JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 7, July 2007, p. 2121 - 2124

Extrinsic tunneling magnetoresistance in thick films of CrO_2-polystyrene composite

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Polystyrene-CrO_2 composite films with extrinsic tunneling magnetoresistance have been obtained. The electric conduction is 2D Mott variable range hopping in the temperature range 77-300 K. The magnetoresistance is negative when the field is aligned parallel to the current (in-plane geometry) and is due to the spin dependent intergrain tunneling of the charge carriers. It reaches a value MR = -10.6 % at room temperature and a magnetic field of 1T. When the field is applied in-plane but perpendicular to the current the magnetoresistivity is positive and has the average value MR = 3.56 %.

Received May 30, 2007; accepted June 27, 2007)

Keywords: Extrinsic tunneling magnetoresistance, Polymer composite films, CrO_2, Polystyrene, Variable range hopping

1. Introduction

The phenomenon known as extrinsic tunneling magnetoresistance (ETMR), i.e., spin tunneling controlled by interfaces, was recently unveiled in $La_{2/3}Sr_{1/3}MnO_3$ [1] and was studied mainly in manganites. Since the very beginning, the phenomenon was attributed to the processes occurring at the grain borders. The electric transport in granular semi metallic ferromagnetic systems occurs by intergrain tunneling controlled by grain surface state. This fact supposes lower fields as compared with single crystals where the basic process is the field reduction of the spin fluctuations, hence, requires rather intense fields.

In a simple model, it is considered that a tunneling barrier excedent appears in granular systems due to the exchange energy involved in spins energetics if the magnetic moments of the two grains are randomly oriented. In these processes the role of the surface spin state is crucial. Spin scattering length is sensitive to the interface related spin clustering and dead areas [1,2]. However, the nature of the mechanisms controlling the spin transfer through the interface is still controversial [3-7].

A control of the interface states in a granular system is difficult to achieve, hence, dilution with a non-magnetic compound should be a solution.

Despite the lack of an appropriate model, the search and findings of materials displaying ETMR proved to be extremely dynamic. More than one hundreds reports were published only in the last year involving new materials or new procedures of fabrication. In a large majority, these methods regard the $La_{1-x}M_xMnO_3$ system, (M: Ba, Ca, Sr) [e.g., Refs. 8, 9], composites with inorganic compounds, e.g., $La_{1-x}Ca_xMnO_3/V_2O_5$, $La_{1-x}Ca_xMnO_3/ZrO_2$, $La_{2/3}Sr_{1/3}MnO_3/CeO_2$, $La_{0.67}Ca_{0.33}MnO3/SrTiO_3$, and $La_{0.7}Sr_{0.3}MnO_3$/glass [10-18], doped manganites like, $La_{1-x}(Bi)Ca_xMnO_3$, $La_{2/3-2x}Eu_xCa_{1/3}Sr_xMnO_3$, $Nd_{1-x}Sr_xMnO_3$/Ag [19-21]. Recently, molybdats $(AA')_2FeMoO_6$ and rheniats $(AA')_2FeReO_6$ (A=A'=Sr, Ca) like Sr_2FeReO_6 [22].

The second type of material but by far the most promising is chromium dioxide CrO_2. It is a metastable compound, difficult to synthesize (needs high pressure) but takes the advantage of 100% spin polarization. This property is due to the fact that minority spin subband has the Fermi level in the gap, hence, is completely empty [23].Reports on the use of this material in ETMR systems are scarce due to a rather bed stability and large grain size. One could mention composites like CrO_2/Cr_2O_3 [24, 25], CrO_2/TiO_2 [26], mechanical compacts CrO_2/RuO_2 [27], and $(Cr\text{-}M)O_2$ (M=V, Mn, Fe, Co) [28, 29]

In few cases, the inorganic matrix was replaced by a polymeric one. By our knowledge, there are only five reports regarding this kind of composites despite the large flexibility of these matrices: $La_{2/3}Sr_{1/3}MnO_3$ in polyparaphenylene matrix [30, 31] and polystyren-CrO_2 composites [32, 33].

In this paper we present the transport properties in magnetic field of composite thick films fabricated from polystyrene-CrO_2. These films display an important tunneling magnetoresistivity at room temperature.

2. Experimental

The films were prepared from CrO_2 powder (Magtrieve from Aldrich) mixed in high purity linear polystyrene solution in chloroform. The mixture, of appropriate CrO_2/matrix ratio is dropped on clean glass supports in a wire frame designated to shape the thick film. After solvent evaporation the film is conditioned 48 hours at 20±2°C. In this way, composite films with thickness ranging from 50 to 300 μm can be obtained. The as resulted film has less than 1% polymer in composition. For electric contacts, we used silver paste.

Transport properties were measured using either Montgomery method [34] which is appropriate for anisotropic systems or by a simply four point method. In both methods, the sample is fed with a current smaller than 1 mA from a current source Keithley 227 and the voltage is measured with a Keithley 182 nanovoltmeter. Magnetoresistivity is defined as $MR = \frac{R(H) - R(0)}{R(0)} 100\%$ where R is the electric resistance and H the applied magnetic field.

There are three geometries used in our measurements: *i*) H perpendicular on the sample surface, *ii*) H parallel with film plane but perpendicular on current, and *iii*) H parallel with both film plane and current. The latter provides the tunneling magnetoresistivity.

3. Results and discussions

Fig. 1 shows the morphology of the composite. The elongated CrO_2 grains are distributed almost randomly. A certain clustering is salient. The clustering is enhanced in thicker films.

The temperature T dependence of the electrical resistance R follows a variable range hopping (VRH) dependence [36] in the temperature range 77-300 K (Fig. 2):

$$R \propto \exp\left[\left(\frac{T_0}{T}\right)^{1/(D+1)}\right], \quad (1)$$

where D the dimensionality of the charge hopping and the scaling temperature T_0 is connected to the localization radius and the density of the localized states at Fermi energy. In the the Mott VRH picture a charge carrier may either hop over a small distance with a high activation energy or hop over a long distance with a low activation energy. This type of conduction is characteristic for localized bands with energy-independent density of state at Fermi level. The good fit of the data with both 3D and 2D equation makes the discrimination between dimensionalities hardly to carry out. However, the best fit is obtained for 2D. For films, 2D would be a natural choice but, in the case of a thick film, 3D hopping might also contribute to the total conduction. The matching with the requirements of percolation theory seems to be less necessary because the amount of ferromagnetic semimetal is much higher than the geometrical percolation threshold. It is to note that despite the low polymer concentration, the transport displays such a strong localization behavior. In polycrystalline films the conduction is almost metallic like both below and above Curie temperature displaying either a quadratic temperature dependence below 240 K [37] or an exponential increase with T typical for a small gap in the excitation spectrum [38]. Following the calculation of Mazin *et al*., the band structure undergoes strong changes that enhance the carrier scattering by spin fluctuations [39]. Therefore, the role of the matrix is not trivial even in the absence of the magnetic field.

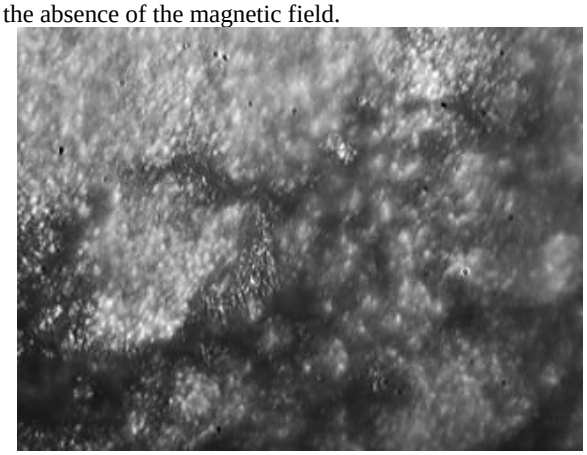

Fig. 1. Morphology of a thick film of the composite polystyrene-CrO_2 (44X).

The magnetoresistance was measured at room temperature in all geometries mentioned above. In the case when the magnetic field is applied perpendicular to the film plane, the magnetoresistance is of orbital origin and in these materials is small. It is noteworthy that a field of 1 T applied in this geometry increases the magnetoresistive response obtained in the geometries with the field applied parallel to the film. It acts like a training procedure preceding a high tunneling magnetoresistance.

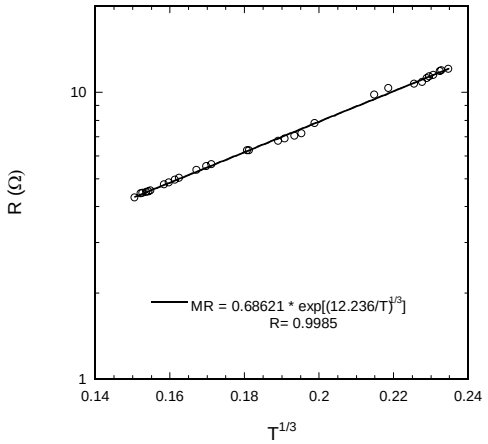

Fig. 2 Temperature dependence of the resistance of the polystyrene-CrO_2 composite.

When the field is applied parallel to the film plane and to the transport current the magnetoresistivity is of pure spin tunneling origin. Indeed, the Lorentz force is zero in this geometry and the change of the resistivity with field is due to the field induced change of the orientation of the magnetic moment of the ferromagnetic grains. As expected, the resistance decreases when the field is applied, i.e., the magnetoresistance is negative with a tendency to saturation at high fields (Fig.3). Roughly, the field dependence obeys the following law:

$$\frac{\Delta R}{R} = A\tanh\left(\frac{H}{H_0}\right) \quad (2)$$

The fit of the data (the solid line in the Fig. 3) with this law provides H_0 = 0.52 T and A = -5.9 %. If one considers that H_0 is related to T in a way typical for magnetic systems, $H_0 = \frac{k_B T}{\mu\mu_B}$, where k_B is the Boltzmann constant, μ_B the Bohr magneton, and μ the average relative magnetic moment of the CrO_2 grain, one obtains μ = 447 for T = 300 K which is of the same order of the moment reported for other granular compounds [40].

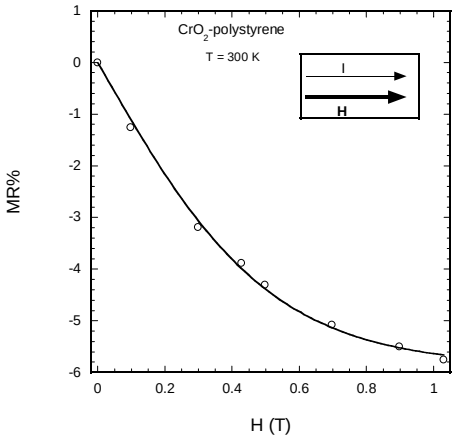

Fig. 3*. Field dependence of the magnetoresistance MR for the field applied parallel to the measuring current I at 300 K. The solid line is a fit with the function MR ~tanh(H/H0).*

The average value of the magnoteristivity in this geometry is -10.6% at room temperature which is the highest value reported in composites with polymer matrix. Such values were reported for thin films at 5 K and 2 T [41]. At room temperature, CrO_2 polycrystalline films need fields as high as 8T to reach a tunneling magnetoresistance of only -4.4 % [42].

It is not clear the origin of the training effect. We can just speculate that either a microscopic arrangement of the grain in the soft matrix occurs or the magnetic field switches some metastable spin states.

When the field is applied parallel to the film surface but perpendicular to the transport current (thereafter *transverse magnetoresistivity*), the magnetoresistance changes the sign, MR > 0 and is three times lower (Fig. 4). The tendency to saturation is salient at fields H > 0.25 T but the field dependence is different from *tanhH*. The average value of the transverse magnetoresistance is 3.56 %. A positive magnetoresistivity cannot be attributed to orbital effects because for a field H ≤ 1T the deviation of the carriers would be larger than the film thickness. A generally accepted explanation is not available in the framework of VRH model yet. Most likely, in the case of strong localization, the field produces an appreciable shrinkage of the wave function reducing its overlap, hence the tunneling probability of the carriers [36].

More elaborated models consider also the spin contribution. A magnetic field could polarize some of the single occupied impurity states blocking the hopping processes involving these states [43]. Consequently, the effective density of state is lowered and the resistance is increased.

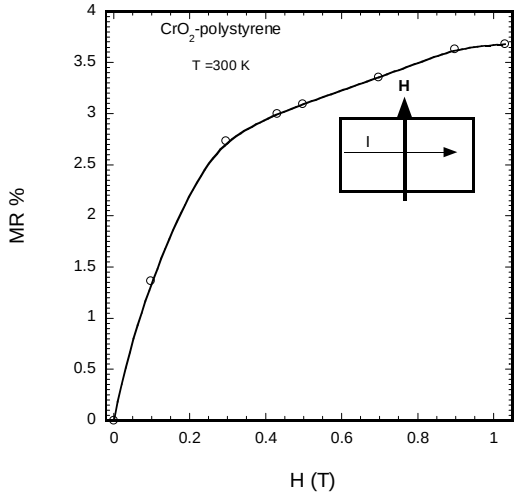

Fig. 4. Field dependence of the transverse resistance of the polystyrene-CrO_2 composite thick film. The solid line is guide for the eye.

Concerning the percolation process, it was difficult to investigate the critical behavior due to the fast increase of the resistance for more than 0.04% polystyrene in the composite that leaves a too narrow range of concentration capable to provide a critical exponent. At this concentration, the geometrical percolation is undoubtedly guaranteed but the intergrain tunneling seems to be extremely low through the polymer layer.

In conclusion, we have obtained thick composite films of polystyrene-CrO_2 displaying extrinsic tunneling magnetoresistance. The charge carrier conduction occurs by 2D variable range hopping in the temperature range 77 – 300 K. When the field is oriented parallel to the film plane and current, the magnetoresistance is of extrinsic tunneling origin, hence, negative whereas it is positive when the field perpendicular to the current and could originate in the impurity wave length shrinkage.

Acknowledgment

This work was supported by the Romanian National Authority for Research and Science under the Project CERES 241/2004.

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