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Growth and Investigation of Oxide Heterostructures Based on Half-Metallic Fe_3O_4

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We report thin films of ferromagnetic Fe_3O_4 (magnetite) grown by a reactive magnetron sputtering at $T = 300 \div 450°C$ on lattice-matched MgO, and bilayer structures composed of Fe_3O_4 and underlying epitaxial films of highly conductive electron-doped $In_2O_3\langle Sn\rangle$, $LaNiO_3$, and antiferromagnetic CoO. The prepared Fe_3O_4/MgO films and the bilayer structures demonstrated clearly defined resistance anomaly at Verwey transition point ($T_V \approx 100-120$ K). Formation of high resistance interlayer was indicated between the adjacent conducting Fe_3O_4 and $LaNiO_3$ layers. However, relatively low interface resistivity of about 0.1 Ω cm^2 (at $T = 300$ K) was estimated for the patterned $Fe_3O_4/In_2O_3\langle Sn\rangle$ bilayer structures. Vertical electrical transport measurements revealed strong nonlinearity in the $I-U$ dependences of the $Fe_3O_4/In_2O_3\langle Sn\rangle$ interface at $T < T_V$.

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1. Introduction

During the last few years, there was increasing interest in various oxide heterostructures as well as electron- and hole-doped diode structures containing ferromagnetic half-metallic oxides with spin-polarized carriers. The heterostructures stacked from ferromagnetic (FM), antiferromagnetic (AFM), highly conducting oxides, and isolating barrier layers are highly desirable for future spintronics applications. However, it is well known that spin-dependent transport in the heterostructures and magnetic tunnel junctions depends crucially on intrinsic

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behaviour of ferromagnetic electrodes and tunnel barriers as well as on quality of interfaces between magnetic materials and usual conductors.

Ferrimagnetic magnetite, Fe_3O_4, with an inverse cubic spinel structure ($a = 0.8396$ nm) is known as a typical half-metallic ferromagnet. It exhibits almost fully spin-polarized carriers both above and below 300 K. Unusually high Curie temperature value of the material ($T_c \approx 850°C$) compared to colossal magnetoresistance (CMR) manganites ($T_c \leq 350$ K) and other known ferromagnetic oxides makes Fe_3O_4 very promising for room temperature applications [1]. It is important to note, however, that growth of high quality magnetite films is complicated due to neighbouring phases, namely, Fe_2O_3 (hematite) and FeO (wuestite) in the Fe–O phase diagram. It means that there is a need to optimize technological conditions precisely in order to grow single phase Fe_3O_4 films. Furthermore, additional requirements might be satisfied to form high quality interfaces between various oxides in the heterostructures.

In this work, we were focussing on high quality Fe_3O_4 thin films and bilayer structures with Fe_3O_4 layers grown on underlaying conductive $In_2O_3\langle Sn\rangle$ (ITO), $LaNiO_3$ (LNO), and antiferromagnetic CoO. ITO is a wide gap ($E_g \approx 3.5$ eV), highly doped n-type semiconductor with typical carrier density (10^{20}–10^{21} cm^{-3}). $LaNiO_3$ is a metallic oxide with the highest carrier density $N \sim 6 \times 10^{21}$ cm^{-3}. Highly conductive ITO and $LaNiO_3$ layers have been used in this work as bottom electrodes to investigate vertical electrical transport in the heterostructures. We believe that high quality Fe_3O_4/CoO bilayer structures could be very promising in future for fabrication of magnetic tunnel junctions.

3. Preparation and characterization of the films and heterostructures

All the films and heterostructures were prepared in this work by a reactive DC magnetron sputtering under various Ar:O_2 mixture pressures using disc-shaped metallic Fe, In (9 mol. % Sn), Co, and ceramic ($LaNiO_3$) targets of 3 cm in diameter.

Series of Fe_3O_4 films ($d = 0.05 \div 0.4$ μm) were grown *in situ* at $T = 300 \div 450°C$ under a fixed Ar:O_2 (30:1) gas mixture pressure of about 5 Pa onto MgO(100) substrates and epitaxial conductive ITO and $LaNiO_3$ underlayers. To find the optimized deposition conditions for single phase film growth, series of MgO substrates were kept in the *off-axis* position at different distances from the target. It is worth noting in this case different deposition rates and different Fe/O_2 ratios (in a gas phase) during film growth on different substrates. Just after deposition, the magnetite films were cooled down slowly to room temperature under the same oxygen pressure conditions. The overlying Fe_3O_4 films were patterned to investigate electrical properties of the interfaces. With this goal in mind, small disc-shaped squares of the material (0.5 mm in diameter) were deposited through a mask on conducting ITO and LNO bottom layers.

The ITO films of epitaxial quality were magnetron sputtered under Ar:O_2 (4:1) pressure of about 5 Pa at 400°C on lattice-matched yttrium stabilized zirconia, YSZ(100). The films were annealed after deposition in vacuum at 525°C to achieve the highest carrier density. The LNO films were grown epitaxially under Ar:O_2 (4:1) pressure of 5 Pa at 550°C on lattice-matched $NdGaO_3$. The films were saturated by oxygen during additional annealing at T = 600°C and $p_{O_2} = 5 \times 10^4$ Pa.

Two phases, namely CoO (NaCl structure, a = 0.426 nm) and Co_3O_4 (normal spinel structure, a = 0.808 nm) are the most stable in the Co–O system. Optimization procedure for growth of high resistive antiferromagnetic single phase CoO films undertaken in this work was similar to that described by us earlier in more detail for the Fe_3O_4 films [2]. Thin CoO films ($d = 0.1 \div 0.2$ μm) were grown by magnetron sputtering on lattice-matched MgO(100) substrates. The deposition conditions of the films mentioned above are summarized in Table.

TABLE

Deposition parameters used in this work for growth of Fe_3O_4, ITO, LNO, and CoO films.

Film	Target	Gas	Deposition pressure [Pa]	Substrates	Substrate temperature [°C]	Film quality
Fe_3O_4	Fe	Ar:O_2 30:1	5.0	MgO(100)	300–450	Epit.
				ITO/YSZ		(113) texture
				LNO/ $NdGaO_3$		(100) texture
				CoO/MgO		Epit.
ITO	In (9 mol% Sn)	Ar:O_2 4:1	5.0	YSZ(100)	525	Epit.
$LaNiO_3$	$LaNiO_3$	Ar:O_2 4:1	5.0	$NdGaO_3$ (100)	550	Epit.
CoO	Co	Ar:O_2 30:1	5.0	MgO(100)	400	Epit.

Crystalline structure of the films and heterostructures were characterized by X-ray diffraction (XRD) and reflected high-energy electron diffraction (RHEED). We were focussing on the characteristic electrical resistance anomaly at the Verwey transition ($T_V \approx 120$ K) to elucidate effects of substrate and deposition conditions on quality of the ferromagnetic material. Vertical electrical transport investigations for the patterned $Fe_3O_4/In_2O_3\langle Sn\rangle$, $Fe_3O_4/LaNiO_3$ bilayer structures were carried out to estimate the interface resistance between the adjacent conducting layers and to study current–voltage ($I-U$) characteristics of the interfaces. The measurements were performed at $T = 80-300$ K by applying three point-probe method for the patterned Fe_3O_4/ITO and Fe_3O_4/LNO bilayer films.

3. Results and discussion

Figure 1 shows typical (004) XRD patterns for series of magnetite films grown simultaneously at 400°C onto several MgO(100) substrates positioned at various distances from the target. Thickness of the films ($d = 0.05 \div 0.4$ μm) and the corresponding deposition rate (40 to about 7 nm/min) decreased systematically with substrate to target distance. The estimated *off-plane* lattice constant of the highest quality Fe_3O_4 films was of about 8.4 Å in a good agreement to recent data for similar Fe_3O_4/MgO films [3–5]. Slight shift of the (004) Fe_3O_4 XRD line toward very intense (002) line of MgO substrate can be seen from the figure. Slight decrease in the off-plane lattice parameter of Fe_3O_4 films observed in this work with decreasing thickness may be easily understood in terms of epitaxial strain.

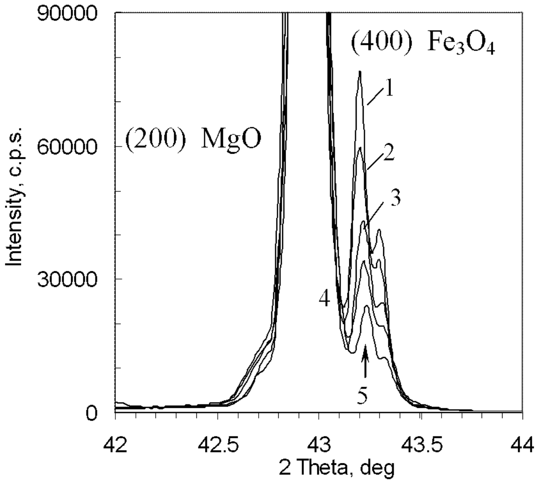

Fig. 1. Typical (004) XRD patterns of $\Theta-2\Theta$ scans (Cu K_α radiation) measured for several Fe_3O_4/MgO films grown at 400°C at various distances from the target. Thickness of the films d [μm]: 0.4 (1), 0.35 (2), 0.15 (3), 0.12 (4), 0.05 (5).

The magnetite films grown at similar deposition conditions on high quality (epitaxial) ITO, LNO demonstrated dominating (100) texture as found from their $\Theta-2\Theta$ XRD scans. Meanwhile, clearly defined RHEED patterns demonstrated epitaxial quality for Fe_3O_4 films grown at similar deposition conditions on lattice matched CoO ($\Delta a/a \approx 0.4\%$) layers. Worse crystalline quality of Fe_3O_4 films on ITO and LNO may be understood taking into account relatively large lattice mismatch of Fe_3O_4 lattice in respect of that of ITO ($\Delta a/a \approx 15\%$) and LNO ($\Delta a/a \approx 8\%$).

Figure 2a shows resistance versus temperature for high quality Fe_3O_4 film prepared on MgO (1) and that buffered by epitaxial CoO layer (2). Room temperature resistivity of both the Fe_3O_4/MgO and Fe_3O_4/CoO/MgO films ranged typically from about 10 to 40 mΩ cm. In both these cases, clearly defined resistance anomalies at the characteristic Verwey transition ($T_V = 120 \div 110$ K) seen in the figure certify unambiguously high crystalline quality of the film material.

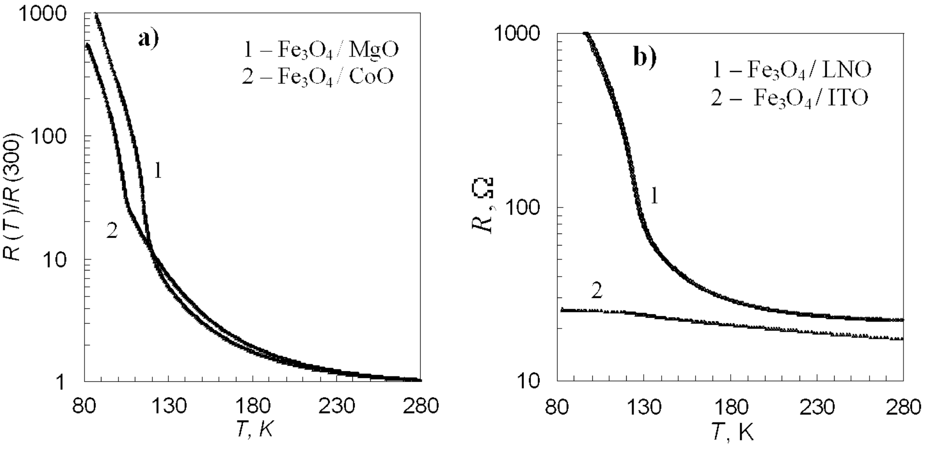

Fig. 2. Resistance versus temperature measured for epitaxial Fe_3O_4 films grown on MgO and CoO/MgO layers (a) and those of the Fe_3O_4/ITO and Fe_3O_4/LNO bilayer structures.

Similar R–T curves for the Fe_3O_4/ITO (1) and Fe_3O_4/LNO (2) bilayer structures are displayed in Fig. 2b. Clearly defined $R(T)$ increase at T_V can only be seen for the Fe_3O_4/LNO films. Meanwhile, only slight resistance increase and saturation behaviour of $R(T)$ dependence below T_V was measured for the Fe_3O_4/ITO samples. To explain the observed difference in the $R(T)$ behaviour, we assume effective shunting of the Fe_3O_4 resistance by the underlaying highly conductive ITO film and possible formation of high resistance interface between Fe_3O_4 and LNO.

Figure 3a, b demonstrates the contact resistivity, R_k, of the Fe_3O_4/ITO and Fe_3O_4/LNO interfaces estimated from the relationship: $R_k = U_{23}S/I_{12}$, where U_{23} is the measured voltage drop between points 2 and 3 when passing current between 1 and 2 and S is the interface square (see inset to Fig. 3a). Thus, following Fig. 3a, b we point out relatively low interface resistance of the Fe_3O_4/ITO interface. It seems likely that high resistance interlayer between Fe_3O_4 and LNO occurs during growth of the Fe_3O_4 top layer.

In Fig. 4a we show typical I–U curves measured at different temperatures for the Fe_3O_4/ITO interface in a case of vertical electrical transport realized in this work by applying 3 point-probe method. It is important to point out strong nonlinearity of the interface resistance at low temperatures, i.e. below the Verwey

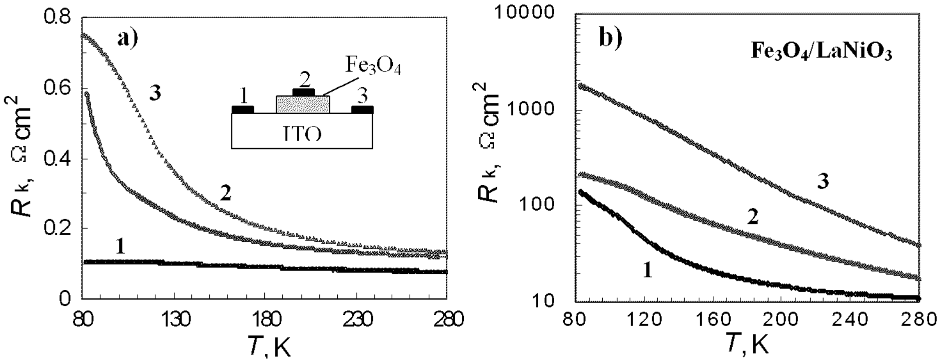

Fig. 3. Contact resistivity of the Fe_3O_4/ITO (a) and Fe_3O_4/LNO (b) interfaces. Thickness of Fe_3O_4 film on ITO, d [μm]: 0.45 (1), 0.25 (2), 0.15 (3) and on LNO: 0.48 (1), 0.20 (2), 0.15 (3).

transition temperature and noticeable asymmetry of the I—U curves in respect of the direction of the bias current. One can conclude that the origin of nonlinearity and asymmetric I—U curves observed in this work for the Fe_3O_4/ITO heterostructure is similar to that reported recently for p—n junctions based on manganites [6]. In contrast to the Fe_3O_4/ITO bilayer structure, almost linear I—U dependences were measured in the whole temperature range for the Fe_3O_4/LNO interface.

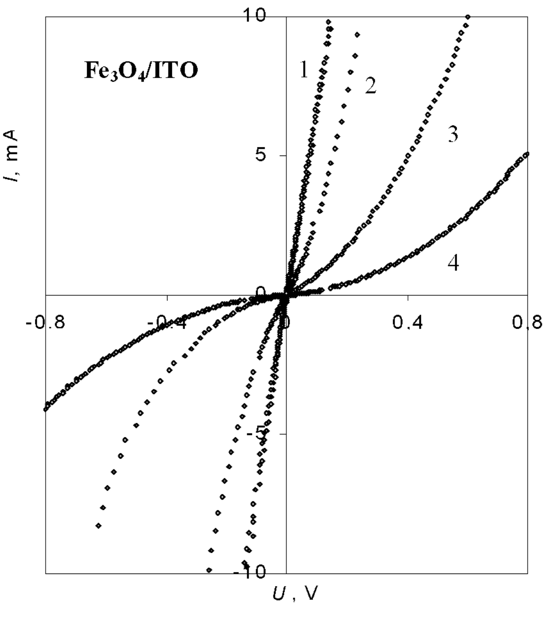

Fig. 4. Typical I—U curves measured at different temperatures for the patterned Fe_3O_4/ITO bilayer structures in a case of vertical electrical transport (by applying 3 point-probe method). Temperature T [K]: 285 (1), 204 (2), 110 (3), and 80 (4).

4. Conclusions

The highest quality (epitaxial) Fe_3O_4 films were grown at 400°C by a reactive dc magnetron sputtering on lattice-matched MgO. Both the highest crystalline quality Fe_3O_4/MgO films and textured magnetite films formed on CoO and $LaNiO_3$ layers exhibited resistance anomaly at the Verwey transition temperature. Formation of high resistance interlayer was indicated between the adjacent Fe_3O_4 and $LaNiO_3$ layers. At the same time, relatively low interface resistivity of about 0.1 Ω cm^2 (at $T = 300$ K) was estimated for the patterned Fe_3O_4/ITO bilayer structures. Vertical electrical transport measurements revealed strong nonlinearity in the $I-U$ dependences of the Fe_3O_4/ITO interfaces at low temperatures, i.e. below the Verwey transition point. The observed nonlinear $I-U$ characteristics of the Fe_3O_4/ITO interface reveal promissing possibilities of the Fe_3O_4 films and bilayer structures for future application in various devices.

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