希薄磁性半導体(Zn,Co)O 薄膜における F ドーピングの磁性への影響

The effect of F-doping on magnetism in diluted magnetic semiconductor (Zn,Co)O thin films

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Co-doped ZnO has been studied extensively as one of the candidates of room-temperature ferromagnetic semiconductors. According to a theoretical prediction, (Zn,Co)O becomes ferromagnetic above room temperature due to co-doping of donor impurity[1]. Experimentally, there have so far been many studies on (Zn,Co)O co-doped with donor impurities Ga or Al, but intrinsic ferromagnetism has not yet been confirmed. In our previous report[2], we showed an increase of magnetization of (Zn,Co)O due to the co-doping of fluorine (F), which is expected to act as donor impurity by substituting the anion site, instead of the cation site in the case of Ga or In. In this study we have investigated the local structure around Co atoms in (Zn,Co)O using X-ray absorption fine structure (XAFS) measurement, with an aim to confirm whether the observed increase in magnetization is the intrinsic magnetic properties originating from Co atoms in the substitutional site.

(Zn,Co)O thin films with 20% of Co were deposited on (11-20) (*a*-plane) sapphire substrate using PLD technique. The deposition was performed at a substrate temperature of 500°C at an oxygen pressure around 0.5Pa. Some of the grown films were annealed after the growth at 500°C in vacuum during one hour, with an aim to introduce O vacancies. Structural properties of the grown films were checked using θ-2θ scan of XRD. XAFS measurement at Co *K*-edge was performed at BL-14B2 of SPring-8. The radial distribution around Co atoms is derived from Fourier transforms of extended X-ray absorption fine structure (EXAFS) oscillation. The magnetization of the films was measured using SQUID.

Figure 1 shows *M*-*H* curves at 2K of as-grown and annealed (Zn,Co)O films with and without (referred to as undoped) co-doping of F. As shown in the figure, the magnetization of the F-doped film is larger than that of the undoped film, and it increases further due to the annealing. In contrast, the magnetization of the undoped film does not increase due to the annealing. In the XRD θ-2θ measurement, we did not detect any trace of secondary phases. Figure 2 shows the radial distribution function (RDF) around Co atoms of the respective films. As shown in the figure, the experimental curves of all the films are very similar to the result of simulation for a single Co atom in the substitutional site in the wurtzite structure. In addition, X-ray absorption near edge structure (XANES) spectra (not shown) do not change due to F-doping or the thermal annealing. These results allow us to conclude that the Co atoms are in the substitutional site in the F-doped and/or annealed films, suggesting the observed increase of magnetization is the intrinsic magnetic properties of the pure diluted phase. As a possible mechanism of the increase of magnetization, the ferromagnetic interaction between Co spins mediated by F impurity or O vacancies is considered. The superexchange antiferromagnetic interaction between Co spins in undoped (Zn,Co)O is considered to be reduced by the ferromagnetic interaction mediated by F impurity or O vacancies, resulting in the increase of magnetization.

[1] K. Sato *et al.*, Jpn. J. Appl. Phys. **40,** L334 (2001) [2] R. Ishikawa *et al.*, 75th Autumn Meeting of JSPS, (2014), 17p-S2-46

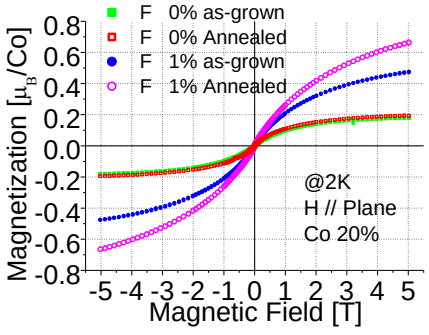

Fig.1 Magnetization curves at 2K of undoped and F-doped (Zn,Co)O films with 20% of Co. The annealing was performed at 500℃.

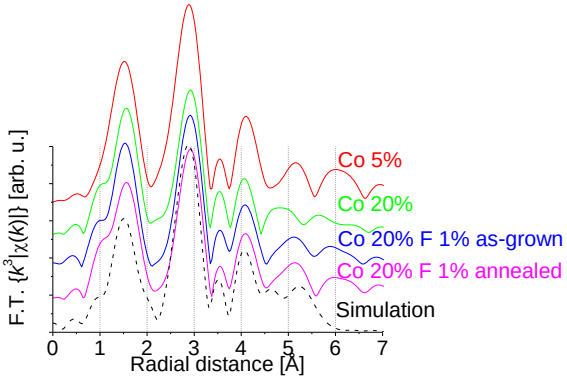

Fig.2 Radial distribution function (RDF) around Co atoms derived from Fourier transforms of EXAFS oscillation. The broken line represents the result of simulation assuming a Co atom at the substitutional site.