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EXAFS Study on Ga-doped in ZnO

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Introduction

ZnO is a wide-gap semiconductor with a direct band gap of 3.4 eV, and it has been extensively studied as a promising material for applications to high performance electronic and optoelectronic devices. Particularly, the development of ZnO-based transparent electrodes has progressed considerably. However, the level of electronic activation of donors is insufficient, and yet the reason is unclear. We have investigated the local structures and valence states of the donor impurities in ZnO by means of XAFS measurements. In this article, we report a result on $Ga_xZn_{1-x}O$ (GZO) from a structural aspect [1].

Experimental

Samples were prepared by laser ablation or RF magnetic sputtering methods on glass (Corning 1737). They were almost completely *c*-axis oriented polycrystalline films. XAFS spectra were measured by collecting the fluorescence X-rays using a 19-element Ge solid-states detector on the Zn and Ga K-edges. To analyze the orientation dependence of the local structure, the measurements were performed with two geometrical settings, the polarization vector of the incident X-rays parallel and perpendicular to the c-axis of the ZnO crystal lattice ($\vec{E} \parallel c$ and $\vec{E} \perp c$, respectively).

Results and Discussion

XANES on the Ga K-edge of GZO films was compared with those of GaN, indicating that Ga^{3+} ions essentially occupied the Zn sites of ZnO substitutionally in GZO films up to x=0.052. On the basis of this result, we compared the local structures of the Ga sites with those of the host Zn sites from EXAFS analysis on the Ga and Zn edges. Using polarization dependence of EXAFS, the distances between the nearest neighbor (NN) sites, O(1) and O(2), and the next nearest neighbor (NNN) sites, Zn(1) and Zn(2), from the Ga/Zn sites were determined .

For the local structure around Zn site, it was found that all of the NN and NNN distances agreed with the distances estimated from the crystal structure, and they showed almost no meaningful dependences on the growth method and condition. On the other hand, the Ga-O distances were shorter than the Zn-O distances: $d_{Ga\text{-}O(1)}$ =1.86 Å and $d_{Ga\text{-}O(2)}$=1.88 Å at x=0.027 while $d_{Zn\text{-}O(1)}$=1.97 Å and $d_{Zn\text{-}O(2)}$=1.99 Å. The Ga-Zn distances were found to be longer than the Zn-Zn distances: $d_{Ga\text{-}Zn(1)}$=3.27 Å and $d_{Ga\text{-}Zn(2)}$=3.24 Å while $d_{Zn\text{-}Zn(1)}$=3.25 and $d_{Zn\text{-}Zn(2)}$=3.21 Å. These results are summarized in Fig. 1.

For the NN sites, the difference in Ga-O and Zn-O distances is consistent with the relative ionic radii; the 4-coordinate radii are $r_{Zn^{2+}}$=0.74 Å, $r_{Ga^{3+}}$=0.61 Å, and $r_{O^{2-}}$=1.24 Å. The NNN sites, however, show an opposite behavior to the NN sites. The elongation of the Ga-Zn distance is attributable to the Coulomb repulsion between the Zn^{2+} and the excess charge at Ga^{3+} ions. The increase of the NNN distance means an enlargement of the Zn^{2+} icosahedron with a Ga^{3+} ion at the center. This is consistent with the fact that the lattice constants of GZO increase with x [2].

References

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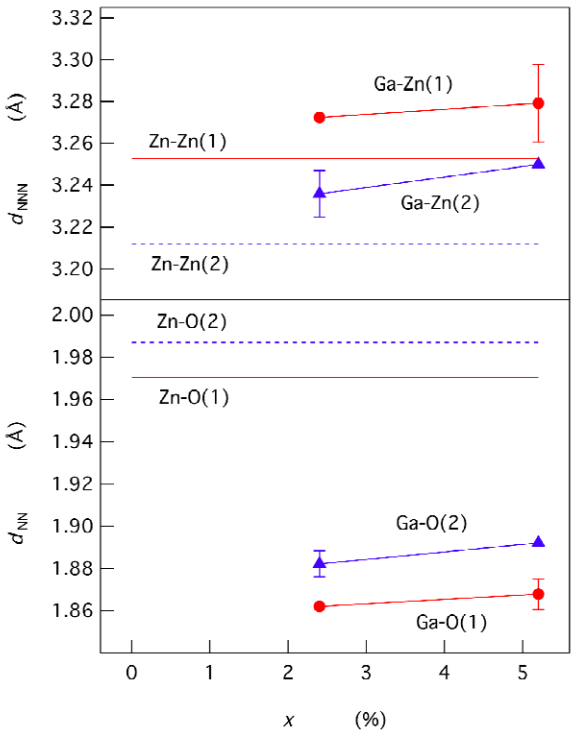

Fig. 1 Interatomic distances from Ga atom to the nearest neighbor (d_{NN}) and the next nearest neighbor (d_{NNN}) sites as functions of Ga concentration x, and those from Zn (independent of x).

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