Electronic structure of $Zn_{1-x}Co_xO$ thin films with controlled surface polarity

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Introduction

Oxide-based diluted magnetic semiconductors (DMS's), in particular ZnO-based DMS's, have attracted much attention due to their potentiality for applications [1]. Codoped ZnO has intensively been studied since the finding of ferromagnetism having Curie temperature near room temperature. Although Co-doped ZnO is a candidate for spintronic device applications, the low reproducibility of ferromagnetism remained as the problem to be solved.

Matsui and Tabata [2] have recently succeeded to obtain a high crystalline pit-free surface in Zn-terminated $Zn_{1-x}Co_xO$ thin film which shows ferromagnetic ordering by means of a new growth technique. In this work, we have investigated the Co 3*d* states of O- and Zn-terminated $Zn_{1-x}Co_xO$ thin films in order to understand the effect of the surface polarity on the electronic structure.

Experimental

 $Zn_{1-x}Co_xO$ (*x*=0.10) thin films were epitaxially grown on O- and Zn-terminated ZnO(0001) substrates, which led to O- and Zn-terminated $Zn_{1-x}Co_xO$ surfaces during the deposition, by the pulsed laser deposition technique using an ArF excimer laser.

Co $3p \rightarrow 3d$ resonant photoemission measurements were performed at BL-18A. Spectra were taken in an ultrahigh vacuum below 5×10^{-8} Pa. Photoelectrons were collected with a VG CLAM hemispherical analyzer in the angle integrated mode at room temperature. The total resolution of the spectrometer including temperature broadening was about 300 meV. Sample surface was cleaned by cycles of Ar⁺-ion sputtering and annealing. Cleanliness of the sample surface was checked by the absence of a high binding-energy (E_B) shoulder in the O 1s spectrum and C 1s contamination by x-ray photoemission spectroscopy (XPS) with Al- $K\alpha$ source ($h\nu = 1486.6$ eV).



Fig.1 Co $2p_{3/2}$ XPS (a) and absorption spectra (b) of the $Zn_{0.9}Co_{0.1}O$ thin films.

Result and discussion

Figure 1 shows Co $2p_{3/2}$ XPS and Co 3p-3d absorption spectra of the thin films. The electronic structure of the Co ions is independent of the surface polarity because the line shape of both the spectra was identical regardless of the polarity. The Co 2p XPS spectra corresponded with a previous XPS measurement [3], indicating that the Co ions are substitute to the Zn site and are divalent under tetrahedral crystal field.

Figure 2 shows the Co 3p-3d resonant photoemission spectra of the O- and Zn-terminated $Zn_{0.9}Co_{0.1}O$ thin films, where on- and off-resonance energies have been chosen to be 62 eV and 57 eV, respectively [see Fig. 1(b)]. The Co 3*d* partial density of states (PDOS) shows a peak near the top of the valence band and a satellite around ~7 eV. These structures are similar to the calculated spectra reported before [3], indicating that the Co ions substituted at the Zn site consistent with the XPS result.

In the O-terminated $Zn_{0.9}Co_{0.1}O$, the intensity of the O 2p band is weaker than that in the Zn-terminated $Zn_{0.9}Co_{0.1}O$. This intensity decrease may be related to crystalline deterioration. The result suggests that the Zn-polar $Zn_{0.9}Co_{0.1}O$ thin film has higher crystalline quality than the O-polar one and the new growth technique has opened the way to solve the reproducibility problem.

References

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Fig. 2 Co 3p-3d resonant photoemission spectra of the $Zn_{0.9}Co_{0.1}O$ thin films. The difference spectra are Co 3d partial density of states in the valence band. The Configuration-interaction (CI) cluster-model spectrum is referred from Ref.[3].