Thin-film heterostructures containing La–Sr manganite and soft ferromagnets: metallorganic chemical vapour deposition, characterization and tunneling magnetoresistance

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A new approach (variant-structure and heterostructures with soft ferrite) to TMR effect of manganites was demonstrated.

Interest in doped manganites $La_{1-x}Sr_xMnO_3$ of a perovskite structure arises from the discovery of their colossal magnetoresistance in certain ranges of doping. The main obstacle for the use of these compounds for magnetic sensoring is a high magnetic field (~1 T) required for a notable CMR effect. Magnetic field concentration with a superconducting lens and the pattering of different tunnelling structures were shown to increase the magnetic sensitivity of CMR materials. Another way is to amplify an external magnetic field using a layer of soft magnets. The latter must meet the following requirements: low coercitivity (Hc < 10 Oe), high magnetic moment, Curie temperature exceeding T_c of CMR material and chemical inertness of ferrite to CMR – material and substrate. In this work, we used spinels $CoFe_2O_4$, $MnFe_2O_4$ and garnets $(La_xNd_{1-x})_3Fe_5O_{12}$ (x = 0, 0.3) as magnetic layers for magnetic field enhancement because they meet all these requirements; in particular, they possess high magnetic moments.

All the films were grown by a single source MOCVD process on single crystal substrates including (110) $ZrO_2(Y_2O_3)$, (111) $ZrO_2(Y_2O_3)$, (001) MgO, (102) $Gd_3Ga_5O_{12}$ and (111) $Gd_3Ga_5O_{12}$. La(thd)$_3$, Nd(thd)$_3$, Mn(thd)$_3$, Co(thd)$_2$, Fe(thd)$_3$, Ca(thd)$_2$, Sr(thd)·2Phen, where thd = 2,2,6,6-tetramethylheptane-3,5-dionate and Phen = *o*-phenanthroline, were used as precursors.[1,2] The deposition temperatures 750–850 °C were used for different compositions, the precursor evaporation temperature was 250 °C, the oxygen partial pressure was 2–5 mbar, and the total gas pressure was 5–10 mbar. The manganite compositions prepared included perovskites $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Sr_{0.3}MnO_3$ spinel $CoFe_2O_4$ and $MnFe_2O_4$. Garnet $(La_xNd_{1-x})_3Fe_5O_{12}$ (x = 0, 0.3) films were deposited as ferromagnetic layers in the heterostructures with the manganites.

X-ray and HREM characterization revealed the dependence of the microstructure of the manganite films prepared on the substrate materials. Films on (110) $ZrO_2(Y_2O_3)$ and (001) MgO were epitaxial, as well with the orientations (110) and (001), respectively, but possessed a block structure with small angle boundaries between the blocks. A difference between these two sets of samples can be explained by switching from 2D to 3D nucleation mode during film growth with the increase of the lattice mismatch and lattice dissimilarity. Manganite films on (111) $ZrO_2(Y_2O_3)$ had out-of-plane orientation (110) with the in-plane variant structure. The orientation relations were found from pole figure XRD measurements and electron diffraction patterns in HREM and can be written as follows (Figure 2):

(111) $[1\bar{1}0]$ $ZrO_2(Y_2O_3)$ // (110) $[1\bar{1}1]$ perovskite.

Orthogonal NCSL is formed for (111) $ZrO_2(Y_2O_3)$ by $[\bar{1}01]$ and $3\cdot[1\bar{2}1]$, for (110) perovskite by $[1\bar{1}1]$ and $4\cdot[1\bar{1}\bar{2}]$, respectively. Lattice mismatch is about 7 or 0%, for the directions. There are totally six variants of the type.

We supposed the growth of variant structures $CoFe_2O_4$ and $MnFe_2O_4$ on $SrTiO_3$, but we found that the spinel layer grows epitaxially on (001) $SrTiO_3$, which excludes the possibility of significant tunnel magnetoresistance because of the absence of high angle boundaries (Figure 1). However, $La_{0.7}Sr_{0.3}MnO_3$ could be grown only in the polycrystalline random state on (001) $CoFe_2O_4$/(001) $SrTiO_3$. Garnet $Nd_3Fe_5O_{12}$ films were grown epitaxially on (102) $Gd_3Ga_5O_{12}$ but only random manganites were deposited on top of both. $Nd_3Fe_5O_{12}$ films were also random on (001) $SrTiO_3$ and (001) $La_{0.7}Sr_{0.3}MnO_3$/(001) $SrTiO_3$. All the heterostructures were used to measure the effect of the crystallinity and magnetic coupling on the magnetoresistance of the manganites.

There are two important low-field phenomena related to the tunnel magnetoresistance in the manganites. One of them is the magnetic reversal transition related to the magnetization hysteresis loop and resulting in the positive magnetoresistance peaks. At a somewhat higher field, the resistance drops sharply to a value lower than that in a zero field (negative tunnel magnetoresistance). Finally, in a much higher field, the resistance switches to the rather weak linear dependence on the field.[3] The latter corresponds to the suppression of the spin fluctuations of scattered or trapped carriers considered to rest in a kind of the paramagnetic state. It demands a rather high field and is not interesting for applications. We consider only negative tunnel magnetoresistance (TMR).

The TMR data for the manganite films and heterostructures are summarised in Figure 3. Three groups of samples can be

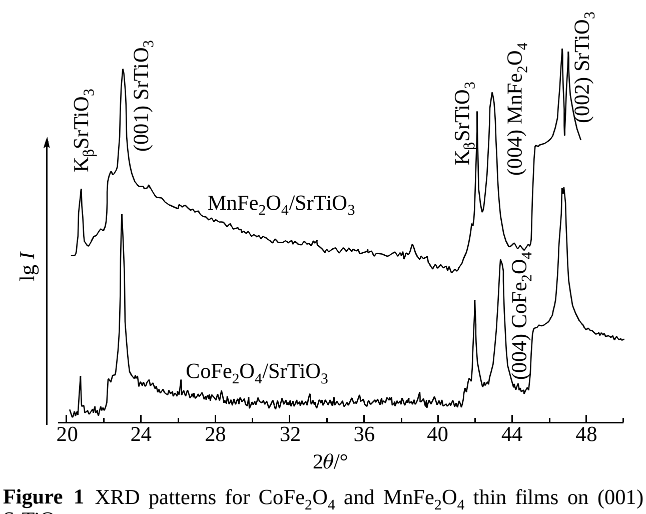

Figure 1 XRD patterns for $CoFe_2O_4$ and $MnFe_2O_4$ thin films on (001) $SrTiO_3$.

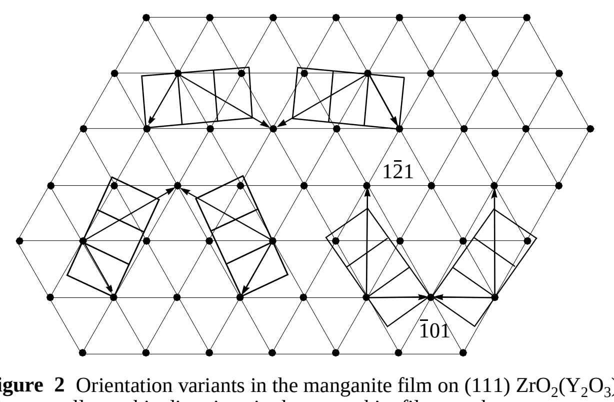

Figure 2 Orientation variants in the manganite film on (111) $ZrO_2(Y_2O_3)$. The crystallographic directions in the perovskite film are shown.

deduced from the data. First, the samples with very low TMR. Those are the films without large-angle boundaries. The second group is formed by the samples with TMR below 10% (at 77 K). Those are all polycrystalline random manganites. This kind of the samples was well described previously.[4–6] The third group of the samples is comprised of films with the variant epitaxial structure. They demonstrate higher magnetic field sensitivity and higher TMR (above 15% at 77 K and 0.1 T) as compared to the polycrystalline samples reported here and elsewhere.

Thus, it can be concluded that special large-angle boundaries formed between the nanodomains of the structural variants allows for high TMR. There is no significant TMR without large-angle boundaries. There is only modest TMR with random large-angle boundaries. The higher TMR was measured in the films on (111) $ZrO_2(Y_2O_3)$ resulting from the higher angles between the domain lattices in the perovskite manganite film as compared to (001) $ZrO_2(Y_2O_3)$ (Figure 2). Also meander structures patterned from the film revealed somewhat higher TMR as compared to the continuous films.

We also found a new possibility for a further increase in the TMR in a low magnetic field. The result was observed with the soft ferromagnetic layer of ferrospinel ($MnFe_2O_4$) grown over the manganite film with the variant structure. We used only Mn-based spinel because magnetization for $MnFe_2O_4$ is higher than that for $CoFe_2O_4$. The magnetic field sensitivity and the magnitude of TMR were increased. Photolithography was used for the pattering of meander structures in the $La_{0.7}Sr_{0.3}MnO_3$ layer for increasing current way. In this case, more tunneling boundaries can impact to overall magnetoresistance [for $La_{0.7}Sr_{0.3}MnO_3$/(111) $ZrO_2(Y_2O_3)$] (Figure 3).

Ferrospinel layers were insulating and possessed no appreciable magnetoresistance. This implies that the effect of the ferrospinel consists in the magnification of the effective external magnetic field applied to the manganite film. The effect of the soft ferromagnetic layer takes place not only for the films with the variant structure but also for the random polycrystalline films (Figure 3). One can consider the perspectives of the approach with the ferromagnetic insulating layers with the higher magnetic induction as compared to the ferrospinels and garnets (Figure 4).

Garnet $(La_xNd_{1-x})_3Fe_5O_{12}$ (x = 0, 0.3) films were deposited on (111) $Gd_3Ga_5O_{12}$, but only random manganites were grown on the top of it. All the heterostructures were used for measuring the effect of the crystallinity and magnetic coupling on the

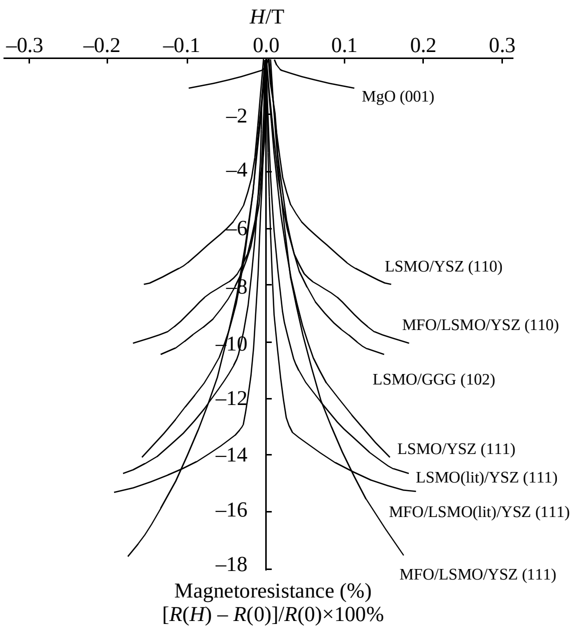

Figure 3 Low field magnetoresistance of different test samples. The abbreviations are as follows: MgO is (001) MgO, YSZ is $ZrO_2(Y_2O_3)$, LSMO is $La_{0.7}Sr_{0.3}MnO_3$, MFO is $MnFe_2O_4$, GGG is $Ga_3Gd_5O_{12}$, 'lit' – measured on the meander obtained by wet chemical lithography.

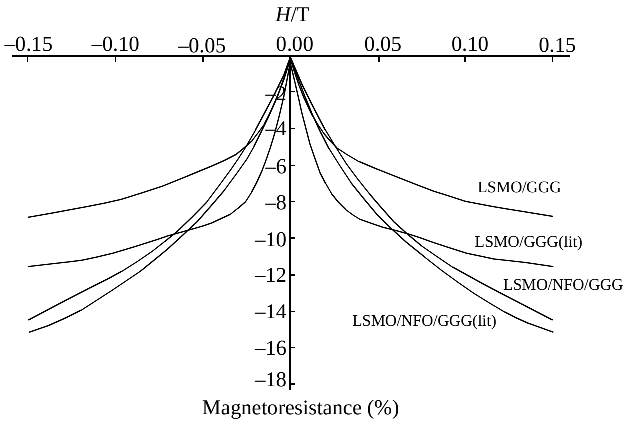

Figure 4 Low field magnetoresistance of the samples including garnet layers. The abbreviations are as follows: GGG is $Ga_3Gd_5O_{12}$, LSMO is $La_{0.7}Sr_{0.3}MnO_3$, NFO is $Nd_3Fe_5O_{12}$, 'lit' – TMR measured on the meander obtained by wet chemical lithography.

magnetoresistance of the manganites. The results of magnetoresistance measurements for the heterostructures consisting of a $La_{0.7}Sr_{0.3}MnO_3$ layer and a $Nd_3Fe_5O_{12}$ garnet layer, which have magnetization higher than that of a La–Nd solid solution, revealed a strengthening influence of the ferromagnetic buffer layer (Figure 4).

The magnetoresistance depends on the chemical composition of a garnet sublayer: with increasing La content of a solid solution $(La_xNd_{1-x})_3Fe_5O_{12}$, the influence of a buffer layer weakens. The application of photolithography to the creation of a meander structure allows us to increase the magnetoresistance for $La_{0.7}Sr_{0.3}MnO_3/Ga_3Gd_5O_{12}$ (Figure 4), while the magnetoresistance does not vary for $La_{0.7}Sr_{0.3}MnO_3/Nd_3Fe_5O_{12}/Ga_3Gd_5O_{12}$. The X-ray diffraction data show that manganites are weakly textured with out-of-plane orientation (001) for $La_{0.7}Sr_{0.3}MnO_3/Ga_3Gd_5O_{12}$. It protects the appearance of special boundaries in a plane of a film, where tunnel magnetoresistance occurs. Manganite films on a buffer layer of $Nd_3Fe_5O_{12}$ are all polycrystalline random. Thus, as well as in the case of heterostructures with ferrospinels, forming of textures in magnetoresistive layer, lengthening current way and amplification of magnetic field sensitivity are promoted for increase $La_{0.7}Sr_{0.3}MnO_3/Ga_3Gd_5O_{12}$.

Thus, we found that the epitaxial variant structure provides a significant advantage over the polycrystalline random films and allows us to reach a higher TMR and a higher magnetic field sensitivity, as well as a lower field of the magnetic reversal transition. They also provide this advantage over monovariant epitaxial films as the latter possess neither TMR nor magnetic reversal transition but only CMR in the high magnetic field near the Curie temperature. This advantage is evidently related to the unique microstructure of the variant epitaxial film with the high density of the special large-angle boundaries.

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