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ELECTRICAL PROPERTIES OF ITO(IO) / Fe_3O_4 HETEROSTRUCTURES

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We describe the preparation and investigation of a heterostructure consisting of electron-doped indium tin oxide (ITO), hole-doped magnetite, Fe_3O_4, and intermediate thin indium oxide (IO) layer. The heterostructures were grown on lattice-matched $ZrO_2 : Y_2O_3(100)$ substrates using dc magnetron sputtering technique. Electrical resistance of the ITO(IO) / Fe_3O_4 heterostructure was investigated at $T = 78$–300 K by applying three-probe method with current passing perpendicularly to a film plane. Off-plane resistance of the ITO(IO) / Fe_3O_4 heterostructures exhibited semiconductor-like behaviour and nonlinear current–voltage characteristics at 78 K.

Keywords: indium tin oxide, iron oxide, magnetron sputtering, p–n heterostructure

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1. Introduction

During the last few years, the precise control of electronic charge rather than that of spin of carriers has been the major task of electronic industry. The group of materials exhibiting spin-polarized carriers (the semi-metallic ferromagnets) is of great importance for novel spintronics applications. The group includes manganites $Ln_{1-x}R_xMnO$ (where R is Ca, Sr, Ba, Ce), magnetite (Fe_3O_4), chromium dioxide, and other ferromagnetic (FM) oxides. Magnetite is unique among all these oxides due to its high Currie temperature ($T_C \sim 858$ K). Below T_C, all spins of carriers in Fe_3O_4 are oriented, and thus the polarization of carriers at room temperature is close to 100%. This feature makes the material promising for room temperature applications [1].

Indium oxide (IO) is a wide band gap ($E_g \simeq 3.5$ eV) semiconductor. The undoped stoichiometric compound could be considered as an intrinsic semiconductor exhibiting high resistance. However, it is well known that certain content of oxygen vacancies occurring in the compound during the film growth results in n-type electrical conductivity. Tin-doped oxide known as ITO (IO doped by Sn up to 9%) is a highly electron-doped ($n \sim 10^{20}$–10^{21} cm^{-3}) semiconductor. ITO is very attractive as a transparent electrode for electronics. It was shown in our previous work [2] that the electrical conductivity and optical properties of this material (depending on density of oxygen vacancies) can be controlled either during the film growth or through its post-deposition annealing.

The p–n structures containing ferromagnetic (FM) materials could be used for fabrication of magnetic field sensors and high-density magnetic access memory elements. The search for optimized growth conditions and investigation of electrical properties of the conducting heterostructures composed of n-ITO and p-Fe_3O_4 layers was the main aim of this work. As both the ITO and Fe_3O_4 exhibit a high carrier density, the intermediate IO layer is introduced to reduce the carrier density at interface to strengthen the nonlinearity and to reveal the rectifying electrical properties of the heterostructures. Up to now there have been only a few reports on the growth and properties of similar heterojunctions consisting of p-Fe_3O_4 layer and n-type Nb-doped conducting $SrTiO_3$, while data on the growth and properties of the ITO(IO) / Fe_3O_4 heterostructures has not yet been reported.

2. Sample preparation

The Fe_3O_4 films were prepared by magnetron sputtering of Fe metallic target (25 mm in diameter) at $T = 350$–$450\,^{\circ}$C onto $ZrO_2 : Y_2O_3(100)$ (YSZ(100)) and MgO(100) substrates mounted perpendicularly to the target (off-axis geometry). The thickness of the

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grown films varied from 30 to 600 nm. The growth was performed in the ambience of Ar : O_2 gas mixture with a lowered oxygen content (30 : 1) under the pressure of 5 Pa (partial oxygen pressure was 0.16 Pa).

Thin ITO and IO films with thickness ranging from 200 to 500 nm were prepared *in situ* by a reactive dc magnetron sputtering using disk-shaped In–Sn (91 : 9 alloy) and In metallic targets with the diameter of 25 mm. Lattice-matched single crystall YSZ(100) substrates ($a_{\mathrm{ITO}} = (1.01–1.03\ \mathrm{nm}) \simeq 2a_{\mathrm{YSZ}}$) were used for film deposition. The temperature of substrates during the film growth was kept at 250–600 °C. The sputtering was performed under Ar : O_2 gas mixtures (4 : 1 and 15 : 1) at a fixed gas pressure of about 5 Pa.

The ITO(IO) / Fe_3O_4 heterostructures were prepared under the optimal growth conditions of both ITO (IO) and Fe_3O_4 films. After deposition, the samples were cooled down slowly (at about 10 degrees per minute) to room temperature in the same ambience. Thin indium oxide interlayer grown between ITO and Fe_3O_4 films was used to reduce the carrier density at the interface and to improve the rectifying electrical properties of the heterostructures.

Microstructure of the films was studied by means of X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED) techniques. Transport properties of the films were measured at 78–300 K by applying standard four-point probe method. The interface resistance and the current versus voltage (I–U) dependences were measured by applying three-point probe method (with current flowing perpendicularly to plane). The method enabled one to study electrical transport through the interface between p- and n-type layers.

3. Results

3.1. Fe_3O_4 films

It was found from the Θ–2Θ X-ray diffraction spectra of the Fe_3O_4 film series that the ratio between Fe and O_2 content in the growth chamber above the film surface played a key role in the growth of single-phase Fe_3O_4. In our case, the Fe and O_2 ratio in the chamber is related to the growth rate and the resultant thickness of film. The optimum growth rate of single-phase Fe_3O_4 (at a fixed partial oxygen pressure of 0.16 Pa) was found to be 20–30 nm/min. XRD measurements revealed a formation of pure metallic Fe clusters when Fe : O_2 ratio above the film surface was higher, i. e. when the growth rate exceeded 40 nm/min. On the other hand, the XRD spectra of Fe_3O_4 films deposited at a rate lower than 15 nm/min showed weak reflexes of Fe_2O_3. Figure 1 demonstrates the characteristic RHEED pattern of the magnetite thin film grown on MgO(100) at 400 °C at a deposition rate of about 20 nm/min. Point-like reflexes demonstrate an epitaxial quality of the film. Both the increase and decrease of the deposition rate resulted in the appearance of additional ring-shaped RHEED patterns demonstrating a polycrystalline quality.

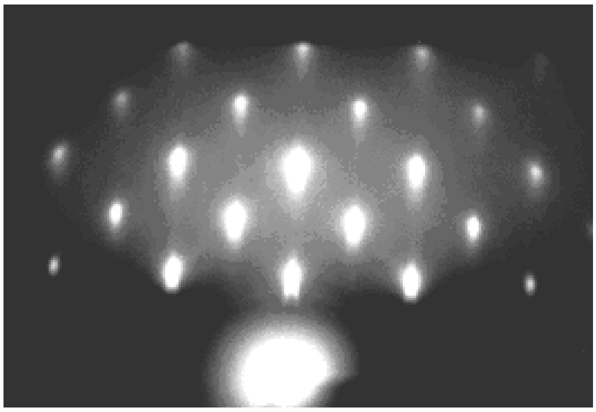

Fig. 1. RHEED pattern of Fe_3O_4 film grown on MgO(100) substrate at 450 °C with deposition rate of 20 nm/min.

Additional data of the prepared film series were obtained by measuring their electrical resistance as a function of film thickness. Both the resistance and resistivity of the films increased with substrate–target distance, i. e. with deposition rate (DR) decreasing. The room temperature resistivity of epitaxial Fe_3O_4 films grown on MgO ranged from 15 to about 40 mΩ cm. However, significantly lower (∼0.25 mΩ cm) and higher (∼100 Ω cm) resistivity values were measured in the cases of the highest and the lowest deposition rates. Significant variation of film resistivity can be easily understood taking into account the presence of metallic Fe and insulating Fe_2O_3 impurity phases in the grown films.

The $R(T)$ plots measured for the Fe_3O_4 films showed significant resistance increase with cooling (see Fig. 2). Clearly defined resistance anomaly (step-like increase of resistance) at 120 K, i. e. in the vicinity of the characteristic Verwey transition point T_{V} was seen for the films in good accordance with recent observations [3, 4]. The resistance versus temperature dependences measured for Fe_3O_4 films grown at three different rates resulting in different thicknesses of the films are shown in Fig. 2. According to our observations, formation of metallic Fe clusters was seen in Fe_3O_4 films when Fe : O_2 ratio above the film surface was higher (growth rate of about 40 nm/min). As we can see from Fig. 2,

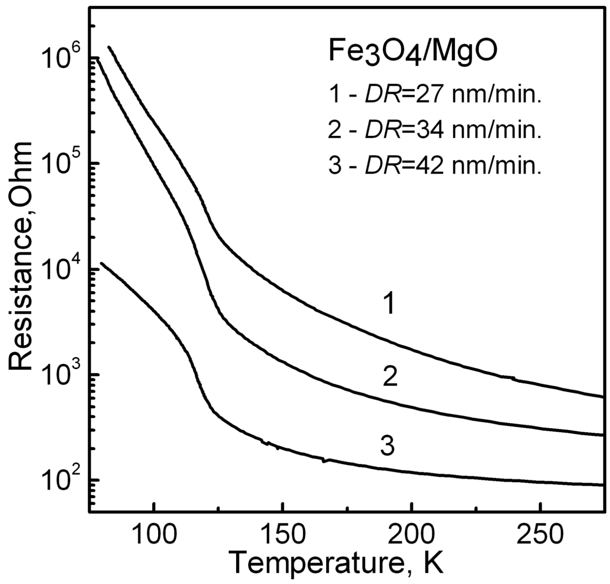

Fig. 2. Resistance versus temperature of Fe_3O_4 films deposited with three different growth rates: *1* at 27 nm/min, *2* at 34 nm/min, and *3* at 42 nm/min.

a small excess of Fe has only negligible effect on T_V value, meanwhile a lowered density of Fe species in a gas phase results in the growth of a Fe-deficient $Fe_{3-\delta}O_4$ phase demonstrating the shift of T_V values from 120 to 103 K.

3.2. ITO and IO films

Crystalline structure of the films was studied by means of XRD and RHEED. Θ–2Θ X-ray diffraction spectra of the ITO and IO films grown onto YSZ substrates revealed (100) in-plane orientation. Point-like reflexes in the electronographs confirmed the epitaxial growth with heteroepitaxial relationships: ITO<100> // YSZ<100> and IO<100> // YSZ<100>. Figure 3 demonstrates a typical RHEED pattern measured for an ITO film of 500 nm thickness.

The ITO films demonstrated a metallic-like resistance versus temperature behaviour, i. e. the resistance of films decreased with temperature decreasing (see Fig. 4). Inset in Fig. 4 shows electrical resistance versus temperature plot of indium oxide film deposited on YSZ. One can see from the inset that IO film exhibits semiconducting properties.

3.3. ITO(IO) / Fe–O heterostrutures

The magnetite films were patterned to investigate the interface resistance between ITO(IO) and Fe_3O_4 layers as well as to study the current–voltage (*I–U*) characteristics. The inset in Fig. 5 demonstrates the

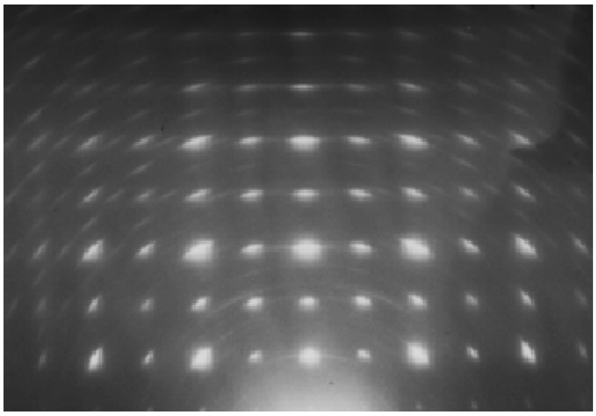

Fig. 3. RHEED pattern obtained for 500 nm thick ITO film deposited on YSZ(100) substrate.

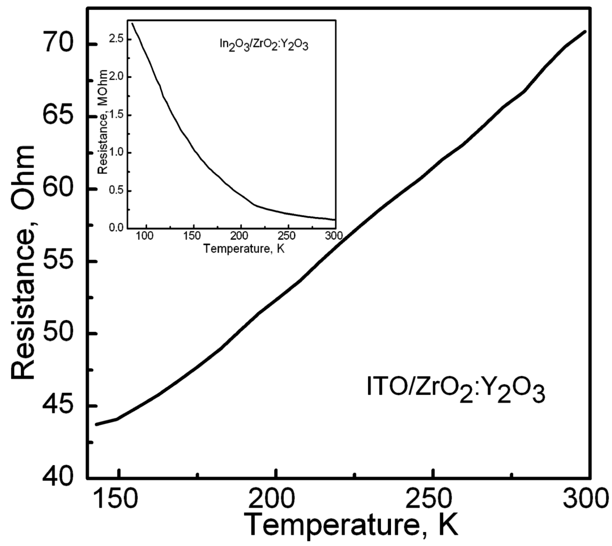

Fig. 4. Resistance dependence on temperature measured for ITO film grown on YSZ(100) substrate. The inset demonstrates the $R(T)$ dependence of IO film deposited on YSZ(100) substrate.

scheme of these measurements. Typical resistance versus temperature plots for the interface of the prepared heterostructures are presented in Fig. 5. The curve *1* in this figure shows the resistance of the interface between ITO(IO) and stoichiometric Fe_3O_4 layers in the temperature range from 300 down to 78 K, while curve *2* has been measured for similar heterostructure containing non-stoichiometric oxygen deficient magnetite. The negligible increase of the interface resistance with temperature decreasing has been observed for ITO(IO) / $Fe_{3-\delta}O_4$ heterostructure. Figure 6 demonstrates the corresponding *I–U* dependences of the ITO(IO) / Fe–O heterostructures measured at room temperature and at 78 K. One can see from the figure that at $T = 78$ K the current flowing through the interface increases non-linearly with forward bias ($U > 0$) increasing. However, the measured *I–U* curves for the heterostructures

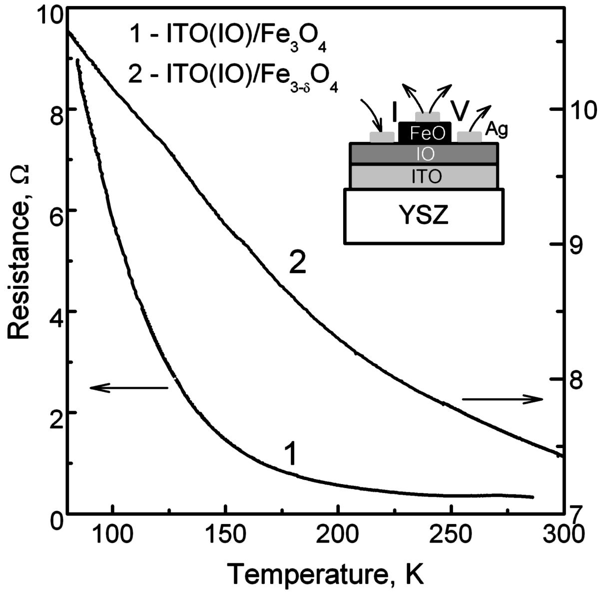

Fig. 5. Interface resistance versus temperature dependences measured for two different ITO(IO) / Fe–O heterostructures. *1* for stoichiometric Fe_3O_4 film and *2* for nonstoichiometric $Fe_{3-\delta}O_4$ film.

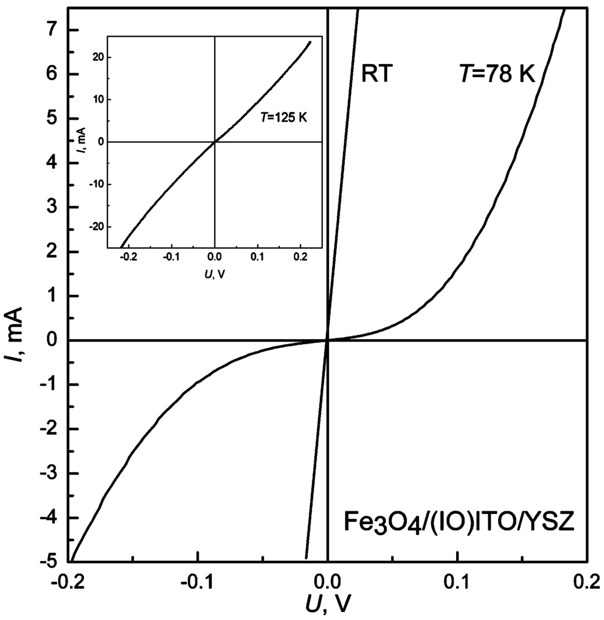

Fig. 6. I–U characteristics measured for ITO(IO) / Fe_3O_4 heterostructure at room temperature and at 78 K. The inset demonstrates the I–U dependence measured for the same heterostructure at 125 K.

were almost linear at high temperatures (see the curve measured at room temperature). Nonlinearity of the I–U characteristics was also seen at temperatures close to T_V (see the inset to Fig. 6). In our opinion, the interface, most probably, appears between the IO and Fe_3O_4, meanwhile the ITO layer in this experiment plays a role of bottom electrode. The highest asymmetry of the I–U characteristics (when measured in forward and reverse directions) has been observed for the ITO(IO) / Fe_3O_4 heterostructures with overlying stoichiometric Fe_3O_4.

One can expect that at room temperature both ITO(IO) and Fe_3O_4 exhibit high carrier concentration resulting in a high density of states at Fermi level. In this case the linear I–U characteristics may be understood assuming the tunnelling of carriers through the interface. At temperatures below the Verwey transition temperature, charge ordering takes place. As a result, the carrier density decreases and an energy gap occurs in the energy spectrum of Fe_3O_4. Nonlinearity and asymmetry of the I–U curves may be explained in this case taking into account the creation of a depletion region with a reduced carrier concentration at the interface similar to a typical semiconductor p–n junction. The forward bias current in such a case may be calculated from the equation obtained by applying the thermionic emission model [5]:

$$J = J_s \left[\exp\left(\frac{eU}{\alpha kT}\right) - 1 \right],$$

where $J_s = AT^2 \exp(-eU_\mathrm{b}/kT)$, and A is a Richardson constant, α is the ideality factor, U_b is the height of barrier, U is an external voltage. The calculated curve fits well the experimental points by inserting $U_\mathrm{b} =$ 1.35 V. Additional experiments are in progress in order to enhance the observed nonlilearity effect and to reveal the rectifying characteristics of the heterostructures.

4. Summary

We point out the Fe : O_2 ratio being one of the most important technological parameters for the growth of high crystalline quality stoichiometric Fe_3O_4 thin films. It has been found in this work that the highest quality Fe_3O_4 films may be grown at 350–450 °C under partial oxygen pressure of 0.16 Pa when deposition rate varies in the range of 20–30 nm/min. The presence of metallic Fe has been indicated in the films when Fe : O_2 ratio over the film surface during the growth exceed the optimal one, while traces of Fe_2O_3 impurity phase occurr in the case of reduced Fe : O_2 ratio. Decrease of Verwey transition temperature T_V from 120 to 103 K has been determined for the films with excess oxygen content.

Heterostructures composed of conducting n-type ITO(IO) and p-type magnetite Fe_3O_4 thin films have been prepared. We point out strong nonlinearity of the interface resistance and significant asymmetry of the I–U curves in respect of the bias current direction below the characteristic Verwey transition temperature for the prepared p–n oxide heterostructures.

Acknowledgement

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ELEKTRINĖS ITO(IO) / Fe_3O_4 DARINIŲ SAVYBĖS

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Santrauka

Buvo siekiama surasti atskirų plonųjų sluoksnių – elektroniniu elektriniu laidumu pasižyminčio alavo oksido In_2O_3, indžio su alavo priemaiša oksido (ITO), p tipo Fe_3O_4 (magnetito), taip pat jų p–n darinių – palankiausias auginimo sąlygas, naudojant nuolatinės srovės magnetroninio dulkinimo būdą. Straipsnyje išanalizuota įvairių technologinių parametrų įtaka Fe_3O_4 sluoksnių, augintų ant įvairių padėklų, kristalinei sandarai ir elektrinėms savybėms. Pastebėta, kad tų sluoksnių fazinė sudėtis ir kristalinė sandara labiausiai priklauso nuo Fe : O_2 santykio dujinėje fazėje virš auginamojo sluoksnio paviršiaus. ITO(IO) ir Fe_3O_4 sluoksnių ribos elektrinės varžos priklausomybės buvo matuojamos 78–300 K temperatūros ruože, naudojant trijų elektrodų metodą, kai srovė teka iš vieno sluoksnio į kitą. Žeminant temperatūrą, užaugintų p–n darinių sluoksnių ribos varža didėjo, o jos I–U charakteristikos, išmatuotos 78 K temperatūroje pralaidžiąja ir atbuline kryptimis, buvo netiesinės ir nesimetriškos.