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Investigation at the atomic scale of the Co spatial distribution in Zn(Co)O magnetic semiconductor oxide

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A sputtered Zn_{0.95}Co_{0.05}O layer was chemically analyzed at the atomic scale in order to provide an accurate image of the distribution of Co atoms in the ZnO matrix. The investigation of the magnetic properties shows that the as-deposited Zn_{0.95}Co_{0.05}O is ferromagnetic at room temperature. Atom probe tomography reveals a homogeneous distribution of all chemical species in the layer and the absence of any Co clustering. This result proves that the ferromagnetic properties of this magnetic semiconductor cannot be attributed to a secondary phase or to metallic Co precipitates within the layer. © 2009 American Institute of Physics. [DOI: 10.1063/1.3152579]

In the field of spintronics, diluted magnetic semiconductors (DMSs) and diluted magnetic oxides (DMOs) have attracted much interest in recent years. These materials, consisting of semiconductor (i.e., GaAs) or oxide (i.e., ZnO and TiO₂) alloys, in which the cation is randomly substituted by a transition metal (Fe, Co, and Mn), present both semiconducting properties required by classic microelectronics and a spin polarization of the carriers in conjunction with macroscopic ferromagnetic properties.^{1,2} The combination of these properties makes it possible to manipulate both the spin and charge of the electron in a single substance, leading to a new class of electronic devices such as spin transistors, ultradense nonvolatile memories and optical emitters with polarized output.^{3,4}

The first scientific publications on DMS focused on Mn doped III-V compounds such as Ga(Mn)As,⁵ which are *p*-type semiconductors and exhibit ferromagnetism. However, practical applications require room-temperature ferromagnetism so that the low Curie temperature ($T_c \approx 130$ K) of Ga(Mn)As alloys has hindered interest in this system.⁶ In 2000, Dietl *et al.*⁷ theoretically predicted the existence of DMS and DMO with a T_c higher than room temperature. Among them a particular attention was given to the oxide ZnO doped with transition metals.⁸ This oxide is a low-cost, wide-band gap ($E_g = 3.37$ eV) semiconductor that is the focus of present research toward applications such as UV light emitters, transparent high-power electronics, windows materials for display and solar cells. In 2001, Ueda *et al.*⁹ reported the first observation of stable ferromagnetic properties of Co-doped ZnO. Since this observation, extensive research has been performed on this material, a large amount of experimental data has been accumulated and a corresponding mechanism to explain the observed magnetism has been proposed. However, the origin of the ferromagnetic behavior remains a matter of debate to this day. Most results on poly-

crystalline powders show no ferromagnetism.^{10,11} Some reports attribute the ferromagnetic properties to the dilute phase,^{12,13} while other reports suggest that ferromagnetism originates from the formation of cobalt clusters.⁸

In this controversial context, highly sensitive characterization techniques are required to elucidate the origin of this experimentally observed ferromagnetism. In addition to conventional techniques such as x-ray diffraction (XRD) or high resolution electron microscopy, many methods have been used to identify the local structure of doping elements such as electron energy loss spectroscopy, x-ray photoelectron spectroscopy,¹⁴ x-ray absorption spectroscopy,¹⁵ and x-ray magnetic circular dichroism (XMCD). Zheng *et al.*¹⁶ suggested using the tomographic atom probe (TAP) to accurately detect secondary phases and very small Co clusters. This paper presents the first three-dimensional (3D) spatial distribution of Co atoms in a ZnO matrix obtained by laser assisted wide angle TAP (LAWATAP). A detailed description of this technique may be found elsewhere.¹⁷

For this study, a Zn_{0.95}Co_{0.05}O thin film was deposited by reactive magnetron cosputtering using pure Zn and Co targets on a prepatterned substrate consisting of an assembly of flat-topped Si (100) pillars ($10 \times 10 \times 100 \mu\text{m}^3$). The base pressure was below 10^{-7} Torr and the working pressure was a mixture of argon at 5×10^{-3} Torr and oxygen at 1.5×10^{-3} Torr. The composition of the film was controlled by adjusting the sputtering power applied to the Co target and by maintaining the power to 75 W for the Zn target. First, a weak etching with the Ar plasma was performed for 2 min with a 200 W power. During the deposition, the substrate was kept at a constant temperature of 600 °C. The thickness was fixed at 100 nm.

The structural characterization was first performed by means of XRD using a monochromatic ($\lambda_{\text{Co } K\alpha_1} = 0.17889$ nm) Brüker diffractometer through θ - 2θ scans and rocking curves. The magnetic properties were investigated using alternating-gradient-field (AGFM) and superconducting quantum interference device (SQUID) magnetome-

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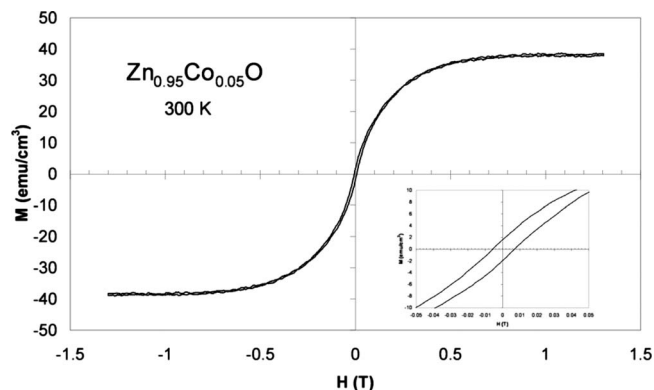


FIG. 1. Magnetization loop of the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film recorded at 300 K by AGFM. The inset shows a zoom between -0.05 and $+0.05$ T.

ters. To perform the atom probe analyses, the silicon pillars were removed from the wafer, mounted on a stainless steel fine tip needle with conductive epoxy glue, and finally shaped into tips using a focused Ga ion beam (30 kV).¹⁸ To reduce Ga implantation and thus avoid damages in the region of interest, the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film was capped with 500 nm of Cr and the final milling was performed at low acceleration voltage (2 kV). Prepared tips were analyzed by LAWATAP at 80 K in an ultrahigh vacuum chamber at a pressure of 10^{-8} Pa. The femtosecond laser pulse system used was an amplified ytterbium-doped laser (AMPLITUDE SYSTEM s-pulse) with a pulse length of 350 fs. Two different wavelengths were tested for the analyses: $\lambda \approx 515$ nm and $\lambda \approx 342$ nm.

The XRD structural characterization shows that the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film exhibits the hexagonal ZnO wurtzite structure with a c -axis perpendicular to the film plane (data not shown here). No peak corresponding to secondary phases or Co clusters is observed. The magnetization loop of the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film recorded at 300 K by AGFM is presented in Fig. 1. The inset shows a zoom between -0.05 and $+0.05$ T. A clear hysteresis loop is observed with a coercive field of 65 Oe and a saturation magnetization (M_S) of 40 emu/cm^3 . This result indicates that our sample exhibits a bulk ferromagnetic behavior at 300 K. Zero-field-cooled and field-cooled (ZFC/FC) magnetization versus temperature curves were also recorded by SQUID magnetometry. No superparamagnetic relaxation is evidenced, suggesting the absence of very small Co clusters.

Figure 2 presents the mass spectrum obtained after atom probe analyses at the 342 nm wavelength of the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film. We note that the mass resolution is better than that obtained using the 515 nm wavelength and enables a higher accuracy of the atomic composition measurements. The peaks corresponding to Zn^{2+} , Zn^+ , O_2^{2+} , and O_2^+ ions are clearly observed and the cobalt ions (Co^{2+} and Co^+) are well detected. Several peaks corresponding to molecular ions such as $(\text{Zn}_2\text{O})^+$, $(\text{Zn}_2\text{O})^{2+}$, $(\text{ZnO})^+$, and $(\text{ZnO})^{2+}$ are also observed. This may be correlated with the wurtzite structure and to the strong covalent bonds of oxygen and zinc atoms. The relative atomic compositions for Zn and Co determined from the mass spectrum are $96.7\% \pm 0.1\%$ and $3.3\% \pm 0.1\%$, respectively.

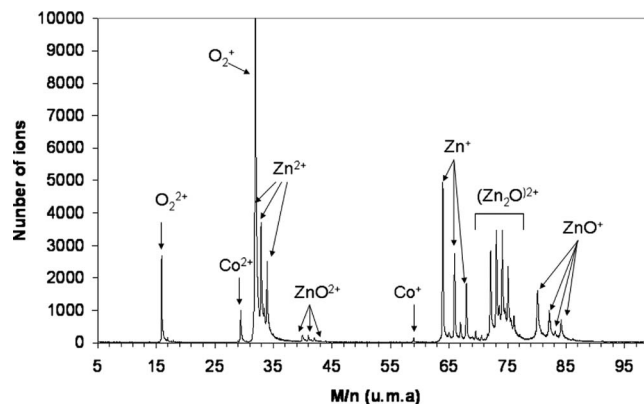


FIG. 2. Mass spectrum of the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film obtained by LAWATAP analyses ($\lambda \approx 342$ nm).

The 3D spatial distributions of Zn, O, and Co atoms in the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film are presented in Fig. 3. Experiments were reproducible and all lead to the same result. Co atoms are distributed homogeneously in the ZnO matrix and absolutely no Co clusters are observed. All detected species show a homogeneous distribution that is synonymous with the absence of secondary phases.

Some prior reports have suggested the presence of very small metallic clusters next to the substrate. Indeed a higher cluster density next to the substrate was observed by Shinde *et al.*¹⁹ in Co-doped TiO_2 . In order to ensure the absence of

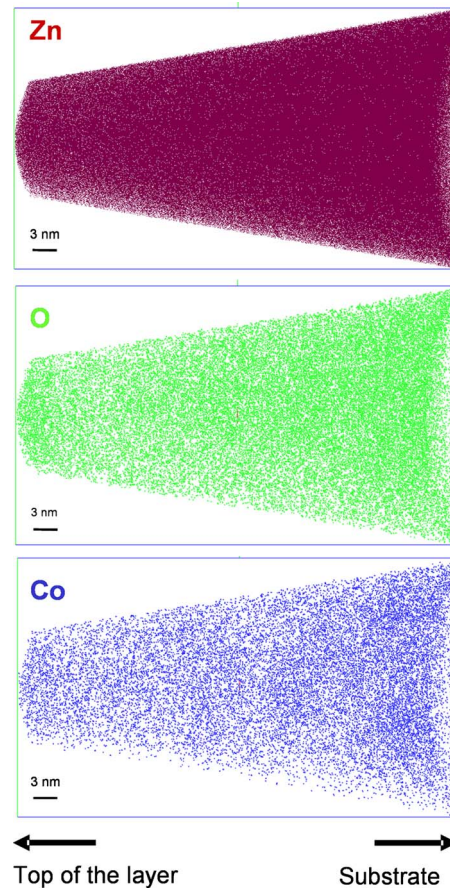


FIG. 3. (Color online) 3D spatial distributions of Co, O, and Zn atoms in the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film obtained by LAWATAP analyses.

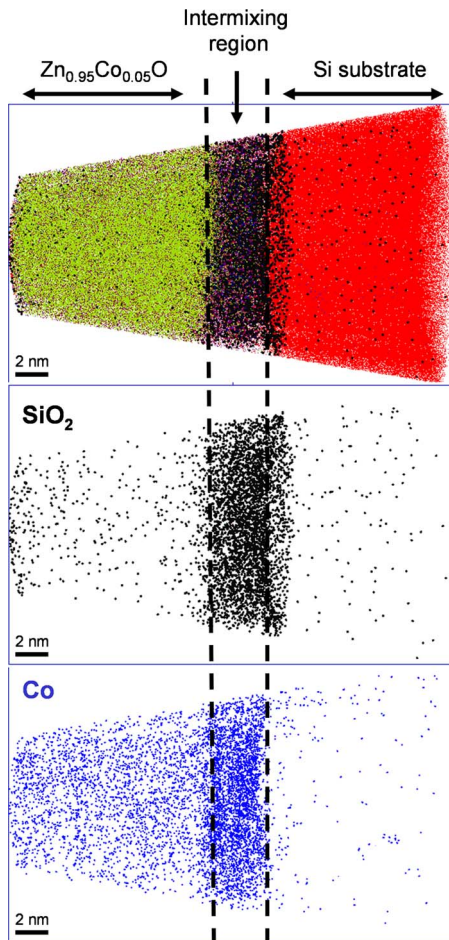


FIG. 4. (Color online) 3D spatial distributions of Co, Zn, O, Si, and SiO_2 species at the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}/\text{Si}$ interface obtained by LAWATAP analyses (Zn and O: same color as in Fig. 3, Si in red).

Co clusters in the whole $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film, the interface between the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film and the Si substrate was also analyzed in this study. The result is shown in Fig. 4. The right side of Fig. 4 corresponds to the Si atoms from the substrate, and the left side to the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ layer. Here again, a clear homogeneous distribution of Co atoms is observed. However, the interface between the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film and the Si substrate reveals a region where a strong chemical intermixing occurs. This region is composed of a mixture of SiO_2 , Zn, and Co atoms. A Co enrichment next to the substrate is also clearly observed in the Co mapping presented in Fig. 4. However, the formation of Co clusters in this Co-enriched region is not observed. This leads to the formation of a thin layer with the following compositions: 3% Co, 49.5% O, 40% Zn, and 7.6% Si. We note that such a concentration of Co atoms in this intermixed region is too small to stabilize long-range-order ferromagnetism. This is supported by recent XMCD results, obtained by Barla *et al.*²⁰ on Co-doped ZnO thin films prepared in the same conditions, that clearly show that diluted Co^{2+} ions in the ZnO matrix are paramagnetic despite the ferromagnetic signal that was observed at room temperature by macroscopic SQUID mag-

netometry. Since the ferromagnetic properties of the sample presented here can be attributed neither to the presence of secondary phases, to ionic Co nor to Co clusters, our results provide good experimental support for the model of defect-induced ferromagnetism recently proposed by Coey *et al.*²¹

In conclusion, we have applied the atom probe technique with atomic-scale resolution on sputter-grown Co-doped ZnO thin films to provide two clear answers regarding the present debate on the origin of the ferromagnetism in these DMSs. First, the distribution of Co atoms is homogeneous within the ZnO matrix, thereby clearly ruling out the presence of metallic Co clusters. Second, there is no experimental evidence of the presence of any secondary phases. In addition, a strong atomic intermixing is observed at the interface between the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ thin film and the Si substrate, which is almost certainly not ferromagnetic despite a slight Co enrichment.

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