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Dependence of Structural and Electrical Properties of Sputtered-Fe_3O_4 Thin Films on Gas Flow Rate

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ABSTRACT

Magnetite (Fe_3O_4) is a potential material for spintronic development due to its high Curie temperature (858 K) and half-metallic structure with only one spin polarization at Fermi level. The bulk properties of Fe_3O_4 make it a big challenge to grow perfectly stoichiometric thin films at a low temperature. Here, we report the structural and morphological evolution of the Fe_3O_4 thin films as a function of gas flow rate. Radio-frequency (RF) magnetron sputtering was used to fabricate Fe_3O_4 thin films on the MgO/Ta/SiO_2 structure at room temperature. Atomic force microscopy (AFM) shows a spherical-like shape, the root-mean-square (RMS) roughness varies from 1.5 nm to 7.5 nm, and grain size increases from 30 nm to 74.3 nm. The structural properties of Fe_3O_4 films are dramatically enhanced by increasing the gas flow rate. Moreover, the resistivity (ρ) versus temperature (T) reveals the existence of a Verwey transition below 120 K, indicating the presence of Fe_3O_4.

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1. Introduction

The ferrimagnetic spinel Fe_3O_4 is well-known for its high Curie temperature (858 K) [1]. Theoretical calculations predicted Fe_3O_4 to have a half-metallic structure with only one spin polarization at the Fermi level [2] - [3]. A metal-insulator transition occurs in Fe_3O_4 at the Verwey temperature, T_V = 120 K [2], which is contributed to by the electron hopping mechanism that governs transport behavior below T_V [1]. The characteristics of Fe_3O_4 make it an attractive candidate for using in a variety of spin-electronic devices.

Growing completely stoichiometric Fe_3O_4 thin films at a low temperature is challenging. High temperature treatment above 500 °C is required to obtain the magnetite phase [4]. However, this action causes inter-diffusion and complexity of the interface between Fe_3O_4 and substrates, as well as the development of amorphous oxides (FeO and Fe_2O_3 phases), which have a major impact on the characteristics of Fe_3O_4 films [2], [5] - [8]. Fe_3O_4 films can be fabricated by various deposition techniques, such as sputtering [9-11], molecular beam epitaxy (MBE) [12] - [15], and pulsed laser deposition (PLD) [16] - [19]. Among these methods, RF-magnetron sputtering is widely used and found suitable for spintronics devices [20], magnetic storage, and spin-polarized current injection [21], [22]. However, sputtering variables, including the applied power density, substrate temperature, argon gas flow, and substrate-to-target distance, have a significant impact on the nanostructure and various properties of Fe_3O_4 thin film in RF-magnetron sputtering. According to the literature of TiN [23] and aluminum zinc oxide [24], the surface morphology and electrical properties are strongly enhanced with increasing the argon flow rate. Here, the aim of this study is to study the influence of the working argon gas flow rate on the structural and morphological properties as well as the conduction mechanism of Fe_3O_4 films. The MgO/Ta double buffer layer has contributed as a buffer layer and a supporting layer to lower the crystallization temperature of Fe_3O_4 film.

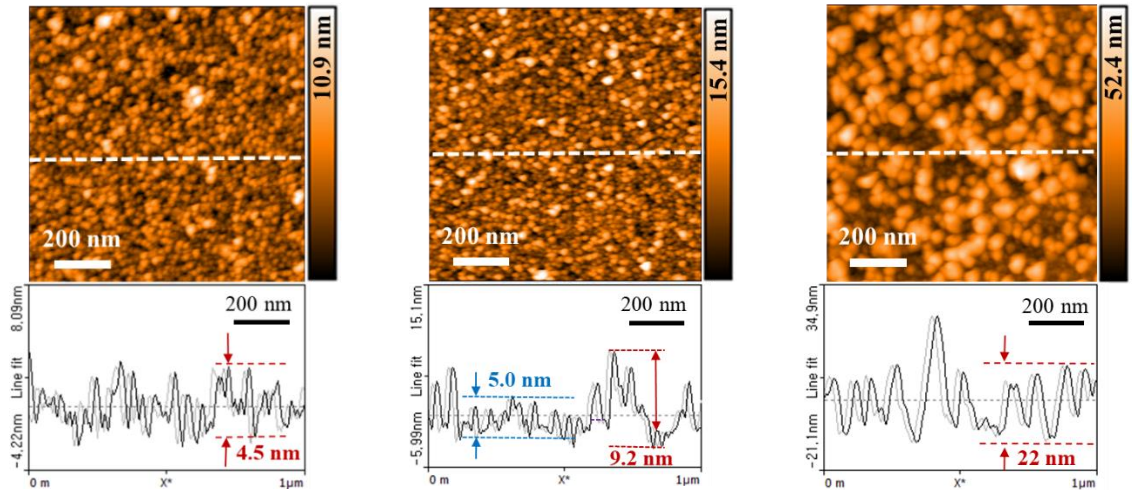
2. Materials and Methods

RF-magnetron sputtering was used to fabricate Fe_3O_4 thin films on SiO_2 substrates with buffer layers of MgO/Ta. Argon gas was used as a background gas and the flow rate ranged from 30.0 sccm to 40.0 sccm. Fe_3O_4 samples were held at 200 °C during deposition. As-grown Fe_3O_4 films were annealed at 450 °C for 1.5 hours without exposure to ambient conditions. X-ray diffraction (XRD) and atomic force microscopy (AFM) were used to examine the structure and the morphology of Fe_3O_4 films, respectively. A four-point probe was used to measure electronic characteristics.

3. Results and Discussion

To understand the effect of argon flow rate on the morphology of Fe_3O_4 films, AFM was used to examine the roughness of the Fe_3O_4 surface. Samples A, B, and C represent the three distinct Argon gas flows: 30 sccm, 35 sccm, and 40 sccm, respectively. They also correspond to three different deposition pressures: 1 mTorr, 5 mTorr, and 10 mTorr.

Fig. 1 shows the AFM scans and their line-profiles of samples A, B, and C. From the cross-sectional AFM profiles for sample A, the average grain size was found to be 30.0 ± 1.0 nm with root-mean-square (RMS) roughness of 1.5 ± 0.3 nm (see Fig. 1a). As the deposition pressure increases, the morphology exhibits drastically increasing RMS roughness. Regarding sample B, the average grain size of 32.0 ± 1.5 nm and rough RMS roughness of 2.3 ± 0.5 nm were observed, while sample C shows the average grain size of 74.3 ± 4.5 nm and the roughest surface with RMS roughness of 7.5 ± 1.2 nm. The line-profiles of samples A, B, and C reveal the evolution of RMS roughness and grain size as a function of the Argon gas flow rate. The results obtained by using AFM scan for three deposition pressures of Fe_3O_4 films are summarized in Table 1.



(a) (b) (c)

Figure 1. *AFM scans (1.0 × 1.0 μm) (upper pannel) and their line-profiles (lower pannel) of samples (a): A; (b): B; and (c): C.*

Table 1. *Morphological analysis of the AFM scans for samples A, B, and C.*

Sample	Argon gas flow rate (sccm)	Deposition pressure (mTorr)	RMS roughness (nm)	Grain size (nm)	Peak to valley (nm)
A	30.0	1.0	1.5 ± 0.3	30.0 ± 1.0	13.0 ± 2.0
B	35.0	5.0	2.3 ± 0.5	32.0 ± 1.5	24.3 ± 3.4
C	40.0	10.0	7.5 ± 1.2	74.3 ± 4.5	49.5 ± 5.8

In order to clarify the effect of gas flow rate on the structure in Fe3O4 thin films, XRD measurements of Fe3O4 thin films were performed. Fig. 2 shows the XRD of Fe3O4 thin films of samples A, B and C.

All the films exhibit a Fe3O4(004) peak at 2θ = 42.43o. This typical peak of Fe3O4 is slightly shifted to a lower angle (42.43o) compared with its theoretical value (43.05o [25]), implying that the tensile lattice strain exists in the film [26]. When increasing the deposition pressure up to 10 mTorr, sample C shows a high-textured Fe3O4 (004) peak, indicating that sample C has the best crystallinity of the three samples. Our results reveal that the quality of Fe3O4 crystallinity strongly depends on the gas flow rate.

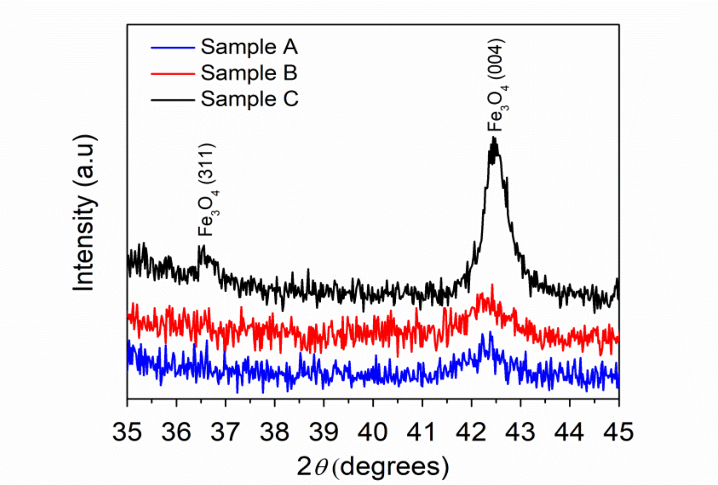
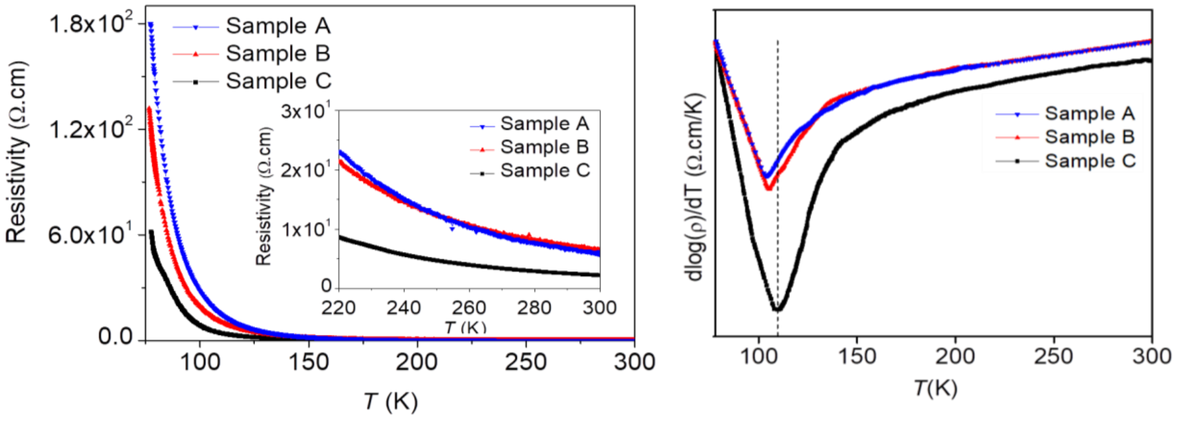


Figure 2. *XRD patterns of samples A, B, and C (deposited at 1, 5 and 10 mTorr respectively)*

After characterizing the morphological and structural properties of Fe_3O_4 films, the electrical transport measurement of Fe_3O_4 films was carried out in the range of temperatures from 77 K to 300 K as shown in Fig. 3a. The resistivity of samples A, B and C as a function of temperature is depicted in Fig 3a. At room temperature (RT), the resistivities of samples A, B and C are 5.9×10^{-2} Ω.cm, 6.5×10^{-2} Ω.cm, and 2.2×10^{-2} Ω.cm, respectively. In particular, at 77 K, the resistivities of samples A, B, and C correspond to 1.80×10^{2}, 1.27×10^{2} and 6.1×10^{1} Ω.cm, respectively. The resistivity of sample C is one order of magnitude lower than the others. When increasing deposition pressures, a drastic fall in the resistivity is observed, which results in an enhancement in crystallinity and grain size. Bigger grain size can decrease grain boundary scattering in Fe_3O_4 thin films, which leads to better conduction [26] - [27].



(a) *(b)*

Figure 3. *(a): Resistivity as a function of temperature of samples A, B and C. The inset shows clearly the resistivity of 3 samples from 220K to 300K; (b): The first derivative curve of log p(T)*

The occurrence of Verwey temperature (T_V) is known as demonstration for high-quality Fe_3O_4 films [28]. To find out the value of T_V, a first derivative of the logarithm of resistivity as a function of temperature was used [29]. The $d\log(\rho)/d$T curves of samples A, B, and C are shown in Fig. 3b. The T_V values of samples A and B are 104.2 K and 105.4 K, respectively, while sample C obtains a T_V of 110.1 K, which is the highest value of the three samples. Samples A, B and C have a lower Verwey transition temperature than the bulk value (~120 K) [6]. Fe_3O_4 thin film deposited at a deposition pressure of 10 mTorr has the highest T_v value, indicating that sample C has a good stoichiometry of Fe_3O_4. This result could be explained by the tensile lattice strain that exists in Fe_3O_4 thin films and antiphase boundaries (APB) caused by the lattice mismatch between Fe_3O_4 thin films and buffer layer or substrate [6] , [30] - [32]. Because T_V strongly depends on strain, APB and the stoichiometry of Fe_3O_4 thin films, according to the previous reports [2], [30], [33] - [34]. When increasing the deposition pressure, electrons in the chamber have a shorter mean free path, giving them more opportunities to collide and ionize Ar gas atoms. It means the number and energy of target particles reaching the substrate surface is adequate enough to build a uniform lattice formation and improve crystallinity [26] - [27].

4. Conclusions

In summary, gas flow rate effects on the structural and electrical properties of Fe_3O_4 thin films were studied. RF-magnetron sputtering was used to deposit Fe_3O_4 thin films on SiO_2 substrates with buffer layers of MgO/Ta at various gas flow rates. A dependence of the morphology, structure and electrical properties of Fe_3O_4 thin films on gas flow rate is observed. When the deposition pressures increase from 1 mTorr to 10 mTorr, the grain size, crystallinity and stoichiometry of Fe_3O_4 samples are improved. Sample C, deposited at 10 mTorr, obtains the lowest RT resistivity of 2.2×10^{-2} Ω.cm and the highest T_v value of 110.1 K, revealing that it has the best crystallinity and the closest stoichiometry to the bulk. Our findings indicate that controlling the deposition pressure is the key factor to grow high-quality Fe_3O_4 thin films.

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