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Effects of Fe impurity on Magnetic and Optical Properties of Spinel Co₃O₄ Thin Films

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It has been investigated the evolution of structural, magnetic, and optical properties as Fe is added to Co_3O_4 . Fe_x $\text{Co}_{3-x}\text{O}_4$ samples were prepared as thin films on Si(100) substrates with thickness of about 1 µm by a sol-gel method employing spin-coating process. The precursor solution for fabricating Co_3O_4 films was prepared by dissolving $\text{Co}(\text{CH}_3\text{CO}_2)_2\cdot 4\text{H}_2\text{O}$ powder in 2-methoxyethanol at 70 °C. For Fe doping, Fe(NO₃)₃·9H₂O was dissolved together with $\text{Co}(\text{CH}_3\text{CO}_2)_2\cdot 4\text{H}_2\text{O}$.

The variation of structural properties with Fe composition in the $Fe_xCo_{3-x}O_4$ films was investigated by X-ray diffraction (XRD). Figure 1 exhibits XRD spectra for the present $Fe_xCo_{3-x}O_4$ films. It is seen that the same spinel structure as Co_3O_4 is maintained up to x = 0.55 with gradual increase of the cubic lattice constant with x. However, the XRD investigation indicates the coexistence of two phases between x = 0.76 and 0.93 as clearly seen in Fig. 2 where the evolution of the (311) peak with x is exhibited.

The result of magnetic-property measurements by vibrating-sample magnetometer (VSM) on the $Fe_xCo_{3-x}O_4$ films is exhibited in Fig. 3. Paramagnetic behavior was observed below x=0.55. Optical properties of the $Fe_xCo_{3-x}O_4$ films were measured by spectroscopic ellipsometry (SE) in the 1.5-4 eV photon-energy range. As shown in Fig. 4, the imaginary part of the dielectric function of $Fe_xCo_{3-x}O_4$ evolves as the Fe composition changes. As the Fe composition increases, the 2.8-eV absorption, due to p-d charge-transfer (CT) transition between O and octahedral Co^{3+} ion,[1] is reduced in intensity. The 1.65-eV structure, due to d-d CT transition between octahedral Co^{3+} and tetrahedral Co^{2+} ions also suffers reduction in strength as x increases. These results indicate that the Fe^{3+} ions substitute octahedral Co^{3+} sites mostly for low Fe compositions. X-ray photoelectron spectroscopy measurements revealed that Fe have Fe^{2+} as well as Fe^{3+} ionic valence at high Fe compositions.

Reference

[1] K. J. Kim, Y. R. Park, D. H. Hyun, S. H. Lee, J. Appl. Phys. 96, 1975 (2004).

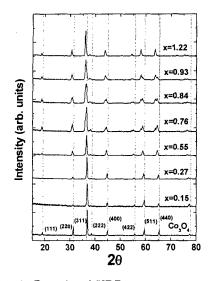


Fig. 1. Result of XRD measurements on $Fe_xCo_{3-x}O_4$ films.

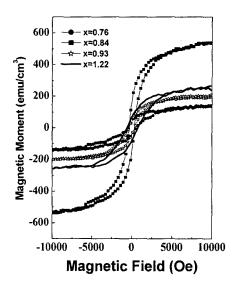


Fig. 3. Result of VSM measurements on $Fe_xCo_{3-x}O_4$ films.

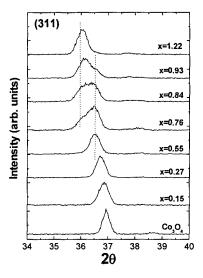


Fig. 2. Evolution of XRD (311) peak of $Fe_xCo_{3-x}O_4$ films.

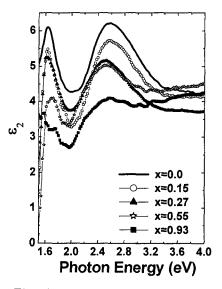


Fig. 4. Imaginary parts of dielectric functions of $Fe_xCo_{3-x}O_4$ films measured by SE.