Tunable ferromagnetism in Ni$_{0.97-\gamma}$Mn$_3$O thin films with hole doping and their electronic structures

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We report $p$-type Li$_{n}$Ni$_{0.97-\gamma}$Mn$_{0.03}$O thin films (LNMO) via a simple solution method on silicon substrates. Magnetization measurements reveal that room-temperature tunable ferromagnetism can be observed in these LNMO thin films. The Mn $L_{2,3}$ x-ray absorption and core-level photoelectron spectra indicate that Mn consists of the Mn$^{2+}$ and Mn$^{3+}$ components. The O $K$-edge x-ray absorption spectroscopy reveals that the majority of holes introduced by the Li doping have mainly O 2$p$ character, and the hole concentration can be enhanced by almost two orders of magnitude by the Li doping, which can tune magnetism and $T_C$. This ferromagnetic behavior in these LNMO thin films may be ascribed to the effective carrier-induced ferromagnetism ($p$-$d$ exchange interaction through the O 2$p$ band).

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Dilute magnetic semiconductors (DMS) have charge and spin degrees of freedom in a single substance, and attract considerable research due to their high potential for applications in spin-dependent semiconductor electronics. Practical spintronic devices require DMS materials that allow electrons and holes of well-defined and long-lived spin states to be generated, injected into useful structures, and controlled at ambient temperature. Especially, the DMS materials should have high Curie temperatures ($T_C$), high spin polarization of the charge carriers, and compatibility with the semiconductors. Spintronic applications require that ferromagnetism has an intrinsic origin, i.e., not from magnetic transition metal (TM) clusters or impurity phases. Recently, a lot of previous theoretical calculations and experimental work on design and exploration of oxide-based DMS or dilute magnetic insulator (DMI) (e.g., various TM ions doped with ZnO, TiO$_2$, In$_2$O$_3$, SnO$_2$, NiO) has been reported for their wide band gap for applications with short wavelength light, high $T_C$ exceeding room temperature, and good physical and chemical stability. Sato et al. used first-principle calculations to reveal that Mn-doped ZnO changed its magnetic state from the spin-glass state to the ferromagnetic (FM) state as a function of carrier density. Dietl et al. used Zener’s model to predict some high $T_C$ DMS materials such as GaN and ZnO containing 5% of Mn with a high hole concentration, and revealed that ferromagnetism can be driven by exchange interaction between hole charge carriers and localized spins. Spaldin et al. predicted that $p$-type doping in (Zn, Co)O could strongly stabilize the FM state by the density functional theory approach.

Normally, DMS materials consist of nonmagnetic semiconducting materials and impurity magnetic cations. For $p$-type DMS, magnetic coupling interactions can occur via $p$-$d$ or $d$-$d$ exchange and lead to antiferromagnetic or ferromagnetic coupling, which depends on the concentration and the localized spin structural environment of the magnetic impurity. Ferromagnetic behaviors of TM-doped oxide-based films are intimately correlated with the local structural defects, carrier concentrations, electronic structure, coupling between localized magnetization, etc. Although many experimental data and corresponding mechanisms have been proposed for understanding the intrinsic magnetic ordering in these oxide-based DMS, the origin of ferromagnetic behaviors in these oxides has still been matter of strong debate. Compared to the TM-doped ZnO, TiO$_2$, and SnO$_2$ systems, which are $n$-type DMSs, it is more feasible to realize the $p$-type doping in NiO system, which could change to FM from antiferromagnetic (AFM) by doping. Thus, NiO can be a good room-temperature $p$-type DMS. However, the mechanism behind and how to tune FM properties of $p$-type NiO DMS are still unclear. In this work, we report Li and Mn codoped NiO thin films (Li$_{n}$Ni$_{0.97-\gamma}$Mn$_{0.03}$O, $y=0$–0.10, abbreviated as LNMO) via a simple sol-gel spin-coating method on Si substrates. Magnetization measurements reveals that all of these LNMO thin films show room-temperature ferromagnetic properties, which can be effectively tuned by the addition of Li. Our observations demonstrate that NiO-based thin films can be a class of promising $p$-type oxide-based DMSs at room temperature.

Three kinds of LNMO thin films (50–80 nm thickness) with nominal compositions of Ni$_{0.97}$Mn$_{0.03}$O (LNMO-1), Li$_{0.04}$Ni$_{0.04}$Mn$_{0.03}$O (LNMO-2), and Li$_{0.10}$Ni$_{0.07}$Mn$_{0.03}$O (LNMO-3), were prepared on Pt(111)/Ti/SiO$_2$/Si (100) substrates by a sol-gel process and rapid thermal annealing as previously reported. Magnetic measurements were examined using a superconducting quantum interference device (SQUID) and a vibrating-sample magnetometer (VSM) in a temperature range of 300–600 K. X-ray absorption spectroscopy (XAS) measurements were performed at the soft x-ray beam line BL23SU of SPring-8. The monochromator resolution was $E/\Delta E=10,000$. XAS signals were measured by the total electron yield method. X-ray photoemission spectroscopy (XPS) measurements were performed using a
Gammatron Scienta SES-100 hemispherical analyzer and a Mg Kα source (hv = 1253.6 eV) in a vacuum below 1.0 × 10⁻⁷ Pa. All the measurements were done at room temperature in the base pressure below 1.0 × 10⁻⁷ Pa. For surface cleaning, Ar⁺ ion sputtering and annealing under oxygen pressure ∼10⁻⁴ Pa were performed. Cleanness of the surface was checked by the absence of a high binding-energy shoulder in the O 1s XPS core-level spectrum and the C core-level 1s contamination signal.

The resultant LNMO thin films are of the single-phase rock-salt structure determined by x-ray diffraction (XRD) with a θ-2θ scan and high-resolution TEM (not presented here). Figure 1 shows the magnetization-field (M-H) loops of the LNMO thin films at room temperature. The results indicate that the magnetization can be enhanced significantly by Li codoping, and the saturated magnetization (Ms) of the LNMO-3 sample (∼43 emu/cm³) is approximately three times larger than that of LNMO-1 sample without Li doping. The coercivity is ∼128.5, 56.0, and 48.1 Oe for the LNMO-1, -2, and -3 samples, respectively, which indicates that the Li doping concentration can also tune the coercivity. Similar behavior was also observed in the Co-doped ZnO films with the addition of Li.21

Figure 2 shows the temperature dependence of magnetization for various LNMO thin films. For a random distribution of the localized spins, the Curie temperature T_C of DMS deduced from the Zener model can be mainly correlated to the TM concentration, the hole concentration, the effective spin moment, and the exchange energy between the holes and magnetic ions.22 T_C obtained from the mean-field theory has the following form:23

\[ T_C \propto S(S+1)Nm^*p^{1/3}, \]  

(1)

where S is the spin and m* is the effective mass of the hole. N is the Mn concentration and p is the hole concentration. It is effective in the weak exchange coupling between the localized moments and the band carriers when the concentrations of carriers and localized spins are relatively low. As seen from Fig. 2, we can observe that T_C can be enhanced by ∼30 K by 10% Li doping. It should be due to the fact that the Li doping increases the hole concentration in NiO-based films, thus enhancing the T_C value. The inset in Fig. 3 shows a plot of T_C as a function of p^{1/3}; a linear dependence is apparent.

It is generally believed that XAS is a powerful tool for investigating the electronic structure of oxide materials.24,25 In order to find the chemical state of the Mn ions, XAS measurements were performed. Figure 3 shows Mn L$_{2,3}$ XAS spectra of the Li$_x$Ni$_{0.97-y}$Mn$_{0.03}$O thin films. The line shapes of the Mn L$_{2,3}$ spectra are similar among them, but the ratio of the intensity of peaks at hν~642 eV to that at ∼640 eV increases with increasing Li content. The positions of the peaks at hν∼640 and 642 eV correspond to those of MnO (Mn$^{2+}$) and LaMnO$_3$ (Mn$^{3+}$), respectively, as shown in Fig. 3(a). Assuming the spectral changes depending on the Li content are caused by the valence changes of the Mn ions, the spectra can be decomposed by into those of the Mn$^{2+}$ (MnO) and Mn$^{3+}$ (LaMnO$_3$) spectra.26 The analysis for the Ni$_{0.97}$Mn$_{0.03}$O thin film is shown in Fig. 3(b), which indicates that the linear combinations well reproduce the Mn L$_{2,3}$ XAS spectra. The Li-content dependence of Mn valence estimated by the fitting is plotted in Fig. 3(c). Although the Mn$^{3+}$ content is dominant in the Li$_x$Ni$_{0.97-y}$Mn$_{0.03}$O films, the Mn$^{2+}$ and the Mn$^{3+}$ content slightly decreases and increases with increasing Li content, respectively. The result indicates that holes induced by the Li doping may change the Mn$^{2+}$ ions to Mn$^{3+}$. However, the increase of Mn$^{3+}$ content is ∼1/20 of the amount of Li content, suggesting that only small portion of doped holes are trapped at the Mn$^{2+}$ site. It is likely that the majority of holes enter the Ni 3d band and/or are compensated by donor defects such as oxygen vacancies.

In order to reveal the character of the charge compensation states in these LNMO thin films, we measured O K XAS spectra for LNMO thin films. Figure 4 shows the O K-edge XAS spectra for these LNMO thin films. In the O K XAS spectra, the empty O 2p states can be probed directly and the Ni 3d structure can also be seen because of the ground-state hybridization between Ni 3d and O 2p. The peak at 531.2 eV observed in the

FIG. 1. (Color online) Magnetization-field (M-H) loop curves of various Li$_x$Ni$_{0.97-y}$Mn$_{0.03}$O thin films; inset is the expanded part.

FIG. 2. (Color online) Temperature dependence of magnetization for Li$_x$Ni$_{0.97-y}$Mn$_{0.03}$O thin films; inset is a plot of T_C as a function of hole concentration p^{1/3}.
FIG. 3. (Color online) Mn $L_{2,3}$ XAS spectra of Li$_y$Ni$_{0.97-y}$Mn$_{0.03}$O. (a) Li concentration dependence. The dashed lines are a guide for the eye. (b) Fitting result for the Ni$_{0.97}$Mn$_{0.03}$O sample, where the spectrum is assumed to be a superposition of the spectrum of MnO ($\text{Mn}^{2+}$) and that of LaMnO$_3$ ($\text{Mn}^{3+}$).26 (c) $\text{Mn}^{2+}$ and $\text{Mn}^{3+}$ contents plotted as functions of Li content.

Of interest to note, as the Li doping content increases, a new peak near 529.1 eV appears in these LNMO thin films, which can be attributed to transitions from O 1$s$ to holes doped into the top of the O 2$p$ band by Li substitution. Similar spectra behavior has also been observed by Kuiper et al. in a Li-doped NiO system.27,29 As for the sample without Li doping, the final state has no states with lower energy to hybridize. However, as doped with Li, the $d^9L$-like final state can hybridize with the lower-energy states where the Li-induced hole is occupied, and such kind of final-state hybridization can shift the spectral weight to the lower-energy state. Additionally, the 529.1 eV prepeak increases obviously with the Li doping content increase, which implies that the holes introduced by the Li doping should have mainly O 2$p$ character. This was also confirmed by the previous bremsstrahlung isochromat spectroscopy (BIS) and XAS spectra.27,30

As is well known, pure NiO is an antiferromagnetic insulator at room temperature, but its conductivity can be tuned by introducing Ni$^{2+}$ vacancies or doping with Li$^+$.31 Normally, the competition between ferromagnetic and antiferromagnetic interactions in metals will lead to a spin glass but not a ferromagnetic ground state. In the case of semiconductors, the mean distance between the carriers is usually much greater than that between the spins, and thus the exchange interaction mediated by the carriers is ferromagnetic for most of the spin pairs.32 As shown in Fig. 1, obvious room-temperature FM behaviors can be observed and the magnetization of LNMO increases as the Li-doped concentration increases. As previously reported, in Mn-doped oxide-based DMS systems, the possible presence of a secondary phase (e.g., metallic magnetic Mn clusters)
can also be the origin of ferromagnetism. Our XAS results reveal that the secondary Mn metal cluster phase as the origin of ferromagnetism can be ruled out. Therefore, the ferromagnetism in these LNMO thin films is most likely attributed to a carrier-induced mechanism. Hall effects measurement results indicate that the holes are major carriers in these LNMO films and show a $p$-type semiconductor. The carrier concentration in LNMO-3 film ($\sim 1.7 \times 10^{17}$ cm$^{-3}$) can be enhanced by almost two orders of magnitude as compared to LNMO-1 film ($\sim 5.7 \times 10^{15}$ cm$^{-3}$). A ferromagnetic exchange interaction between the magnetic Mn ions and a spin-polarized hole trapped at a Ni vacancy can occur. With increasing the Li doping concentration, more hole carriers will be generated. The increased hole carriers are expected to enhance the exchange coupling between the hole carriers and the Mn 3d spins, thus make FM coupling interaction more effectively, which gives an obvious enhancement of FM properties for these LNMO thin films. Similar phenomena have also been observed in the Li-codoped ZnO: Co and Cu-codoped ZnO: Fe thin films.

In summary, all $p$-type Li and Mn codoped NiO thin films show room-temperature ferromagnetism, and can be tuned by Li doping. Our XAS experimental data reveal that Mn ions are composed of Mn$^{2+}$ and Mn$^{3+}$ ions, and no metallic Mn is observed. The holes compensating the Li doping in LNMO films are located primarily in the O 2p states. These holes have a great influence on the Curie temperature and ferromagnetic properties. The observed ferromagnetism in these LNMO thin films may be originated from carrier-induced ferromagnetism.

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