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Properties of $Zn_{1-x}Co_xO$ thin films grown on silicon substrates prepared by pulsed laser deposition

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Abstract

$Zn_{1-x}Co_xO$ ($x=0.05$, 0.10) thin films are formed on silicon (100) substrates using pulsed laser deposition (PLD). The as-deposited films show ferromagnetic behaviors with Curie temperature higher than room temperature. Homogeneous film with a wurtzite structure has been formed when $x=0.05$, whereas inhomogeneous film with a wurtzite phase mixed with cubic Co phase has been formed when $x=0.10$. A significant increase in the magnetism is observed for the $Zn_{0.90}Co_{0.10}O$ film because of the presence of Co clusters. After thermal annealing in O_2, the carrier concentration of the $Zn_{0.95}Co_{0.05}O$ film decreased three orders of magnitude from 10^{20} to 10^{17} cm^{-3} and the film became paramagnetic. The electronic structure of $Zn_{1-x}Co_xO$ ($x=0.125$) was studied using full-potential linearized augmented plane-wave (FP-LAPW) method. Both the annealing experiments and calculation suggest that the double-exchange mechanism is the possible origin of the ferromagnetism in the $Zn_{0.95}Co_{0.05}O$ film.

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1. Introduction

Diluted magnetic semiconductors (DMS), in which some atoms of host semiconductors are randomly substituted by magnetic atoms, are regarded as key materials for spintronics because they have charge and spin degrees of freedom in a single substance [1]. As an II–VI oxide DMS, transition-metal-doped ZnO is currently attracting much attention due to the proposed possibility of room temperature ferromagnetism [2,3]. ZnO is also suitable for fabricating carrier-controllable ferromagnetism because carrier-controlling techniques for ZnO have been well established. It is well known that heavy electron doping in ZnO can be easily achieved up to 10^{21} cm^{-3} by Al^{3+} or Ga^{3+} doping [4,5]. Among the methods used for deposition of thin film, PLD is effective and has the advantage that the ratios of the elemental components of the bulk and film are almost the same, even for chemically complex systems [6].

There are several papers reporting ferromagnetic $Zn_{1-x}Co_xO$ thin films using PLD method [4,7–10]. However, the origin of the ferromagnetism in $Zn_{1-x}Co_xO$ thin films remains an issue of debate. Ueda et al. [4] reported that ZnO could be ferromagnetic above room temperature by doping of Co and considered that double exchange mechanism is the most possible origin of the ferromagnetism. Kim et al. [7,8] studied the relationship between growth conditions (growth temperature and oxygen gas pressure) and magnetic properties of Co:ZnO films grown by PLD and showed that the films grown at 700 °C are predominantly ferromagnetic at room temperature due to the existence of ferromagnetic cobalt clusters. Rode et al. [9] reported that the ferromagnetism is, at least, partially due to the intrinsic properties of $Zn_{1-x}Co_xO$ and does not result from segrega-

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tion effects. Prellier et al. [10] showed the magnetization–temperature curves of the films, which are ferromagnetic with a Curie temperature around 300 K, and found no evidence of the metallic cobalt cluster. The discrepancy could be caused by the differences in the preparation of targets and the growth conditions. So far, almost all substrates for depositing ZnCoO thin films using PLD method are sapphires and it is well known that the properties of the films are influenced by the substrates. It is therefore worthwhile investigating the properties of ZnCoO films grown on other types of substrates. In this paper, we prepared $Zn_{1-x}Co_xO$ thin films grown on silicon substrates using PLD method and the films show ferromagnetic behaviors with Curie temperature higher than room temperature. Various properties of the films were investigated and the origins of the appearance of ferromagnetism are discussed.

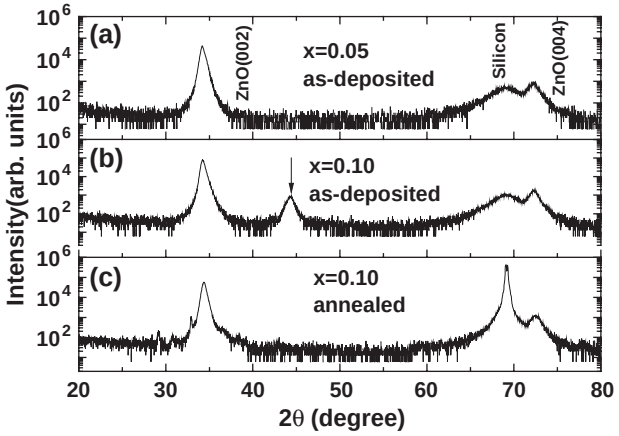

Fig. 1. (a and b) X-ray diffraction patterns of as-deposited $Zn_{1-x}Co_xO$ ($x=0.05$ and 0.10) films. The substrate temperature was fixed at 700 °C and the oxygen pressure was 4×10^{-3} Pa. (c) The XRD pattern of the annealed $Zn_{0.9}Co_{0.1}O$ film. The film was annealed at 700 °C in an oxygen-ambient pressure of 13 Pa for 30 min after deposition.

2. Experimental details

$Zn_{1-x}Co_xO$ ($x=0.05$, 0.10) thin films were fabricated on Si (100) substrates using PLD from ceramic targets with prescribed compositions. Before deposition, the substrates were ultrasonically cleaned using acetone for 12 min and then using ethanol for 10 min. Al was added to the targets at 1 wt.% as the electronic dopant. The chamber was evacuated by a turbo pump to a base pressure of 1.3×10^{-4} Pa. All the films were formed at 700 °C in an oxygen-ambient pressure of 4×10^{-3} Pa using a pulsed laser with peak energy density of 2 J/cm^2 (Nd: YAG laser, $\lambda=266$ nm, 8 ns, 10 Hz). The target-to-substrate distance was fixed at 4 cm. A clamp was used to fix the substrate. There was no film deposited underneath the clamp and steps were formed on the substrate. The thickness of the films was measured using a stylus profilometer (Tencor alpha-step 500). After deposition, the $Zn_{1-x}Co_xO$ films were annealed at 700 °C in an oxygen-ambient pressure of 13 Pa for 30 min. The crystal structure of the films was characterized by conventional X-ray diffraction (XRD) using Cu K_α radiation ($\lambda=1.5406$ Å) (MAC MXPAHF). Magnetic measurements were performed using a vibrating sample magnetometer (VSM) and superconducting quantum interference device magnetometer with a magnetic field applied parallel to the film surface. The resistivity of the samples was measured using a four-probe method. The carrier concentration was deduced from Hall effect using the van der Pauw method. All the electrical measurements were carried out at room temperature.

3. Results and discussion

The XRD patterns of the as-deposited $Zn_{1-x}Co_xO$ films are shown in Fig. 1(a) and (b). All of the films have a c-axis-preferred orientation. When $x=0.05$, homogeneous film of single wurtzite ZnO phase is found, whereas inhomogeneous films of wurtzite phase mixed with a new phase ($2\theta=44.3°$, indicated by an arrow) were formed when $x=0.10$. The corresponding parasitic phase is most probably cubic cobalt or $ZnCo_2O_4$. In order to identify this new phase, the structure of the annealed $Zn_{0.90}Co_{0.10}O$ thin film was studied. Fig. 1(c) is the XRD pattern of the annealed sample. The peak located at 44.3° disappears after annealing. Therefore, the new phase in $Zn_{0.90}Co_{0.10}O$ film is metallic cobalt rather than $ZnCo_2O_4$ because $ZnCo_2O_4$ phase will not change after thermal annealing in ambient oxygen. This indicates that metallic cobalt phase separates from the $Zn_{0.90}Co_{0.10}O$ film. The average size of cobalt clusters is 11 nm, which is estimated from the full width at half maximum of the peak at 44.3° using the Scherrer formula [11].

In Fig. 1(c), the small peaks at 30.9°, 36.5°, and 38.2° are from cubic Co_3O_4 due to the oxidation of cobalt clusters and the peak at 29.1° is from SiO_2 due to the oxidation of the substrate during the annealed process. The high Si(400) peak is from the Si substrate which was uncovered by the film due to the clamp during the deposition process. The Si(200) second order peak at 33° also appears.

The XRD results show that the solubility of cobalt ions in ZnO was less than 10% in our experiments. Kim et al. [7] found that solubility limit of cobalt ions in ZnO was around 40% using an optimized condition of substrate temperature of 600 °C and oxygen pressure of 10^{-3} Pa on sapphire (0001) substrates. We suggest that the solubility of cobalt in ZnO not only depends on the growth conditions but also depends on the properties of the substrate. The high deposition temperature of 700 °C in our experiments reduces the solubility [7] and the tetrahedral silicon structure may also reduce the solubility limit.

The measurement of magnetization vs field (M–H) curves on the as-deposited $Zn_{1-x}Co_xO$ films was carried out by VSM system at room temperature with a magnetic