Fabrication and Characterization of Rocksalt $Zn_{1-x}Ni_xO$ Thin Films

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Zinc oxide (ZnO) has been attracting attentions as a promising widegap semiconductor. Among its polymorphs, wurtzite ZnO (w-ZnO), which forms under ordinary pressure, has been widely studied. In contrast, there is a few report about rocksalt ZnO (rs-ZnO) known as a high-pressure phase, because rs-ZnO is unstable at atmospheric pressure and transforms to w-ZnO below 2 GPa [1]. rs-ZnO has Zn ions octahedrally coordinated with O ions, which is an untypical characteristic among Zn compounds. Therefore, rs-ZnO is expected to have unique physical properties and functions. Maintaining the rocksalt single phase at atmospheric pressure helps us to characterize its properties. The alloying of ZnO with rocksalt oxides such as NiO and the epitaxial growth on the single-crystalline substrates of rocksalt oxides can be effective for obtaining rocksalt phase. In this study, we fabricated rs-ZnO thin films with low-level Ni alloying and investigated their physical properties.

The $Zn_{1-x}Ni_xO$ thin films were fabricated on MgO(001) substrates by pulsed laser deposition (PLD). Four PLD targets were prepared, in which Ni concentrations were 0, 5, 8, and 26 cation%. The substrate temperature and the oxygen partial pressure were kept at 473 K and 0.05 Pa, respectively, during the deposition. The Ni concentrations in the thin films were measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES). The crystal structures of the thin films were investigated by X-ray diffraction (XRD). To estimate the optical band gaps of the thin films, absorption coefficients were measured by optical transmission spectrometry.

The Ni concentrations in the $Zn_{1-x}Ni_xO$ thin films were 0, 9, 15 and 36 cation%, respectively, which are 1.4-1.9 times larger than those in targets. The increase of the Ni concentration might have resulted from the faster evaporation of Zn atoms from the growth front. The XRD 2θ–θ profiles of the undoped and $Zn_{1-x}Ni_xO$ films are presented in Fig. 1. The profile of the undoped film exhibits peaks of w-ZnO and MgO. On the other hand, the films with more than 9 cation% Ni are suggested to be a single phase of the rocksalt structure. A systematic XRD analysis indicated that the rs-$Zn_{1-x}Ni_xO$ thin films have been epitaxially grown on the substrates with a cube-on-cube relationship.

The values of the indirect and direct band gaps of rs-ZnO have been reported to be 2.5 eV at 13.5 GPa and 4.5 eV at 10 GPa at room temperature, respectively [2].

However, the absorption of the indirect band gap could not be observed in our measurements because of the very week absorption of thin film. Meanwhile, the direct optical gaps of the thin films could be estimated using a Tauc relation. The direct band gaps of the rs-$Zn_{1-x}Ni_xO$ thin films at room temperature are presented in Fig. 2. While the undoped film with the wurtzite structure has the direct band gap of 3.3 eV, the values of the rs-$Zn_{1-x}Ni_xO$ thin films with 9, 15, and 36 cation% Ni are 4.4, 4.5 and 4.6 eV, respectively. These values of the rocksalt films are close to the reported direct-band gap of undoped rs-ZnO [2]. The band gap of the rs-$Zn_{1-x}Ni_xO$ is found not to change monotonically with the Ni concentration, considering that the band gap of NiO is 3.8 eV [3].

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References

[1] K. Kusaba et al., Proc. Jpn. Acad. Ser. B 75 (1999) 1.

[2] A. Segura et al., Appl. Phys. Lett. 83 (2003) 278.

[3] D. Adler and J. Feinleib, Phys. Rev. B 2 (1970) 3112.

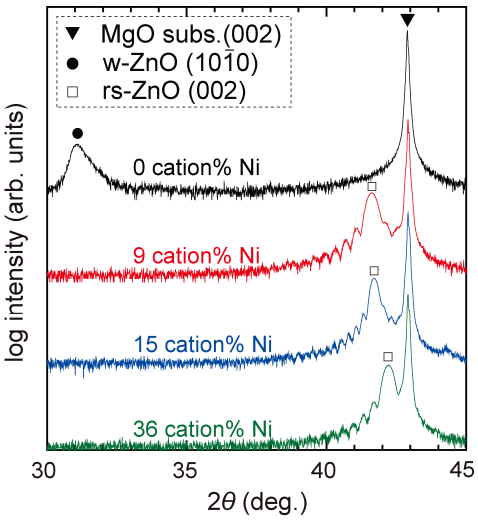

Fig.1 2θ–θ XRD profiles of $Zn_{1-x}Ni_xO$ thin films.

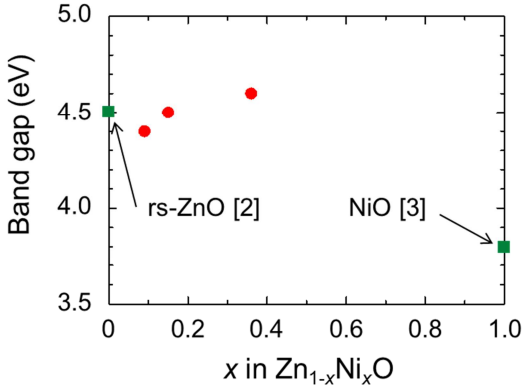

Fig. 2 Direct band gaps of rs-$Zn_{1-x}Ni_xO$ thin films.