1-1-2016

Robust ferromagnetism of single crystalline CoxZn1−xO (0.3 ≤ x ≤ 0.45) epitaxial films with high Co concentration

Qiang Cao  
*Shandong University*

Dapeng Zhu  
*Shandong University*

Maxiang Fu  
*Shandong University*

Li Cai  
*Shandong University*

Ping Yang  
*National University of Singapore*

*See next page for additional authors*

Follow this and additional works at: [https://ro.uow.edu.au/aiimpapers](https://ro.uow.edu.au/aiimpapers)

Part of the Engineering Commons, and the Physical Sciences and Mathematics Commons

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
Robust ferromagnetism of single crystalline CoxZn1−xO (0.3 ≤ x ≤ 0.45) epitaxial films with high Co concentration

Abstract
In contrast to conventional dilute magnetic semiconductors with concentrations of magnetic ions of just a few percent, here, we report the fabrication of epitaxial Cox Zn1−xO single crystalline films with Co concentrations from x = 0.3 up to 0.45 by radio-frequency oxygen-plasma-assisted molecular beam epitaxy. The films retain their single crystalline wurtzite structure without any other crystallographic phase from precipitates, based on reflection high energy electron diffraction, X-ray diffraction, transmission electron microscopy, and Raman scattering. The results of X-ray diffraction, optical transmission spectroscopy, and in-situ X-ray photoelectron spectroscopy confirm the incorporation of Co2+ cations into the wurtzite lattice. The films exhibit robust ferromagnetism and the magneto-optical Kerr effect at room temperature. The saturation magnetization reaches 265 emu/cm3 at x = 0.45, which corresponds to the average magnetic moment of 1.5 μB per Co atom.

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

Authors
Qiang Cao, Dapeng Zhu, Maxiang Fu, Li Cai, Ping Yang, Shuang Li, Yinlian Zhu, Xiuliang Ma, Guo-Lei Liu, Yan-Xue Chen, Shi-Shen Yan, Liang-Mo Mei, and Xiaolin Wang

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/2174
Robust ferromagnetism of single crystalline Co$_x$Zn$_{1-x}$O (0.3 ≤ x ≤ 0.45) epitaxial films with high Co concentration

Qiang Cao,1,2,a) Dapeng Zhu,1 Maoxiang Fu,1 Li Cai,1 Ping Yang,3 Shuang Li,4 Yinlian Zhu,4 Xiuliang Ma,4 Guo lei Liu,1,3a) Yanxue Chen,1 Shishen Yan,1 Liangmo Mei,1 and Xiaolin Wang5
1School of Physics and National Laboratory of Crystal Materials, Shandong University, Jinan 250100, China
2School of Physics and Engineering, Qufu Normal University, Qufu 273165, China
3Singapore Synchrotron Light Source, National University of Singapore, 5 Research Link, Singapore 117603, Singapore
4Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
5Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Innovation Campus, North Wollongong, New South Wales 2500, Australia

(Received 27 June 2016; accepted 26 July 2016; published online 4 August 2016)

In contrast to conventional dilute magnetic semiconductors with concentrations of magnetic ions just a few percent, here, we report the fabrication of epitaxial Co$_x$Zn$_{1-x}$O single crystalline films with Co concentrations from x = 0.3 up to 0.45 by radio-frequency oxygen-plasma-assisted molecular beam epitaxy. The films retain their single crystalline wurtzite structure without any other crystallographic phase from precipitates, based on reflection high energy electron diffraction, X-ray diffraction, transmission electron microscopy, and Raman scattering. The results of X-ray diffraction, optical transmission spectroscopy, and in-situ X-ray photoelectron spectroscopy confirm the incorporation of Co$^{2+}$ cations into the wurtzite lattice. The films exhibit robust ferromagnetism and the magneto-optical Kerr effect at room temperature. The saturation magnetization reaches 265 emu/cm$^3$ at x = 0.45, which corresponds to the average magnetic moment of 1.5 $\mu_B$ per Co atom. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4960555]

Ferromagnetic semiconductors have been attracting considerable attention for several decades because they combine two mainstream components of modern information technology, semiconductors for logic and magnetism for memory, within a single material. In particular, a ferromagnetic semiconductor with high Curie temperature ($T_C$) and large magnetization is highly desirable for practical applications of semiconductor spintronic devices that exploit both charge and spin to carry data.1,2 Hence, extensive experimental searches have been performed via magnetic doping of various semiconducting materials, such as Ga$_{1-x}$Mn$_x$As,3 Mn$_x$Ge$_{1-x}$4 Ti$_{1-x}$Co$_x$O$_2$,5 etc. Owing to the very low thermodynamic miscibility (typically ≤10%) of transition metals (TMs) in semiconductors, however, high $T_C$ ferromagnetic semiconductor research to date have been confined to dilute magnetic compounds containing minute amounts of magnetic ions. These are the so-called dilute magnetic semiconductors (DMSs). Despite considerable experimental efforts, the lack of high $T_C$ and/or large magnetization has up to now impeded the application of DMS in practical spintronics devices.6,7

In order to realize high $T_C$ and large magnetization in a semiconductor, the most direct way is to incorporate a higher concentration of magnetic ions by overcoming the obstacle represented by the low solid solubility of TM elements in semiconductors by means of non-equilibrium growth techniques. An extra high concentration (≥30%) of magnetic ions must be introduced into the semiconductor matrix, substitutionally and uniformly. Moreover, the high dopant concentration should persist in the crystal structure of the semiconductor host in order to fit into current electronic techniques. Although a few research activities have been directed towards the development of heavily doping ferromagnetic semiconductors,8–10 the technical realization of single phase semiconductor material with high concentration of magnetic dopants remains a challenge. In this work, we grew single crystalline wurtzite Co$_x$Zn$_{1-x}$O epitaxial films with Co concentrations from x = 0.3 up to 0.45 under conditions far from thermodynamic equilibrium. A systematic study of the structural, optical, and magnetic properties of the films is herein presented. The single crystalline wurtzite structure, robust ferromagnetism, and magneto-optical effect indicate the great potential of the Co$_x$Zn$_{1-x}$O films for practical spintronic devices operable at room temperature (RT).

The Co$_x$Zn$_{1-x}$O epitaxial films were grown on Al$_2$O$_3$ (0001) substrates by radio-frequency oxygen-plasma-assisted molecular beam epitaxy (RF-MBE). Metal fluxes were provided by evaporating high purity elemental solid sources (5N cobalt and 6N zinc). Oxygen flux was supplied in form of active oxygen (5N5) radicals by a radio-frequency plasma source. Before deposition, the Al$_2$O$_3$ substrates were thermally annealed at 800°C for 10 min in the growth chamber with a base pressure of 1 × 10$^{-9}$ mbar. A 40 nm ZnO buffer layer was first grown to relax the lattice mismatch, and then a Co$_x$Zn$_{1-x}$O epilayer 200 nm thick was deposited. During growth, Co$_x$Zn$_{1-x}$O epilayers were grown at the relatively

---

a)Authors to whom correspondence should be addressed. Electronic addresses: qiangcao@126.com and liu-guolei@sdu.edu.cn

0003-6951/2016/109(5)/052404/5/$30.00 109, 052404-1 Published by AIP Publishing.
low temperature of 400 °C, and the partial oxygen pressure was reduced to 10⁻⁷ mbar by using a liquid nitrogen trap. The film growth was monitored in real time by reflection high energy electron diffraction (RHEED). The Co concentration was manipulated by the flux ratio of Co and Zn, and cross-checked by energy dispersive x-ray analysis. The results of quantitative analysis are in good agreement with nominal compositions. The crystal structure of the films was characterized by high resolution XRD (Cu Ka radiation) and transmission electron microscopy (TEM). Non-resonant and resonant Raman measurements were performed to verify the single crystallinity of the films. The evolution of the lattice parameters a/b and c for the CoₓZn₁₋ₓO with various Co concentrations shows a close behaviour to Vegard’s law. As shown in Fig. 1(c), c increases with increasing Co concentration, whereas a/b decreases, indicating that Zn atoms are replaced by Co atoms. Otherwise, if Co atoms are in interstitial sites, both a/b and c will increase. The slight deviation from Vegard’s law for higher Co concentration can be attributed to more lattice defects introduced by increasing Co concentration. The microscale and atomic structures of the films were investigated by TEM. A low-magnification TEM image is shown in Fig. 1(d), and the inset shows a representative cross-sectional high-resolution TEM image. The total thickness of the CoₓZn₁₋ₓO film is about 200 nm. No phase segregation or Co-rich precipitates are found. Overall, the experimental results indicate that the CoₓZn₁₋ₓO films retain the single crystalline wurtzite structure with Co concentration x from 0.3 up to 0.45.

Non-resonant Raman spectra of the CoₓZn₁₋ₓO films with various Co concentrations are shown in Fig. 2(a). Besides the mode of the sapphire substrate at 750 cm⁻¹, three other Raman peaks are observed at 437, 576, and 240 cm⁻¹, respectively. According to the Raman selection rules in the wurtzite crystal structure, the modes at 437 and 576 cm⁻¹ are separately assigned to the E₂ high frequency branch (E₂H) and A₁ longitudinal optical (LO) mode, respectively. Neither of the modes is shifted with increasing Co concentration. An additional mode around 240 cm⁻¹ has also been reported for Mn doped ZnO, manifesting it is not an element sensitive mode. The intensity of this peak increases with Mn concentration and decreases after annealing, which indicates that the mode is probably related to damage or disorder of the crystal lattice induced by doping. The damage to the crystal lattice disrupts the long-range ordering in the ZnO crystal and separates by 60°, which demonstrates that the CoₓZn₁₋ₓO films are single domain epitaxial films without other orientations.

![Figure 1](image_url)  
**FIG. 1.** (a) XRD and corresponding RHEED patterns of the CoₓZn₁₋ₓO films with x = 0.3, 0.4, and 0.45, respectively. (b) (102) ϕ-scans of Co₀.₄Zn₀.₆O and Co₀.₄₅Zn₀.₅₅O films. (c) Experimentally (exp) determined lattice parameters of a/b and c for the CoₓZn₁₋ₓO films with various Co concentrations. The dashed lines are plotted with lattice parameters taken from the reference standards of bulk ZnO and wurtzite CoO. (d) Cross-sectional high-angle annular dark field scanning TEM image of Co₀.₄₅Zn₀.₅₅O film. The inset shows a high-resolution TEM image of the same film.
Co concentration, which is due to radiative absorption by color centers in the Co\(^{2+}\) ions,28–30 \(\text{Zn}_x\text{Co}_{1-x}\text{O}\) films are semitransparent in the visible light region, however, and the transmittance decreases with increasing excitation photon energy. Three characteristic absorptions are observed at 1.86, 2.01, and 2.17 eV, which are indicated by the arrows in Fig. 3(a). They are correlated with the \(d-d\) transitions of Co\(^{3+}\) ions with the \(3d^7\) high-spin configuration in a tetrahedrally coordinated Zn ions.

The oxidation states of Co in the \(\text{Co}_x\text{Zn}_{1-x}\text{O}\) films were characterized by \textit{in-situ} XPS spectra. Co metal clusters near the film surface can be identified if they exist, since they cannot be oxidized to Co\(^{2+}\) without air exposure. As shown in Fig. 3(b), the XPS spectra of the \(\text{Co}_x\text{Zn}_{1-x}\text{O}\) films are in sharp contrast to those of Co metal or Co clusters. Their Co\(^{2+}\) character can be deduced from the presence of a satellite structure 5 eV above the Co 2p\(_{3/2}\) main line.\(^{31}\) The difference in energy between the Co 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks is about 15.5 eV, which also matches that for standard Co\(^{3+}\) ions,\(^{31,32}\) indicating the divalent state of Co, as expected for substituted Co ions at Zn sites.

Figure 4(a) presents the temperature dependent hysteresis loops of the \(\text{Co}_{0.3}\text{Zn}_{0.7}\text{O}\) film. When the films were cooled from 300 K to 5 K, the coercivity was enhanced from 232 Oe to 740 Oe, but the increase in the saturated magnetization \((M_s)\) was very slight from 38 emu/cm\(^3\) at 300 K to 41 emu/cm\(^3\) at 5 K. The long range ferromagnetic order is dominant in our \(\text{Co}_x\text{Zn}_{1-x}\text{O}\) films at RT. Furthermore, the \(\text{Co}_x\text{Zn}_{1-x}\text{O}\) films exhibit stronger magneto-optic properties, as revealed by the MOKE spectra. The hysteresis measured from the MOKE spectra at RT for \(\text{Co}_{0.3}\text{Zn}_{0.7}\text{O}\) film is shown in Fig. 4(b). For comparison, magnetization data measured for the same film using a SQUID are also included. The SQUID and MOKE hysteresis results are in excellent agreement. In addition, obvious magnetic anisotropy with the hard axis perpendicular to the film is.
shown in Fig. 4(c), indicating a continuous magnetic layer rather than a magnetic granular film or magnetic clusters embedded in a ZnO matrix. As shown in Figs. 4(a)–4(c), the $M_s$ and remnant magnetization are both remarkably enhanced with increasing Co concentration. $M_s$ reaches 265 emu/cm$^3$ at $x = 0.45$. Assuming that the magnetic moments purely come from Co atoms, the average magnetic moment is 1.5 $\mu_B$ per Co for the Co$_{0.45}$Zn$_{0.55}$O film at RT. It is worth to mention that there is no deterioration of magnetic moment with time at least for one year, indicating a stable ferromagnetism for our films. Moreover, the resistivity of Co$_x$Zn$_{1-x}$O films increases with decreasing temperature from RT down to 5 K, showing a clear semiconducting, rather than metallic character.

In summary, we have grown single crystalline Co$_x$Zn$_{1-x}$O epitaxial films with high Co concentration by RF-MBE. The films retain their single crystalline wurtzite structure with Co concentrations from $x = 0.3$ up to 0.45. No phase segregation or Co-rich precipitates are found. The films exhibit robust ferromagnetism and the magneto-optical Kerr effect at RT. The saturation magnetization reaches 265 emu/cm$^3$ at $x = 0.45$, which corresponds to an average magnetic moment of 1.5 $\mu_B$ per Co atom. As an alternative to conventional diluted magnetic semiconductor, the approach of growing single crystalline semiconductor films with a high concentration of magnetic atoms opens up a dimension in the search for ferromagnetic semiconductors that work at RT.

This work was supported by the State Key Project of Fundamental Research of China under Grant Nos. 2013CB92303 and 2015CB921400, the NSFC for Distinguished Young Scholar No. 51125004, the NSF Grant Nos. 11374189 and 51231007, 111 project B13029. P.Y. was supported by the SSLS via NUS Core Support C-380-003-001.

References