metal concentrations were compared. The characterization was performed with Rutherford Backscattering Spectrometry (RBS) to obtain the metal content, grazing incidence x-ray diffractometry (GIXRD) to establish the existence of crystalline phases and to estimate grain size. In the case of the $Ti-SiO_2$ film, this also allowed Scanning Transmission Electron Microscopy (STEM). The characterization of the Fe and Co granular in alumina had been reported before [12, 13] and will be summarized below.

The $Fe-Al_2O_3$ granular samples were deposited by co-evaporation at room temperature onto pre-oxidized Si wafers with 0.48 metal volume fraction and a thickness of 1000 Å. The Fe arranged itself in grains with body centered cubic (bcc) structure and mean size of 43 Å within the amorphous Al_2O_3 matrix. More details on the fabrication of the $Fe-Al_2O_3$ samples can be found elsewhere [11, 12]. The $Fe-Al_2O_3$ samples presented tunnel magnetoresistance, an effect that is expected in ferromagnetic metal/insulator granular [12], but would not be present if the metal fraction had established a continuous metallic network, as could be presumed in a sample with that high volume fraction of iron.

The $Co-Al_2O_3$ granular sample was co-sputtered at room temperature from $Co-Al_2O_3$ targets onto a glass substrate with a metal fraction of *x*~ 0.50 and a thickness of 2000 Å. The Co atoms formed grains with 16 Å mean diameter, showing a closed-packed hexagonal atomic structure. This sample presented superparamagnetism and tunnel magnetoresistance indicating the non-percolation of sample [13].

The $Ti-SiO_2$ granular sample presented in this paper was obtained on a glass substrates by co-sputtering Ti and SiO_2 targets at room temperature. RBS showed a sample thickness of 1300 Å, and a metal fraction of *x*=0.32. XRD was performed, showing that Ti and SiO_2were non crystalline. Analyses were carried out in an FEI Titan 80/300 transmission electron microscope operated at 300 kV, equipped with a spherical aberration correction system. The cross section images were obtained using a high-angle annular dark-field detector (HAADF).

Fig. 1 shows the cross section of the $Ti-SiO_2$ sample but it didn't observe clearly defined grains. One possibility is the Ti grains (light grey contrast in Fig. 1) are smaller than 1nm. The electrical resistance experiments were carried out using the four-point method with a distance of approximately 2 mm between the electrical contacts. Direct current was injected parallel to the sample plane. The resistance (*R*) vs. voltage (*V*) measurements were performed in the range from 0 to 15 V. The resistance as a function of temperature (*T*) was measured between 4.2 K and 300 K. Assuming that the samples had a 0.32 metal volume fraction, grain size of approximately 10-20 Å and grains homogeneously distributed along the insulator in a hexagonal packing of non touching spheres, the distance between the spheres was estimated to be ~3-6Å. In this somewhat idealized configuration the maximum voltage drop between neighboring grains would bearound 15μV and the system would be in the low field regime even at the 4.2 K measurements, considering that k_BT/ein this case would be 350μV.

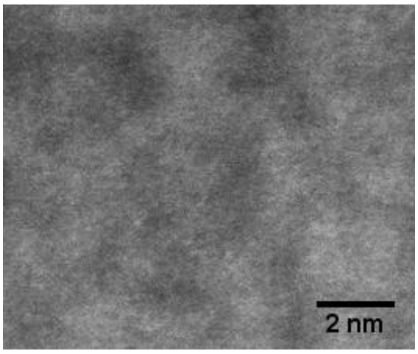

Fig. 1 Cross section STEM-HAADF images of the Ti–SiO_2 sample

III. RESULTS AND DISCUSSIONS

The resistance measurements at room temperature of the Ti-SiO_2 sample with x=0.32 are shown in Fig. 2. It can be seen that the resistance reduced with increasing voltage, with a variation of approximately 140 Ω over the voltage range. The Fe-Al_2O_3 [12] and Co-Al_2O_3 [13] systems had shown an analogous behavior, with the strongest variation in the Fe-Al_2O_3 sample.

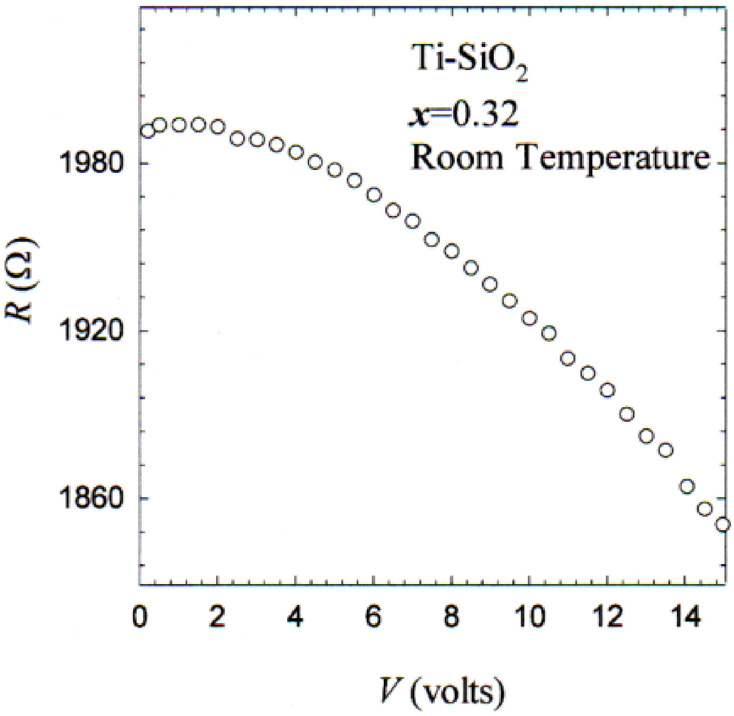

Fig. 2 Non-ohmic resistance versus voltage behavior at room temperature of the Ti–SiO_2 sample

The resistance measurement as a function of temperature of the Ti-SiO_2 sample is shown in Figs. 3a and 3d. To enable easy comparison with the results of the Fe-Al_2O_3 and the Co-Al_2O_3 samples, those are reproduced from references [12, 13]. In the upper row (Fig. 3 a-c) the curves are shown as a plot of Ln R vs. $T^{-1/2}$, in the bottom row (Fig. 3 d-f), the curves are plotted as Ln R vs. $T^{-1/4}$ according to the Mott VRH model. It is clearly visible, that the α coefficient of the Mott VRH fits the curves much better and over a broader temperature range than the α=1/2 does. The temperature range considered for the fitting was between 100 K and 150 K, and adjusted well over the whole measured range in the case of α=1/4. It is believed that the fitting with Mott-VRH adjusted better to the experimental results because the samples were not homogenous, i.e., *s*/*d* was not constant.

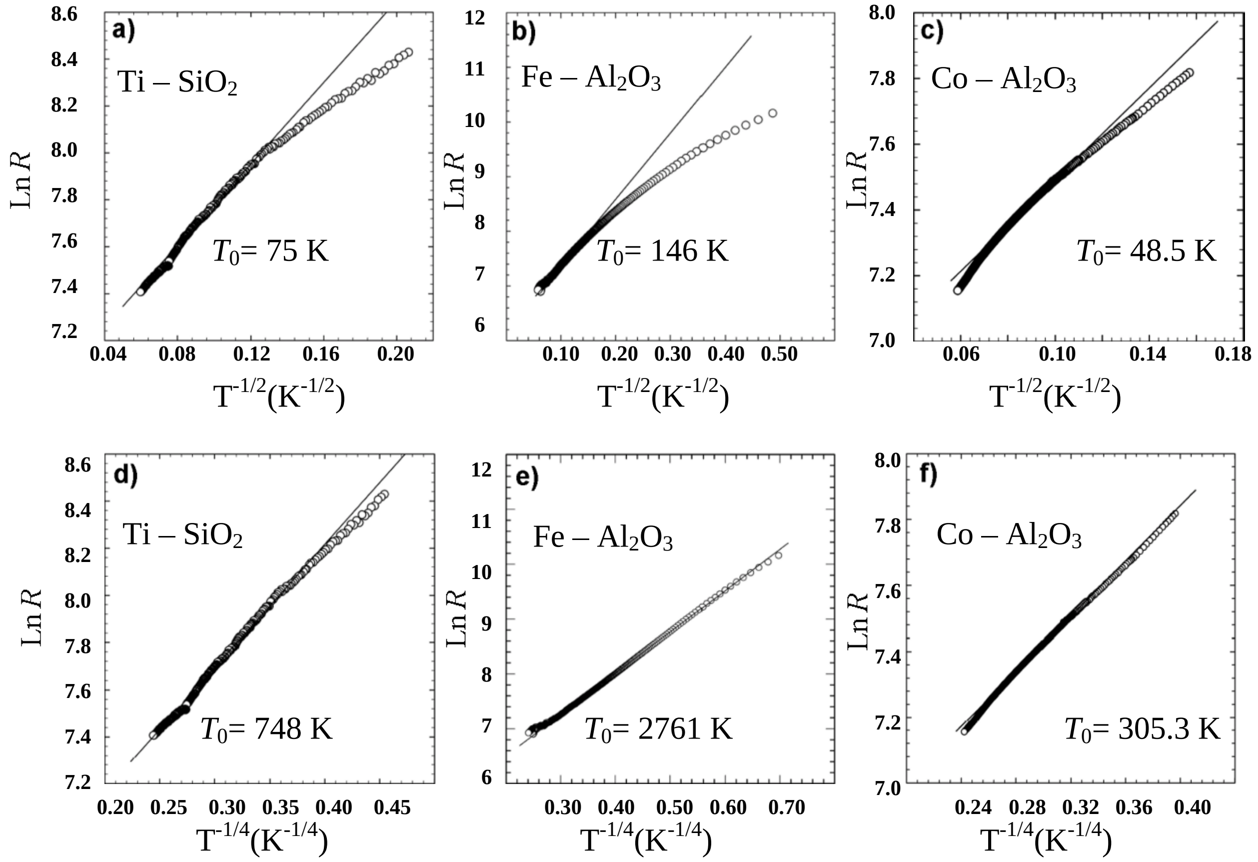

Fig. 3 Plots a-c show the Ln R vs. $T^{-1/2}$ fit of the three granular systems: a) Ti-SiO_2 with x=0.32, b) Fe-Al_2O_3 with x=0.48, c) Co-Al_2O_3 with x~0.50. Plots d-f show the same data with Ln R vs. $T^{-1/4}$ straight line fit according to the Mott-VRH model. The solid lines are least squares fittings of the experimental data between 100 K and 150 K using Eq. (1) with α=1/2 (upper row) and α=1/4 (lower row)

In Fig. 4a different currents were used in the Ti-SiO_2 system to obtain the Ln R vs. $T^{-1/4}$ curves in the 100-150 K temperature range. Again the analogous curves for Fe-Al_2O_3 and Co-Al_2O_3 from former reports [12, 13] are shown in Figs. 4b and 4c, respectively. The steeper inclinations of the low current lines in each plot show that the resistance variation at low currents is bigger than at high currents. It can be verified that T_0 was higher for lower applied current in all cases.

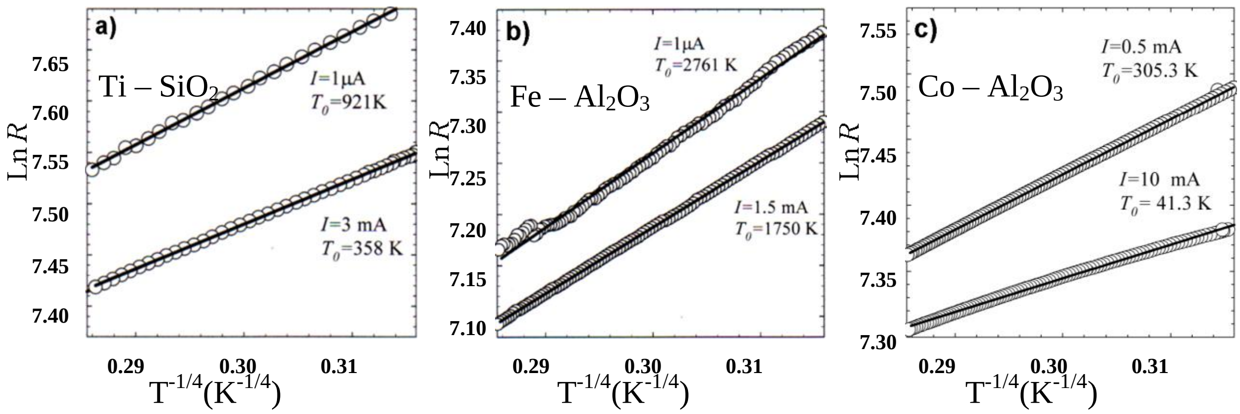

Fig. 4 Comparison of the resistance behavior as a function of temperature between 100 and 150 K, with high and low injected currents. a) Ti-SiO_2using 1 μA and3 mA; b) Fe-Al_2O_3using 1μA and 1.5 mA; c) Co-Al_2O_3using 0.5 mA and 10 mA

The good adjustment of the $T^{-1/4}$ lines with the experimental data gives an indication that the Mott variable range hopping is consistent with the measurements in low current as well in high current conditions.

To clarify the reasons why it was applied the Mott VRH model, originally developed for semiconductors, to the metal/insulator granular, it was reviewed the concepts of the model below. It seems clear to us that it can be used analogously for metallic grains separated by insulating barriers when the dimensions of grains and barriers are in the tens of Å range.

According to [6], the wave function of an electron tunneling between two states in metallic grains separated by an insulating barrier is proportional to

$$\psi(r_{ij}) \propto \exp(-\frac{r_{ij}}{\xi}) \tag{2}$$

Where r_{ij} is the distance between the two grains, $\xi = \hbar/(2m|\varepsilon|)^{1/2}$ is the localization length, m is the effective mass, and the bound particle energy is defined as $\varepsilon<0$.

The electrical resistance (R_{ij}) of an electron tunneling between a metallic grain with state i and another grain with state j can be written as

$$R_{ij} \propto \exp(2\frac{r_{ij}}{\xi} + \frac{\varepsilon_{ij}}{k_B T}) \tag{3}$$

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.

According to Mott [6] variable range hopping only occurs when the exponent in Eq. (3) is minimized. Keeping in mind that the distance between the metal grains can be written as $r_{ij}\approx \xi(T_0/T)^{1/4}$ and the typical energy difference between states ε_{ij} equals $\Delta_M=\Delta/(Nr_{ij}^3)$, where $\Delta_M \approx a\ k_B T_0^{1/4} T^{3/4}$ and N is the number of randomly distributed localized states in a band with energy width Δ, centered at the Fermi level ε_F. In the Mott-VRH model, T_0 is related to the localization length via the formula $T_0=\beta\Delta/N\xi^3$, a and β are numerical factors.

For any electron pathway, the total electrical resistance is the sum of resistances of the individual hoppings. In the Mott-VRH the resistance is given by Eq. (1) with $\alpha = 1/4$,

$$R = R_0 \exp(\frac{T_0}{T})^{1/4} \tag{4}$$

According to the relationship $T_0=\beta\Delta/N\xi^3$, when T_0 decreases, the localization length ξ increases. This is consistent with the behavior observed in Fig. 4, where R and T_0 are shown as a function of the bias potential and the injected current. In all cases T_0 decreases with higher current, showing that the localization length is bigger with higher current. This effect is consistently observed in the Ti-SiO_2, Fe-Al_2O_3, and Co-Al_2O_3 granular thin films.

Two interpretations could possibly explain the modifications of the electrical properties with higher current:

(i) Additional electrons tunnel on the same paths between the grains;

(ii) Additional electrons tunnel on additional new paths between more distant grains.

In the first explanation, if the same paths are being used, and considering that $r_{ij}\approx \xi(T_0/T)^{1/4}$and $T_0=\beta\Delta/(N\xi^3)$, than the keeping the same constant r_{ij} imply that ξ and T_0should not change. The additional term of the exponent in Eq. (3) is related to ε_{ij}, which equals $\Delta_M=\Delta/(Nr_{ij}^3)$ and remains the same as well. So the final value of R_{ij} in Eq. (3) would remain constant and the overall resistance R would not change. Therefore, the interpretation (i) does not describe the experimental results.

In the second explanation, if new paths are enabled between more distant grains, r_{ij} increases and each new path, being longer, and having higher resistance. Since the new paths, even though more resistant, would be turned on in parallel, the overall resistance R would drop. Since these new paths would form between more distant grains, according to $r_{ij}\approx \xi(T_0/T)^{1/4}$, the localization length ξ must increase too. So this interpretation does explain the drop of $R$and the increase of ξ with the increase of bias potential or applied current.

The interpretation (ii) also explains the increase of resistance variation with current or bias potential at lower temperatures. If a new path is turned on in parallel at room temperature, the total resistance of the sample decreases. If the same path is turned on at a lower temperature, it will have a higher resistance and the overall resistance variation will be higher.

It is important to note that the localization length, a mean value for the electrons on all activated paths, is given by $\xi = \hbar/(2m|\varepsilon|)^{1/2}$, and is supposed to be constant. However, when the bias is increased, T_0 obtained from the fitting of the experimental data decreases. As T_0 by definition is equal to $\beta\Delta/N\xi^3$, when T_0 decreases, ξ has to increase.

IV. CONCLUSIONS

This study of several different metal/insulator granular thin films showed that:

(i) The experimental results fitted better with $\alpha = 1/4$ than with $\alpha = 1/2$ for Ti-SiO_2, Fe-Al_2O_3, and Co-Al_2O_3 samples, indicating that the transport mechanism is equivalent to Mott-VRH;

(ii) When the current was increased in the low-field regime, *R*and T_0 decreased. Using the Mott-VRH model, the decrease of T_0 was associated with an increase of the localization length ξ;

(iii) The resistance variation as a function of the current or the bias potential was higher at lower temperatures;

(iv) The non-ohmic behavior of the metal/insulator granular thin films in the low-field regime was interpreted as being associated to new electronic paths between more distant grains, which decreased the total resistance of the samples and increased the localization length ξ;

(v) It is proposed that these modifications of R and ξ, when the current and/or bias potential are increased in the low-field regime, are universal properties of metal /insulator granular thin film.

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