Growth and investigation of p-n structures based on Fe$_3$O$_4$ thin films

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Abstract. We report preparation and investigation of p-n heterostructures based on Fe$_3$O$_4$ thin films grown on n-Si(111) substrates as well as indium oxide (IO) and tin doped indium oxide (ITO) layers deposited on lattice-matched monocrystalline ZrO$_2$:Y$_2$O$_3$(100). Thin Fe$_3$O$_4$ films with thickness ranging from 100 to 300 nm were grown in situ at 400 K using dc magnetron sputtering technique. The measurement of microstructure revealed polycrystalline quality of Fe$_3$O$_4$ films on silicon substrate and epitaxial growth on (IO)ITO/YSZ. Investigation of surface composition by X-ray Photoelectron Spectroscopy (XPS) showed that Fe 2p peak consists of three main peaks, namely, metallic iron Fe(0), Fe(II) and Fe(III). Transport measurements of Fe$_3$O$_4$/n-Si heterostructures demonstrated rectifying behaviour in a wide temperature range ($T=78$÷$300$ K) while those prepared by growing Fe$_3$O$_4$ layers on indium oxide (IO) demonstrated nonlinear current-voltage ($I$-$V$) dependencies at low temperatures ($T<120$K).

1. Introduction

Ferrimagnetic magnetite, Fe$_3$O$_4$, with an inverse cubic spinel structure ($a=0.8396$ nm) is a self-doped highly conductive ($\rho\cong10$ m$\Omega$cm at $T=300$K) oxide demonstrating p-type conductivity due to a hopping of spin-polarized electrons between ferrimagnetically ordered Fe$^{2+}$ and Fe$^{3+}$ ion states [1]. The attracting properties, such a high Curie temperature value ($T_c \cong 858$ K) and almost 100% of spin-polarized carriers, make this oxide one of the most promising materials for room temperature spintronics applications [2]. Over the past few years, there was an increasing interest in fabrication of various device structures containing Fe$_3$O$_4$ [3]. However, up to now only a limited number of reports are known on preparation of magnetic p-n junctions using Fe$_3$O$_4$ films.

In this work, we report the results of preparation and investigation of p-n heterostructures consisting of hole-doped thin Fe$_3$O$_4$ films and electronically doped Si(111) substrates as well as highly conducting n-type ITO underlayered by IO.

2. Film growth and characterization

The p-n device structures were prepared by growing p-type Fe$_3$O$_4$ layers on both n-Si(111) substrates and n-type layers of indium oxide (IO) on highly conducting tin-doped indium oxide (ITO). The Fe$_3$O$_4$ thin films with thickness ranging from 100 to 300 nm were grown in-situ at 400 K using dc reactive magnetron sputtering technique. A disk of metallic Fe (35 mm in diameter and 0.5 mm thick) was used as a target. Film growth was performed in Ar:O$_2$ gas mixture (10:1) ambient keeping partial oxygen pressure in the vacuum chamber of about 0.16 Pa. After deposition, the films were cooled down slowly to a room temperature under the same oxygen pressure conditions. To prevent possible film bombardment by high energy ions during deposition, the substrates were positioned in the off-axis configuration at a distance of 30-60 mm from the symmetry axis of the discharge and 20-25 mm above the target plane. It is important to note that in our case, both thickness of the grown films and film composition (Fe and oxygen ratio) depended on the distance between the target and a growing film on the substrate.
ITO films ($d = 200\div500$ nm) were magnetron sputtered from In-Sn (91:9) alloy target onto lattice-matched ZrO$_2$:Y$_2$O$_3$(100). Temperature of the substrates during film growth was kept at $250\div600$ °C. Sputtering was performed in Ar:O$_2$ gas mixture (4:1) at a pressure of about 5 Pa. As far as both ITO and Fe$_3$O$_4$ exhibit high carrier density, the intermediate In$_2$O$_3$(IO) layer was introduced in order to reduce carrier density at the interface and to reveal rectifying electrical properties of heterostructures.

Crystalline structure of the grown films was revealed by measuring their $\Theta$-2$\Theta$ X-ray diffraction (XRD) spectra, and studying high-energy electron diffraction (RHEED) images. X-ray photoelectron spectroscopy (XPS) was employed to study surface composition of the films. X-ray photoelectron spectra were recorded using XSAM 800 (KRATOS Analytical, UK) spectrometer. The aluminum anode Al K$_\alpha$ radiation with photon energy of 1486.6 eV and hemispherical energy analyzer with pass energy of 20 eV in a fixed analyzer transmission (FAT) mode were used. The energy scale of the spectrometer was calibrated using Au 4f/2 and Cu 2p$_{3/2}$ Ag 3d$_{5/2}$ peak positions. Charge effects were compensated assuming that adventitious carbon peak position is at 285 eV. Carbon, oxygen, and iron core level spectra acquired with 0.1 eV energy increment. The “XPSPEAK41” software was employed for the peak fitting procedure. The Shirley background with Lorenz to Gauss rate 50:50 and asymmetric line shape (asymmetry parameters TS: 0.25; TL: 30) for metallic iron Fe 2p peak were used. For other peaks were used Lorenz to Gauss rate 30:70 and symmetric line shape. All fitting procedures are made using the Gaussian-Lorentzian sum function.

Transport properties of the films were investigated in a wide range of temperatures ($T = 78\div300$ K) by applying four point-probe method. Meanwhile three point-probe method (with current flowing through the interface between $p$- and $n$-type materials) was applied to investigate interface resistance and current versus voltage ($I$-$V$) dependencies of the prepared $p$-$n$ device structures. The $I$-$V$ curves were measured by passing dc current of about $0\div100\mu$A and using metallic In pads as electrodes.

3. Results and discussion

3.1. Microstructure and surface chemical composition of thin Fe$_3$O$_4$ films

The measurements of microstructure carried out by X-ray diffraction and reflection high energy electron diffraction techniques demonstrated the polycrystalline quality of thin Fe$_3$O$_4$ films on silicon substrates and epitaxial growth on (ITO)/ITO/YSZ. The analysis of XRD spectra measured for Fe$_3$O$_4$ films deposited on substrates kept at different distances from the discharge symmetry axis, showed both thickness variation of the grown films and film composition (Fe and oxygen ratio) deviation from the stoichiometric compound. The XRD plots of the films grown on the substrate kept near the symmetry axis of the discharge (in a distance of about 30-35 mm) demonstrated reflexes corresponding to the Fe$_3$O$_4$ phase and traces of reflexes corresponding to a negligible amount of Fe clusters. Spectra of the films prepared on substrates positioned at a distance of 45 mm from the symmetry axis of the discharge exhibited XRD peaks attributed only to the stoichiometric Fe$_3$O$_4$, meanwhile weak reflexes of Fe$_2$O$_3$ phase appeared in the spectra with increasing the distance up to 60 mm.

Due to the fact that both Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ crystallize in the same cubic inverse spinel structure and the phases are characterized by similar lattice parameter $a=0.8396$ nm and $a=0.8350$ nm, respectively, the diffraction rings can not be attributed either to polycrystalline Fe$_3$O$_4$, and polycrystalline $\gamma$-Fe$_2$O$_3$, or their mixture. Therefore, it is difficult to clarify the presence of phases in polycrystalline Fe$_3$O$_4$ films. In order to analyze surface composition of the deposited films, XPS measurements have been accomplished for the Fe$_3$O$_4$ films. Figure 1 demonstrates the Fe 2p core-level X-ray photoelectron spectrum and peak fitting procedure results. It was found, that Fe 2p peak consists of three main peaks, namely - metallic iron Fe(0), Fe(II) and Fe(III), accompanied with typical Fe(II) peaks at 715 eV and 728 eV and small Fe(III) peak at 719 eV [4]. From this picture it is clear that some amount of metallic iron is present on the film surface. After appropriate peak area calculation it was found that Fe 2p$_{3/2}$ peaks ratio of metallic iron Fe(0), Fe(II) and Fe(III) ions is 14.6%, 46.4% and 39.1%, respectively.
3.2. Transport measurements
The overlaying Fe$_3$O$_4$ films were patterned to investigate both the interface resistance between layers and $n$-Si substrate or underlaying (IO)ITO layers and to study the corresponding current-voltage ($I$-$V$) characteristics. The patterning of magnetite films was performed by putting metallic foil mask with opened squares of about 1x1 mm$^2$ on the substrates prior to film deposition.

3.2.1. Fe$_3$O$_4$/n-Si heterostructures
Electrical measurements of the prepared Fe$_3$O$_4$/n-Si heterostructures demonstrated a semiconductor-like increase of the interface resistance with temperature decreasing down to 78 K. Figure 2 demonstrates current-voltage dependencies measured for the Fe$_3$O$_4$/n-Si heterostructure at $T= 300$ K and 78 K. The rectifying behaviour typical for semiconductor $p$-$n$ diode structures have been indicated for the heterostructures either at room temperature and at $T = 78$ K. It can be seen from figure 2 that differential resistance of the heterostructures at zero bias ($R_d= dV/dI$) increases significantly with cooling down to $T = 78$ K. In all cases, current through the interface was found to increase steeply with forward bias ($V>0$) at a certain critical value $V_d$ (diffusion voltage) corresponding to the mismatch between band structures of $p$- Fe$_3$O$_4$ and $n$-type Si.

3.2.2. Fe$_3$O$_4$/(IO)ITO heterostructures
Figure 3 demonstrates current-voltage I-V dependencies measured at room temperature and $T=78$ K for a set of Fe$_3$O$_4$/(IO)ITO heterostructure. It can see from the figure, that current flowing through the IO/Fe$_3$O$_4$ interface increases nonlinearily with bias voltage $V$ increasing than $T=78$ K. The asymmetry of I-V characteristic (in a case of forward and reverse bias) is clearly defined. Slight non-linearity of the I-V characteristics were also seen above the characteristic Verwey transition temperature ($T_v \sim 120$ K). However, almost linear I-V dependencies were measured for the prepared Fe$_3$O$_4$/(IO)ITO heterostructures at room temperature. The observed linear I-V characteristics of the Fe$_3$O$_4$/(IO)ITO heterostructures at 300 K may be understood assuming tunneling of carriers through the interface between highly doped n-IO and p-Fe$_3$O$_4$ layers. Significant resistance increase observed usually for high quality magnetite thin films at $T \approx T_v$ (the Verwey transition temperature) may be associated to charge ordering and occurance of energy gap in the energy spectrum of Fe$_3$O$_4$. Nonlinearity and asymmetry of the I-V curves of the Fe$_3$O$_4$/(IO)ITO heterostructures at $T < T_v$ may be explained taking into account creation of a depletion region due to reduced carrier concentration at the interface.
We conclude that p-n heterostructures containing p-type Fe₃O₄ layers on n-type Si substrates demonstrate rectifying behaviour in a wide temperature range (T=78÷300 K) while those prepared by growing Fe₃O₄ layers on indium oxide (IO) demonstrate nonlinear current-voltage (I-V) dependencies only at low temperatures (T<120K).

Acknowledgements
This work has been supported partially by Lithuanian State Science and Studies Foundation (Grant No T-102/07 and Grant No C-18/2007 project MULTIMA) and EC Project No BPD2004-ESF-2.5.0-03-05/0029 (Post Doc).

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