Hydrogen-induced ferromagnetism in ZnCoO

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(Received 16 August 2005; accepted 15 December 2005; published online 8 February 2006)

We have investigated experimentally the effects of n-type impurities such as Al and H on the magnetic properties of ZnCoO. The carrier density changes slightly upon the introduction of hydrogen but increases significantly in the case of Al. A measurement of magnetic circular dichroism indicates that, of the two impurities, only H induces ferromagnetism in ZnCoO. Our experimental data suggest that, unlike Al, H plays an important role in the enhancement of ferromagnetic spin-spin interactions that goes much beyond a carrier-mediated effect. © 2006 American Institute of Physics. [DOI: 10.1063/1.2171789]

Since dilute magnetic semiconductors (DMS) were introduced in the early 1980s, their study has attracted much attention among researchers because of their potential utilization in novel electronic devices which rely on both the charge and spin of electrons.

Many theoretical models have been suggested to explain ferromagnetism in DMS and extensive experimental efforts have been directed at improving their magnetic properties.

Recently, the influence of H on the magnetic properties of several DMS was extensively investigated. This was motivated by the fact that in the fabrication of electronic devices or thin films, samples actually are rarely free from H contamination and H impurities are inevitably introduced into thin films. Baik et al. reported that in hydrogenated (Ga,Mn)As, H-plasma exposure produces an increase of 20% in residual magnetization with no evidence for the formation of Mn–H complexes in n-type samples. It is well-known that H is an important unintentional impurity in ZnO, and should also occur in significant concentrations in ZnCoO. Wan et al. and Walle have investigated H storage capacity and H doping in ZnO, respectively. Furthermore, a theoretical study indicates that hydrogenation in ZnO-based DMS can lead to ferromagnetism even if the carrier density is low. Attempts to intentionally increase the H content of ZnO and a few other DMS have already been carried out by several experimental groups.

In this study, we investigate the effects of the n-type dopants H and Al on the magnetic properties of ZnCoO in order to test the influence of extra carriers on the magnetic properties of this material. Hydrogen and Al are well-known donor-type impurities in ZnO. We find that the unintentional H contamination in ZnCoO is quite serious. Our MCD measurements indicate that H induces ferromagnetism in ZnCoO but Al doping does not change the magnetic properties even when the carrier density is significantly increased. We find through x-ray-photoelectron-spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) measurements that H is strongly coupled to Co in hydrogenated ZnCoO.

We fabricated the ZnCoO, artificially hydrogenated ZnCoO:H, and ZnCoO:Al (1.6 mol %) samples using the rf magnetron sputtering process under an argon-hydrogen mixed-gas environment, and compared their properties with those that did not go through the hydrogenation process. All of the samples were grown on a (0006) Al₂O₃ and on a (111) n-Si substrate, in a rf magnetron sputtering system having a base pressure over \(10^{-7}\) Torr. Sputtering was administered in a pure Ar (~99.999%) and O (~99.999%) atmosphere of 5.6 mTorr at 450–500 °C with a rf input of 100 W for the ZnCoO target. The Co concentrations (4–9 mol %) were determined by integrating the Co signals via XPS and the hydrogen concentrations by SIMS. The free electron concentrations in ZnCoO:H and ZnCoO:Al at room temperature were estimated by Hall measurements to be of the order of \(~10^{18}\) cm⁻³ and \(~10^{19}\) or \(10^{20}\) cm⁻³, respectively. The magnetic properties of the samples were studied by MCD and a commercial superconducting quantum interference device (SQUID).

We first measured the magnetic properties of a ZnCoO thin film without the hydrogenation process. Only paramagnetic behavior was observed at all temperatures in the SQUID measurements. By contrast, hydrogenated ZnCoO samples showed a ferromagnetic behavior. In order to verify whether this was related to a secondary phase or whether it was an intrinsic effect, we performed the MCD measurement for the hydrogenated ZnCoO from 13 to 300 K. Figure 1(a) shows the MCD signals of each sample, ZnCo(9.1%)O:H, ZnCo(5.0%)O:H, ZnCo(6.1%)O, and ZnCo(4.1%)O, mea-
FIG. 1. The magnetic properties of pure ZnCoO, ZnCoO:H, and ZnCoO:Al samples. (a) The MCD signals of the ZnCoO:H samples are dependent on the magnetic field. By contrast, pure ZnCoO has no MCD signal at 13 K and 370 nm. The MCD signals without hydrogen treatment are difficult to distinguish compared to hydrogenated sample. (b) ZnCoO as well as ZnCoO:Al samples have small MCD signals and depend on the magnetic field just linearly.

FIG. 2. Spontaneous MCD signals of ZnCoO, ZnCoO:H, and ZnCoO:Al. The spontaneous MCD signal of ZnCoO(5.0%)O:H has larger value than that of ZnCoO(9.1%)O:H, and the samples without hydrogenation (ZnCoO, ZnCoO:Al) do not have any spontaneous MCD values at whole temperature region.

FIG. 3. XPS spectra of Co 2p states. (a), (b) XPS data of ZnCoO(4.1%)O and ZnCoO(6.1%)O show four peaks P2, P3, P5, and P6, respectively. P2 and P5 correspond to Co 2p1/2 and Co 2p3/2, respectively. P1 and P4 reflect the Co metallic state that was detected at (c) ZnCoO(5.0%)O:H and (d) ZnCoO(9.1%)O:H. Hydrogen contamination induces the metallic state and shifts the oxidized cobalt peaks (P2 and P5) as well as increases the FWHM.

The magnetic field dependence for the two samples without hydrogenation, as shown in Figs. 3(a) and 3(b), it seems that H in ZnCoO without hydrogenation, as shown in Figs. 3(a) and 3(b). It seems that H in the value of the spontaneous MCD signal at room temperature was not zero. This means that the curves at room temperature are not linearly proportional to the magnetic field. The samples without hydrogenation (ZnCoO, ZnCoO:Al) showed null MCD values over all measured temperature range. The variation of the spontaneous MCD signals is different from the traditional behavior with temperature from the ferro- to the paramagnetic phase. This behavior, similar to the $M$-$T$ curve of paramagnetic matter, has been reported by a few researchers of ZnO-based DMS. The difference was caused by the different mechanism of magnetic origin in each case, as recently suggested by the results of theoretical calculations.

We found that the H is strongly coupled with the Co in the ZnCoO:H by XPS measurements and measured the change of the chemical bonding states of cobalt when H is added to ZnCoO. Figure 3 compares the Co 2p core-level photoemission spectrum of pure ZnCoO with the spectrum from a hydrogenated sample. The measured spectra could be deconvoluted into six peaks (P1, P2, P3, P4, P5, and P6), as shown in Fig. 3. Peaks P2 and P5 correspond to Co 2p1/2 and Co 2p3/2, respectively, and the position of these primary peaks is similar to that of CoO. The Co 2p3/2 signals of ZnCoO:H shifted to a higher energy level by 0.5–0.8 eV, and the full width at half maximum (FWHM) of these peaks was 1.2–1.4 times broader than that of pure ZnCoO. Generally, the energy of Co–O bonding is 780.1 eV and that of the Co metallic state is 777.3 eV. It is known that when Co binds to hydrogen, the binding energy increases by 1–781.0 eV. Co 2P3/2 (P2) and Co 2P1/2 (P5) correspond to the peaks of oxidized cobalt, and P3 and P6 correspond to the shake-up satellite lines of P2 and P5, respectively. This means that H-doping affected the Co states in the Co–O bonding. The satellite peaks, in the spectrum of all the samples, which are due to the interaction between the core hole and the valence electrons resulting in a change in the potential seen by the valence electrons upon the creation of the core hole, were well defined and this reflects the fact that substituted Co is in the +2 oxidation state. It is expected that Co +2 would incorporate into the wurtzite lattice at the Zn +2 sites. Peaks P1 and P4, corresponding to the Co metallic state, reflect the H-induced reduction in oxidized cobalt and the formation of a Co metallic state. The Co metallic precipitation was not detected in the ZnCoO without hydrogenation, as shown in Figs. 3(a) and 3(b).
hydrogenated ZnCoO forms a Co metallic precipitation due to the reduction of oxygen. Hence, it is expected that Co doped into hydrogenated ZnCoO would incorporate into the wurtzite lattice at the Zn +2 sites as well as into the precipitation as the Co metallic phase. The Co metallic phase obtained from the hydrogenation process could contribute to the ferromagnetism, but the ferromagnetism induced by the metal Co is not detected by MCD.

The concentrations of H for samples without unintentional hydrogenation and those that went through the hydrogen cosputtered process were determined by SIMS measurements. The depth profiles shown in Fig. 4 were taken by a Cameca ims-4f spectrometer, using Cs+ as the primary ions. It is remarkable that the pure ZnCoO had already contained relatively significant amounts of hydrogen impurities in which the hydrogenation could come from the ubiquitous surface hydrocarbon contamination. The concentration of H in the hydrogenated ZnCoO was increased by one order of magnitude. We especially note that the amount of H in the high-Co-concentration sample is much larger than that in the low-Co-concentration one even though in pure ZnCoO the high-Co-concentration sample is much larger than that in the low-Co-concentration one even though in pure ZnCoO the density of H does not depend on the Co-doping concentration, as shown in Fig. 4(a). This means that the capacity for H uptake is affected by the presence of Co ions. Figure 4(b) shows the amount of Co and Co compounds of ZnCo(9.1%)O:H with depth. The results of the SIMS measurements, shown in Fig. 4(b), provide evidence that H is coupled to a Co ion and that (Co+H)x complexes are uniformly distributed within the hydrogenated sample. The consistent experimental results by XPS and SIMS, that the H doping affects the Co state and that H is coupled to Co ions, would support the idea that Co–H bonding affects the ferromagnetic properties of ZnCoO:H.

A proposed mechanism for ferromagnetism in ZnCoO is the carrier-mediated double exchange interaction through conduction carriers. Hydrogen in ZnO has been suggested to be a shallow donor impurity and it was expected therefore that it would provide extra conduction electrons. However, it is remarkable that the carrier density is measured to be little changed by H contamination. The carrier concentration is measured to be only of the order of 10^{18} \text{cm}^{-3} in both ZnCoO and artificially hydrogenated ZnCoO, much below the actual H concentration. On the other hand, when Al is added to ZnCoO, the carrier concentration is significantly increased up to 10^{20} \text{cm}^{-3}. The carrier concentration is 10^3–10^5 times larger as compared to hydrogenated ZnCoO.

However, it is interesting that no ferromagnetic MCD signal was observed in the ZnCoO:Al samples for various Co concentrations in sharp contrast to the case of ZnCoO:H, as shown in Fig. 1(b). The result for ZnCoO:H are in good agreement with the recent theoretical prediction from first-principles calculations showing that H contamination does not necessarily increase the carrier concentration since when H is coupled with a Co dimer, it creates a deep level differently from the shallow level in pure ZnO. The XPS and SIMS data for the ZnCoO:H provide strong evidence for a significant amount of the H–Co coupling. These data indicate that the H can enhance the ferromagnetic spin-spin interaction in the ZnCoO:H.

In summary, we have experimentally investigated the effect of donor-type impurities, hydrogen and Al, on the magnetic properties of ZnCoO. We find that hydrogenation can be serious even in undoped ZnCoO and is enhanced in the Zn_{1−x}Co_{x}O with high alloy ratio x. Through a MCD measurement, the ferromagnetism is significantly enhanced by the H addition to ZnCoO. Therefore, the controversial ferromagnetism could be explained by the hydrogen effect in DMS system as one of possible origins of ferromagnetism.

This work was supported by Grant No. R14-2002-029-01000-0 from the ABRL Program, and partially financially supported by Pusan National University in the program (Post-Doc. 2005) and by the Korea Research Foundation Grant No. (KRF-2004-005-C00044).