STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF $FeGa_2O_{4-\delta}$ EPITAXIAL FILM ON MgO(100) SUBSTRATE

TÍNH CHẤT CẤU TRÚC, ĐIỆN VÀ TỪ CỦA VẬT LIỆU MÀNG MỎNG $FeGa_2O_{4-\delta}$ MỌC TRÊN ĐẾ MgO (100)

Duong Van Thiet[1,*], Nguyen Xuan Chung[2], Nguyen Quoc Tuan[1], Nguyen Tien Tung[1], Nguyen Minh Quang[1]

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ABSTRACT

In this paper, we reported on the growth, structural, electrical and magnetic properties of $FeGa_2O_{4-\delta}$ thin film on MgO(100) substrate by using Molecular Beam Epitaxy method. The Reflection-High-Energy-Electron Diffraction image indicates that epitaxial film was grown in layer-by-layer mode along the MgO(100) plane. The crystal structure in single phase with cubic structure of $FeGa_2O_{4-\delta}$ was pointed out by the X-ray diffraction whereas their inverse spinel characterization was revealed by analysing Raman spectrum. We find that the films exhibit the semiconductor behaviour and magnetoresistance with the maximum value of 9% at 150K under external magnetic field of 8kOe. The magnetization hysteresis (M-H) loops of film observed at room temperature like ferrimagnetism state with easy magnetization axis in perpendicular to the film surface.

Keywords: *Ferrimagnetism, Spintronics, $FeGa_2O_{4-\delta}$, thin film, MBE.*

TÓM TẮT

Trong bài báo này, chúng tôi nghiên cứu quá trình mọc và phân tích các đặc tính cấu trúc, điện và từ của vật liệu $FeGa_2O_{4-\delta}$ màng mỏng được lắng đọng trên đế MgO bằng cách sử dụng phương pháp bốc bay chùm phân tử. Các kết quả đã chỉ ra rằng, màng mỏng $FeGa_2O_{4-\delta}$ được mọc dưới dạng 'epitaxial' trên đế MgO với cơ chế mọc lớp từng lớp. Kết quả này đã được quan sát bằng phương pháp kiểm tra nhiễu xạ chùm tia điện tử năng lượng cao trong quá trình mọc. Kết quả nhiễu xạ tia X chỉ ra, màng mọc trên đế MgO là đơn tinh thể với cấu trúc cubic và sự định hướng mọc là mặt phẳng (400). Bằng phép phân tích Raman cũng kết luận được rằng cấu trúc tinh thể của màng thuộc loại cấu trúc spinel oxít đảo một phần khi tại vị trí tứ diện có sự chiếm chỗ của Fe^{3+} và Ga^{3+}. Trạng thái hóa trị của các nguyên tố Fe, Ga và O trong mẫu được phân tích bằng phương pháp phân tích quang phổ quang điện tử tia X đã chỉ ra rằng trong mẫu tồn tại cả hai trạng thái hóa trị Fe^{2+} và Fe^{3+}. Tính chất điện của màng thể hiện tính chất bán dẫn và hiệu ứng từ điện trở âm đã đo được trong mẫu với giá trị lớn nhất đạt được là 9% tại nhiệt độ đo 150K trong điều kiện tác dụng từ trường ngoài là 8kOe. Phép đo từ độ dưới tác dụng của từ trường ngoài trong cả hai trường hợp vuông góc và song song với mặt phẳng màng thể hiện tính chất của trạng thái ferít từ, trong đó trục từ hóa dễ theo hướng vuông góc với mặt phẳng màng.

Từ khóa: *Ferít từ, Spin điện tử, $FeGa_2O_{4-\delta}$, màng mỏng, MBE.*

[1]School of Mechanical and Automotive Engineering, Hanoi University of Industry, Vietnam
[2]Department of Physics, Hanoi University of Mining and Geology, Vietnam
[*]Email: dvthiet86@haui.edu.vn
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1. INTRODUCTION

The spinel oxide structure is represented by $(A_{1-x}B_x)[B_{2-x}A_x]O_4$ while A, B cation arrangements in tetrahedral site (T - denoted by round brackets) and octahedral site (O - denoted by square brackets), here x is called the inversion parameter. The case of x = 0 is called normal spinel, x = 1 is full inverse spinel and 0 < x < 1 is mixed spinel [1]. The AGa_2O_4 (A = Fe, Ni, Zn,...) has shown great

promise as potential phosphors, photocatalysis and spintronics materrials [2-5]. Among them, the $FeGa_2O_4$ possesses unique physical properties such as magnetic, piezo electric, magnetoelectric, and magneto-optical properties and cathodoluminescent features [6-9]. Furthermore, $FeGa_2O_4$ exhibits remarkable properties as anode material in Li-ion capacitors and biomedical application [10, 11]. In thin films form, $FeGa_2O_4$ has been studied in various application as photocathodes, spintronics because their physical properties such as transparency to visible light, p-type electrical conducting [12,13] and have high junction magnetoresistance value, which can be useful in magnetic-tunnel junctions (MTJ) device [2]. The structure of $FeGa_2O_4$ is a cubic spinel crystal with a space group of Fd-3m and a lattice parameter of a = 8.385Å [14]. It was reported on both full inverse and mixed spinel oxide [8, 15, 16]. The magnetic properties of $FeGa_2O_4$ were analyzed in previous reports: J. Ghose *et al.* reported the superparamagnetism above 10K [8], Huang *et al.* reported on $FeGa_2O_4$ nanostructured particles exhibited superparamagnetic above 247K and ferromagnetic property below this temperature [9], Lyubutin *et al.* indicated that $FeGa_2O_4$ reveals the spin-freezing temperature of T_{SG} = 26K [16]. While other report presented anti-feromagnetic property with freezing temperature T_f = 12.42K [17]. Up to now, the research on structural, electrical and magnetic properties of thin film form have been very limited. So, in this study, we report on fabrication of $FeGa_2O_4$ thin film by using Molecular Beam Epitaxy (MBE). Details of the results will be presented followings.

2. MATERIALS AND METHODS

The $FeGa_2O_{4-\delta}$ film was grown on a MgO(100) substrate by MBE system (VG Semicon. Inc.) in a low-pressure chamber (around 10^{-9} Torr) with the growth temperature of 400°C. Atomic oxygen gas was applied into chamber by using an oxygen cracking cell. Evaporation of Ga, Fe was conducted by using effusion cells under pressure of 9 x 10^{-6} Torr. During growth, the film quality was monitored by *in-situ* Reflection High-Energy Electron Diffraction (RHEED), while the film's surface was inspected by *ex-situ* Scanning Electron Microscope (SEM). X-ray Diffraction (XRD) was used to investigate the phase and growth orientation of the films, the scanning angle range (2θ) was set from 10° to 80°. Raman spectroscopy was conducted at room temperature, in the range of wave numbers from 200 to 800cm^{-1} by using an Ar+ laser with wave length of 532nm, power of 5mW and a diameter beam size of 50μm. X-ray Photoelectron Spectroscopy (XPS) was used to investigate the valence states of Ga, Fe and O. The resistivity and magnetoresistance (MR) were measured by using low-temperature transport measurement system (TPMS) with four-probe van der Pauw configuration. The magnetic properties were measured by a Vibrating-sample magnetometer system(VSM).

3. RESULTS AND DISCUSSION

Fig. 1(a) shows the streaky RHEED pattern of the MgO(100) substrate, indicating the clean and flat surface. Fig. 1(b) presents the Kikuchi RHEED patterns after the growth of about 100nm $FeGa_2O_{4-\delta}$ film on MgO(100) substrate, demonstrating the film was epitaxial growth with a layer-by-layer mode.

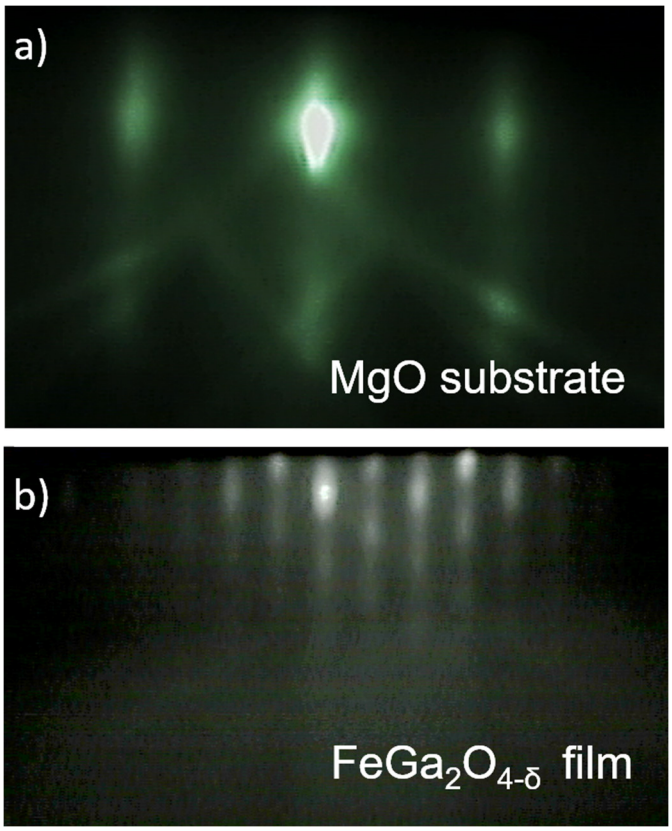


Figure 1. (a) RHEED patterns of the MgO(100) substrate before growing film and (b) $FeGa_2O_{4-\delta}$ film with the substrate of MgO(100) at growth temperatures 400°C

Fig. 2(a) presents film's secondary electron image (SEI) by using SEM. The film's surface is characterized by arrangement of like nano-sheets, nano-structured particles and no cracks or pores. Fig 2(b-c) show the compositional image and energy dispersive X-ray spectroscopy (EDX). It appears the peaks of Ga and Fe elements with the atomic ratio of Fe : Ga = 3.29 : 6.87 ≈ 1:2.

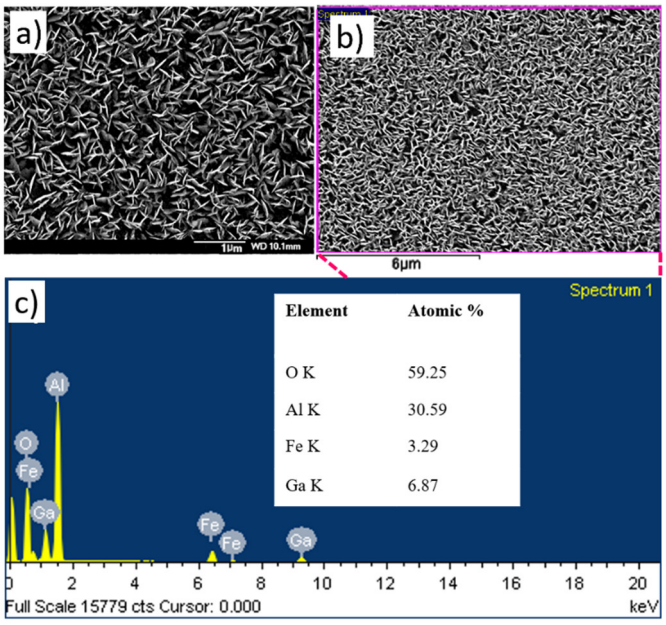


Figure 2. (a) SEM $FeMn_2O_{4-\delta}$ films; (b) BEI-COMPO image and (c) energy dispersive X-ray spectroscopy of $FeGa_2O_{4-\delta}$ film

The crystalline of film was investigated by X-ray diffraction, which is presented in Fig. 3(a). The scanning angle was set in the range from 10 to 80°. There is only one peak at 43.48° nearby (200) diffraction peak of the substrate. This peak matches to the (400) peak of $FeGa_2O_4$ bulk material in JCPDS standard card: #74-2229. The values of distance between the lattice planes d along c axis of bulk and film material are 2.0907 and 2.0809Å, respectively. This result shows film's out-of-plane d spacing under compression strain compared to bulk material.

The Raman spectrum of Fe_3O_4 and $FeGa_2O_{4-\delta}$ films were measured at room temperature to investigate depth regarding to local structure in Fig. 3(b). A wavelength of 532nm laser beam was used, the range of wave numbers was set from 200 to 800cm^{-1}. In cubic spinel structure, there are five Raman active modes: A_{1g}, E_g and $3T_{2g}$ [18]. To understand more about local structure of $FeGa_2O_{4-\delta}$ film, Raman spectra of Fe_3O_4 film are compared. It is well known that Fe_3O_4 has completely inverse spinel structure. The A_{1g} Raman mode appears a symmetric peak due to only Fe^{3+} cation fully occupies at tetragonal sites [19]. This Raman mode is the result of the vibration between the cation and oxygen at T position. The structure of partially inverse spinel oxide (at T site the cation co-exist different valence states of +2 and +3), the A_{1g} Raman mode appears the splitting, shouldering or broadening [20-26]. The A_{1g} Raman mode of $FeGa_2O_{4-\delta}$ film appeared asymmetric peak which may be the co-exist of both Ga^{3+} and Fe^{3+} at T site. Note that the atomic radius of Ga^{3+} and Fe^{3+} are close so Ga^{3+} cation easily occupies Fe^{3+} site. In previous reports by using Mossbauer diffraction method, the cation distribution at T and O show that s partially inverse spinel oxide [15, 16].

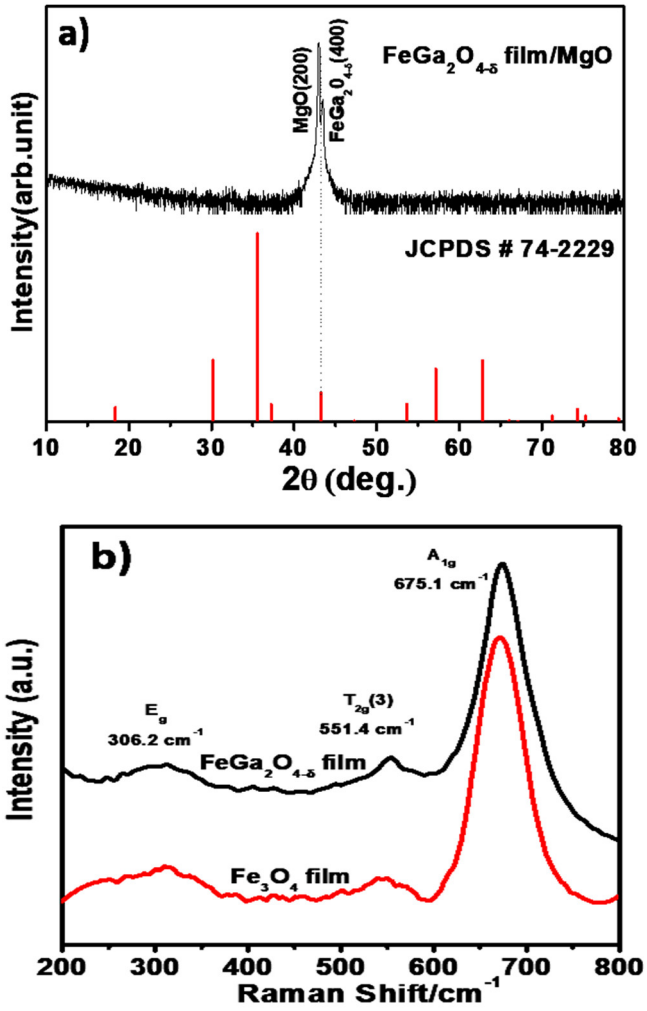
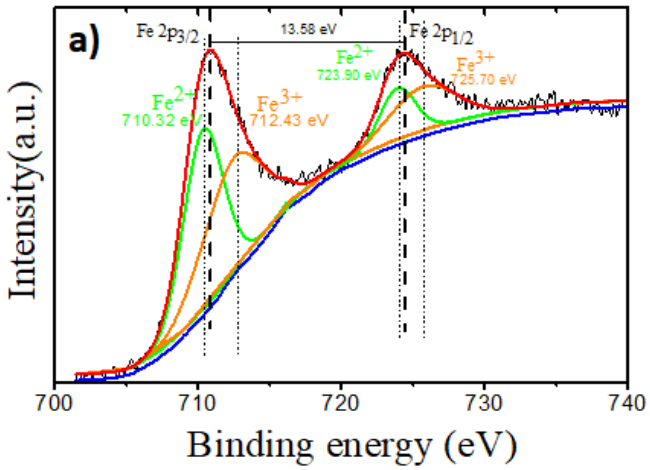


Figure 3. (a) The θ-2θ X-ray diffraction patterns of the $FeGa_2O_{4-\delta}$ film; (b) Raman spectrum active vibration modes of Fe_3O_4 and $FeGa_2O_{4-\delta}$ films



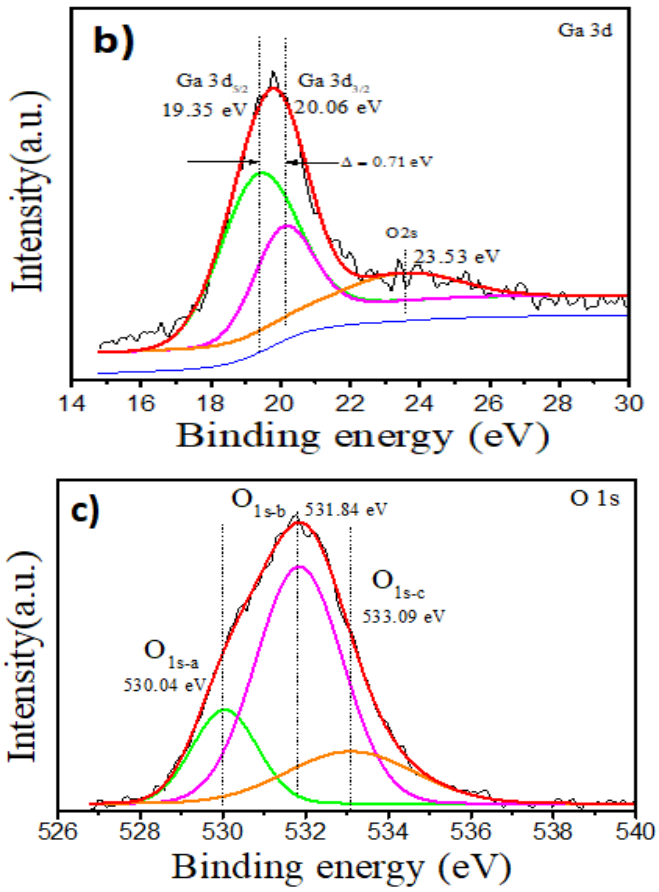


Figure 4. (a) XPS spectra of Fe 2p, (b) Ga 3p and (c) O1s of $FeGa_2O_{4-\delta}$ films

The valence states of cations and anions on film's surface were investigated by XPS spectra. Fig. 4(a) presents the Fe 2p core-level spectra with two main peaks of $Fe2p_{3/2}$ and $Fe2p_{1/2}$; the spin-orbit spliting value of 13.58eV. By applying Gaussian distribution fitting, the peak positions at 710.32eV and 723.90eV confirms oxidation states of Fe^{2+} while peaks at 712.43eV and 725.70eV assign to oxidation states of Fe^{3+}. There are appearance of Fe^{2+} and Fe^{3+} valence states in $FeGa_2O_{4-\delta}$ film. Fig. 4(b) shows the Ga 3d core-level spectra; two main peaks of Ga $3d_{5/2}$ and Ga $3d_{3/2}$; the spin-orbit spliting of 0.71eV, which is larger than bulk's one of 0.46eV. Fig. 4(c) presents O 1s core-level spectra with peak positions of 530.04, 531.84 and 533.09eV corresponding to bonds between oxygen and cations, deficiency of oxygen and –OH functional group, which absorbed on film's surface.

Fig. 5(a) indicates a variation of the resistivity vs temperature in 255 - 410K range. The value of resistivity could not be measured below 255K due to limitation of measurement system. The resistivity value decreases as measurement temperature increases, indicating that the sample's conductivity like semiconductive behaviour. The relation between resistivity of semiconductor as well as spinel oxide and measurement temperature has been reported to be exponential [27, 28]. During the measurement of temperature dependence of resistivity an external magnetic field of 0.6T applied perpendicular to sample surface, the resistivity value decreases, which proved the existence of magnetic domains. This results can be explained by re-orientation of magnetic domain under external magnetic field, which decreases scattering of carriers so the resistivity value decreases. Fig. 5 (b) shows negative magnetoresistances at various measurement temperature under external magnetic field from 0 to 8kOe. The negative magnetoresistances show clearly that orientation of magnetic domains in sample is rotated according to the external magnetic field. The highest MR value achieved of 9% at 150K. This value is higher than of Fe_3O_4 thin film [29].

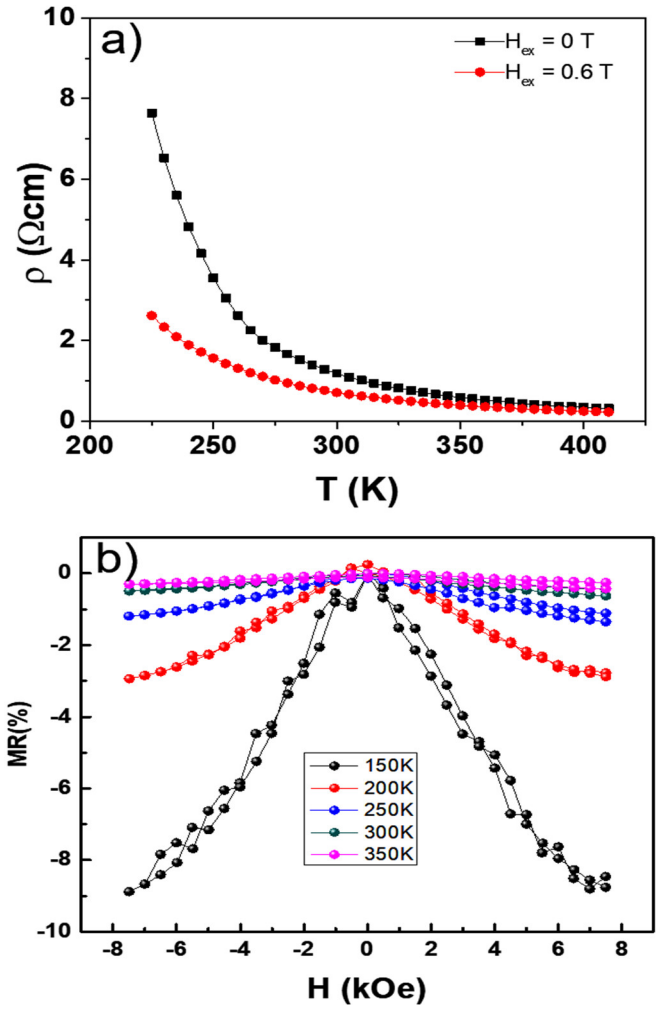


Figure 5. (a) The temperature dependence of resistivity of $FeGa_2O_{4-\delta}$ film; (b) Magnetoresistance vs. magnetic field measured at various temperatures

Fig. 6 presents magnetization hysteresis (M-H) loops of $FeGa_2O_{4-\delta}$ film at room temperature under perpendicular and parallel external magnetic fields. The

magnetization saturation can be obtained at lower magnetic field as magnetic field is perpendicular to film plane. In previous literature, magnetic properties of $FeGa_2O_{4-\delta}$ shows spin-glass state at low temperature [16, 17] or ferromagnetism state below 247K [9]. However, in this study we observed ferrimagnetism at room temperature. In the limitation of measurement methods, this result can relate to some possibilities: *i)* appearing strain between film and substrate, which modifies the magnetic properties of film compared to bulk material [30, 31]; *ii)* the distributions of Fe^{2+} và Fe^{3+} at T and O site. The ferrimagnetism state in $(A_{1-x}B_x)[B_{2-x}A_x]O_4$ spinel oxide originates from the interaction between total moment of T and O, A-B, B-A in T, O site, while the interaction between total moment of T and O is antiferromagnetism, A-B or B-A is ferromagnetism. In this case, Ga^{3+} has diamagnetism, the appearance of Ga^{3+} at tetrahedral site or on both T and O. Previous reports have shown that $FeGa_2O_4$ is antiferromagnetism or ferromagnetism at low temperature [9, 16, 17].

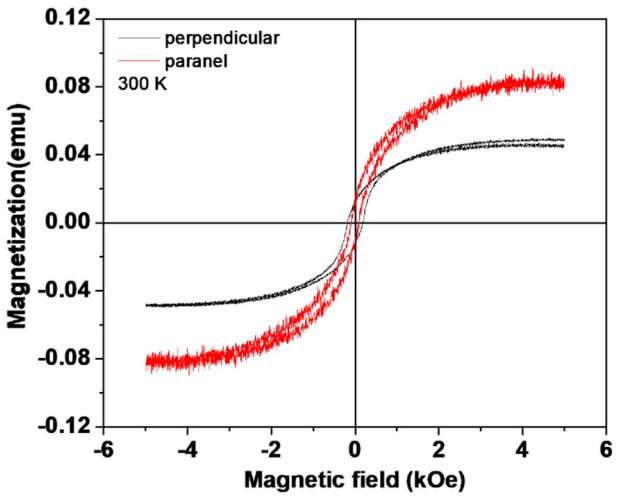


Figure 6. Out-of-plane and in-of-plane magnetization hysteresis (M–H) loops at room temperature

4. CONCLUSION

In summary, $FeGa_2O_{4-\delta}$ epitaxial film on MgO(100) substrate was successfully grown by using MBE. The film is oriented (400) with cubic structure and single crystal properties. There are appearance of cation valence Fe^{2+}, Ga^{3+} and Fe^{3+} in film, while at tetrahedral site there are appearance of both Ga^{3+} and Fe^{3+} cations. The film presents semiconductor behaviour and negative magnetoresistance effect with highest value of 9% at 150K. The magnetic property of $FeGa_2O_{4-\delta}$ film exhibits ferrimagnetism at room temperature, the magnetization easy axis is perpendicular to film's surface. The obtained results in this work include the structural, electrical and magnetic of $FeGa_2O_{4-\delta}$ spinel oxide film, which will be useful for the research and fabrication of spintronics devices.

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THÔNG TIN TÁC GIẢ

Dương Văn Thiết[1], Nguyễn Xuân Chung[2], Nguyễn Quốc Tuấn[1], Nguyễn Tiến Tùng[1], Nguyễn Minh Quang[1]

[1]Trường Cơ khí - Ô tô, Trường Đại học Công nghiệp Hà Nội

[2]Khoa Vật lý, Đại học Mỏ - Địa chất