

Valence Band Structure of Co-Doped Fe₃O₄(100) Films

Fan-Yong RAN*, Yasushi TSUNEMARU, Takahide HASEGAWA, Yasuo TAKEICHI, Ayumi HARASAWA, Koichiro YAJI, Sung-Hun KIM, and Akito KAKIZAKI

Synchrotron Radiation Laboratory, Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan

Introduction

Magnetite (Fe₃O₄) has been widely studied due to its predicted spin polarization of -100%[1]. On cooling through ~122K (T_v), it undergoes a first-order phase transition, named Verwey transition[2]. Co-doped Fe₃O₄ has attracted particular attention because of its enhanced structural anisotropy and magnetic anisotropy. The magnetocrystalline anisotropy constant of Fe₂CoO₄ is about 1.8×10^5 J/m³[3]. It is reported that Co ions mainly substitute the Fe²⁺ ions in magnetite[4]. Co doping changes magnetic properties, destroys Verwey transition and reduces magnetoresistance[5]. So far, there is still lack of evidence on the valence band structure of Co-doped Fe₃O₄, which is significant to understand its physical and chemical properties.

Experimental

High quality 200 Å thick Co-doped Fe₃O₄ (100) films were deposited on MgO(100) substrates using molecular beam epitaxy method. The base pressure of the preparation chamber is $< 2 \times 10^{-10}$ mbar. The growth rate is about 3 Å/min. During the growth, the O₂ pressure was maintained at 2×10^{-6} mbar, and a substrate temperature of about 250 °C was used. After preparation, the films were *in situ* transferred into an analysis chamber (base pressure, $< 8 \times 10^{-11}$ mbar). Then, the structural properties were investigated by low-energy electron diffraction (LEED). Using a photon energy of $h\nu=48$ eV, angle-resolved photoelectron spectroscopy (ARPES) spectra were measured at RT to investigate the valence band structure along $\bar{\Gamma}-\bar{M}$ direction in the surface Brillouin zone of Co-doped Fe₃O₄ films.

Results and Discussion

Figure 1(a) shows LEED pattern of surface of pure Fe₃O₄ films. Clear $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction (white solid square) and (1×1) unit cell (white dashed square) are visible, indicating clean and well-ordered surface. The Brillouin zone and $\bar{\Gamma}-\bar{M}$ direction of Fe₃O₄(100) surface are schematically represented in Fig. 1(a) (black solid line). LEED investigation on Co doped films suggests that the Co doping blocks the reconstruction. X-ray photoelectron spectroscopy analysis reveals that the Co²⁺ ions substitute the Fe²⁺ ions of Fe₃O₄.

Figure 1(b) shows the ARPES spectra near E_F . It is found that the photoelectron intensity in the range of 0-0.5 eV is reduced with Co doping, and become nearly 0 for Fe₃O₄ film doped with about 33% Co. Especially, density of states (DOS) at E_F is found to be 0 for Co doped films, suggesting a metal-insulator transition

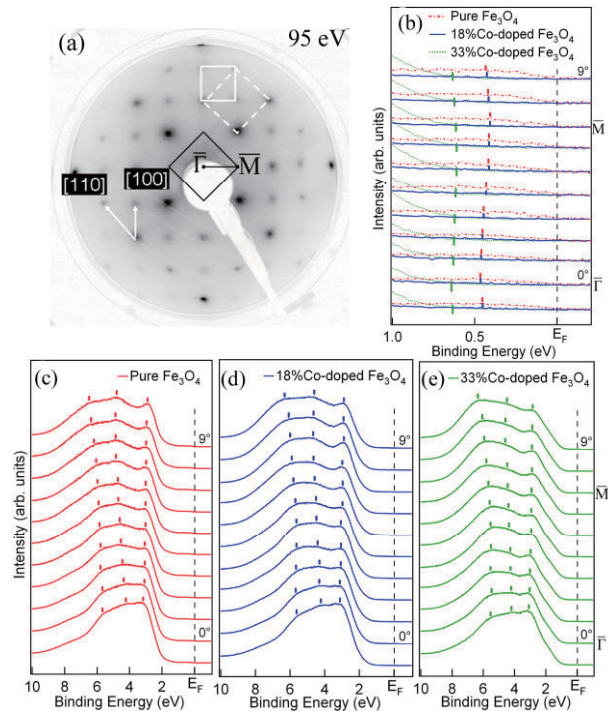


Fig. 1 (a) LEED pattern of pure Fe₃O₄ films; (b)-(e) ARPES spectra of pure and Co-doped Fe₃O₄ films.

induced by Co doping. As can be seen in Figure 1(c)-(e), dispersions of O *2p*-derived features above 2.5 eV are nearly not changed by Co doping. However, the spectral intensity at 0.5-3 eV is enhanced by Co doping, which are assigned to the *d* states originated from doped Co ions.

Conclusion

We have investigated valence band structure of Co-doped Fe₃O₄(100) films. Co²⁺ ions substitute the Fe²⁺ in Fe₃O₄. The DOS near and at E_F is reduced by Co doping due to the decrease of Fe²⁺ in Fe₃O₄, which might be responsible for the decrease in conductivity and magnetoresistance, as well as disappearance of Verwey transition in Co-doped Fe₃O₄.

References

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* fyran80@gmail.com