Mn-doped Cu$_2$O thin films grown by rf magnetron sputtering

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Cu$_2$O has excellent optical properties and could be a good host semiconductor for dilute magnetic semiconductors because doped Cu$_2$O is a p-type and direct wide-band-gap semiconductor. In this work, Mn-doped Cu$_2$O thin films were deposited on thermally oxidized silicon substrates by radio-frequency magnetron sputtering. X-ray diffraction results show that highly (200) oriented (Mn$_{0.06}$Cu$_{0.94}$)$_2$O films can be achieved at elevated substrate temperature. X-ray photoelectronic spectroscopy confirms that the valence of copper in the films is only +1, and no other valence states. The Mn-doped Cu$_2$O films show primary paramagnetic behaviors above 25 K. Very weak ferromagnetic property interspersed with paramagnetic phase appears near 5 K. The high magnetic moment of 5.3$\mu$B per Mn ion and high resistivity suggest the valence state of manganese is mainly +1. © 2005 American Institute of Physics. [DOI: 10.1063/1.1852319]

I. INTRODUCTION

Dilute magnetic semiconductors (DMSs) have attracted a great deal of attention recently because of their potential applications in spintronics$^1$ and the discovery of ferromagnetism in III-V-based DMSs such as Ga$_{1-x}$Mn$_x$As.$^2$ Ferromagnetic semiconductors promise efficient spin injection and transport and potential seamless integration with current semiconductor technology.$^3$ The development of room-temperature (RT) ferromagnetism in DMSs is the first step towards semiconductor-based spintronic devices. Early efforts in this field have concentrated on compound semiconductor materials doped with transition elements, and ferromagnetism was realized in some cases, but the Curie temperatures are rather low. Oxide semiconductors are a natural class to explore in view of their diverse properties.

Recently, considerable effort has been focused on achieving ferromagnetism in oxide semiconductors, such as transitional metal-doped ZnO,$^4$-$^6$ TiO$_2$,$^7$-$^8$ and SnO$_2$.$^9$-$^{10}$ While the ferromagnetism has been observed in these systems, the exact origin and the specific transport properties are not clearly understood.

Cuprous oxide (Cu$_2$O) is a p type direct band-gap ($E_g$ = 2 eV) semiconductor with excellent optical properties. For instance, it has a high absorption coefficient for solar energy,$^{11}$ excitons, consisting of an excited electron and hole bound together in semiconductors, can propagate coherently through Cu$_2$O.$^{12}$ These properties make Cu$_2$O an attractive material that may combine the optical and magnetic properties for new devices. There are limited researches to develop DMS based on Cu$_2$O.$^{13}$ RT ferromagnetism is reported in Co-doped Cu$_2$O films codoped with Al.$^{14}$ In this manuscript, we report the preparation and properties of highly oriented Mn-doped Cu$_2$O films. The details of chemical valence of ion and magnetic properties of Mn-doped Cu$_2$O thin films have been examined.

II. EXPERIMENT

The Mn-doped Cu$_2$O thin films were grown on thermally oxidized silicon (TOS) substrates or silicon wafers coated with 100-nm-thick Cu films by radio-frequency (rf) magnetron sputtering deposition. Ceramic targets of (Mn$_{1-x}$Cu$_{0.5}$)$_2$O used for magnetron sputtering were synthesized by the standard solid-state reaction techniques. Thin-film growth was carried out at room temperature, 593, 693, and 793 K, respectively. The base pressure of the chamber was less than 1 $\times$ 10$^{-7}$ Pa. The pressure of working Ar gas and the sputtering power were kept at 0.6 Pa and 80 W during the deposition, respectively.
The structure of the Mn-doped Cu$_2$O films was characterized by scanning electron microscopy (SEM) (Jeol JSM-6335FEG) and x-ray diffraction (XRD) (Philips 3100 Diffractometer). The composition of films and chemical states of ions were studied using x-ray photoelectron spectroscopy (XPS) (PHI-5300/ESCA). A Mg $K_{\alpha}$ line at 1253.6 eV was used with the x-ray source operating at 14.5 kV. The vacuum of the analysis chamber was less than $3 \times 10^{-7}$ Pa. All binding energies have been corrected for sample charging effect with reference to the C $1s$ line at 284.6 eV. The XPS peak areas and peak decomposition were determined using Gaussian–Lorentzian curve fitting. The magnetic properties of the films were characterized by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc.) in the temperature range of 5–300 K.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns for the films deposited at RT, 593, 693, and 793 K. All samples have good structural quality and high degree of (200) orientation, which improves with substrate temperature. The cross-sectional SEM images show that the films are uniform and smooth, no presence of Mn clusters. The line scan using energy dispersive x-ray spectroscopy shows that the Mn distribution is uniform. However, the stoichiometry of the films was characterized by x-ray diffraction (XRD) (Philips 3100 Diffractometer). The composition of films and chemical states of ions were studied using x-ray photoelectron spectroscopy (XPS) (PHI-5300/ESCA). A Mg $K_{\alpha}$ line at 1253.6 eV was used with the x-ray source operating at 14.5 kV. The vacuum of the analysis chamber was less than $3 \times 10^{-7}$ Pa. All binding energies have been corrected for sample charging effect with reference to the C $1s$ line at 284.6 eV. The XPS peak areas and peak decomposition were determined using Gaussian–Lorentzian curve fitting. The magnetic properties of the films were characterized by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc.) in the temperature range of 5–300 K.

FIG. 1. XRD patterns for (Mn$_{0.06}$Cu$_{0.94}$)$_2$O films deposited at RT, 593, 693, and 793 K.

The chemical valence states of Cu and Mn atoms of the films are analyzed by XPS. The high-resolution Cu 2$p$ and Mn 2$p$ core-level spectra of the films prepared at 673 K are shown in Figs. 2 and 3, respectively. The 2$p$ core levels are split into 2$p_{1/2}$ and 2$p_{3/2}$ components due to the spin-orbit coupling. The line shape of 2$p_{3/2}$ reflects the chemical valence and is fitted using a Shirley background and a convolution of 20% Gaussian and 80% Lorentzian functions. The dashed lines denote the fitted curves. In Fig. 2 only one peak at 932.7±0.1 eV is needed to match the experimental data well, which agree well with literature data. This indicates that the film consists of single (MnCu)$_2$O phase, i.e., Cu$^{+1}$ is the only chemical valence state for copper. However, the chemical valence state of Mn is not easy to determine because Mn has various valence states and their binding energies are intermixed. In Fig. 3, we also use one peak at 640.7±0.1 eV to fit the experimental results. Because Mn is chemically active, Mn$^{+1}$ seldom appears in any stable oxides and the binding energy for Mn$^{+1}$ is not found in the literature. Although we cannot ascertain the valence state of Mn, it is still clear that this peak does not correspond to Mn$^{3+}$ or higher Mn valence state, which is greater than 641 eV, suggesting that the valence of Mn predominantly $+1$.

Figure 4 shows the temperature dependence of the magnetization in a field of 100 mT. The inset in Fig. 4 shows the plot of the reciprocal magnetic susceptibility $\chi^{-1}$ vs temperature $T$. The almost linear behavior with increasing tempera-

FIG. 2. High-resolution Cu 2$p$ core-level spectra of the films prepared at 673 K. The inset is the fitted curve for Cu 2$p_{1/2}$.

FIG. 3. High-resolution Mn 2$p$ core-level spectra of the films prepared at 673 K. The inset is the fitted curve for Mn 2$p_{1/2}$.

FIG. 4. Magnetization as a function of the temperature of for (Mn$_{0.06}$Cu$_{0.94}$)$_2$O films.
ture except around 5 K suggests that the film is paramagnetic at high temperature. The hysteresis loops also confirm the paramagnetic behavior for all temperatures above 5 K. The hysteresis loops at 5 and 35 K are compared in Fig. 5. There is a clear hysteretic behavior at 5 K although the magnetization is not saturated in 5 T. The hysteretic behavior disappears at 35 K. Very weak ferromagnetic property interspersed with paramagnetic phase appears at the temperature near 5 K. This observation is consistent with $\chi^{-1}$ vs $T$ results, where a visible deviation from linear behavior below 25 K is present. The straight line in the inset of Fig. 4 is fitted using the Curie–Weiss law in the temperature range of 25–135 K. The moment of Mn ion was calculated to be 5.3$\mu_B$ per Mn ion. It should be noted that only Mn$^{1+}$ or Mn$^{2+}$ in their high spin states could have these high moments.

The films exhibit high room-temperature resistivity of about $3 \times 10^6$ $\Omega$ cm. The room-temperature resistivity of cuprous oxide films is in the range of $10^2$–$10^7$ $\Omega$ cm \cite{16,17} depending on the preparation condition. The high resistivity of Mn-doped Cu$_2$O shows that deep energy levels are formed due to Mn doping and few Mn$^{3+}$ ions are excited to the Mn$^{2+}$ state.

**IV. CONCLUSIONS**

The single phase, highly oriented \(\text{Mn}_{0.06}\text{Cu}_{0.94}\) \(_2\text{O}\) thin films were successfully grown on TOS and Cu/Si substrates by rf magnetron sputtering. The films show paramagnetic behavior in all temperatures above 5 K. Very weak ferromagnetic signal interspersed with paramagnetic phase is observed at the temperature near 5 K. The valence of Cu and Mn, determined by various techniques, is believed to be mainly +1.

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