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Crystalline effect on ferromagnetism and magneto-transport of epitaxial semiconducting Co:ZnO films

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ABSTRACT

We have studied the magnetic origin and the effect of crystallinity of epitaxial semiconducting Co:ZnO films on ferromagnetism and magneto-transport properties by comparing signal-type domain (SD) and twin-type domain (TD) structure films grown in the same conditions. A higher saturation magnetization in TD films than that in SD films is observed, suggesting that bound charge carriers, produced mainly by defects in films, play a dominant role in ferromagnetism. A lower concentration of itinerant carriers in TD films than that in SD films is detected, which helps separate the effects of bound and itinerant carriers on ferromagnetism and magneto-transport. We hypothesize the interaction of the spin moments of itinerant carrier with the bound carrier mediated ferromagnetic domain results in the weaker strength of the anomalous Hall effect in TD films than that in SD films. It is likely that both itinerant and bound carriers are important for spintronic application in diluted magnetic oxides and could be modified by control of crystal structure.

1. Introduction

The claim to have made nonmagnetic oxides such as TiO_2 or ZnO that are ferromagnetic at room temperature (RT) is one of the most surprising and controversial claims of the 21st century [1]. To realize spintronics devices based on these ferromagnetic oxides, the spin-related transport property, in addition to the ferromagnetism, is also a key factor to be developed. Although d^0 ferromagnetism has also been observed in undoped and/or non-magnetic ion doped ZnO system, however, the lack of spin polarized carriers in these systems will limit the potential in spintronics applications [2].

The expectation that doping magnetic elements into these oxides would have important applications in semiconductor spintronics has motivated considerable research in recent years.

Unfortunately, a transition metal-doped oxide is not necessarily a dilute magnetic oxide (DMO), as originally expected. In various cases, the observed ferromagnetism in DMOs is attributable to uncontrolled magnetic clusters or secondary phases [3]. The rigorous structural measurements [4,5], the anomalous Hall effect (AHE) [6–8], and magnetic circular dichroism (MCD) [9–11] characterizations have indicated the absence of magnetic clusters and secondary phases in carefully grown DMOs, supporting intrinsic ferromagnetism. A key issue is the connection between the ferromagnetism and the magneto-transport properties in DMOs.

Ferromagnetism in Mn-doped III–V semiconductors has been identified as itinerant carrier-mediated [12]. The III–V diluted magnetic semiconductor (DMS) carriers are highly spin-polarized and have been used to realize semiconductor spintronics devices at temperatures that are far below RT. However, the physical origin of the RT ferromagnetism of DMOs is presently unclear. In some cases, the observation of very low electrical conductivity along with a considerable magnetic saturation moment indicates that delocalized free carriers are not easily accessible in DMOs [13,14]. The difference between the electric field effects of the magnetism in III–V DMSs and DMOs show that their ferromagnetism has two fundamentally different origins [15–17]. Physical models of the insulation of the magnetic state of DMOs are thus important.

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These involve the percolative bound magnetic polaron (BMP), discussed in the context of strongly insulating disordered DMO materials [18], defect state percolation [19], and combined percolative BMPs at lower temperatures and itinerant carrier-mediated ferromagnetism at elevated temperatures [20]. For example, Behan et al. demonstrated two distinct mechanisms that can give rise to ferromagnetism in (Co, Al) doped ZnO:BMP in the insulator region and carrier-mediated exchange in the metallic state. However, MCD and AHE were only observed in the metallic (degenerate) state. Accordingly, they concluded that when ZnO is doped into the metallic regime, it can behave as a genuine DMO [21]. The material-related challenge is still serious because both magnetic doping and electronic doping are required [22]. We have also carried out detailed studies about the origins in Co (magnetic doping) and Ga (electronic doping) doped ZnO single crystalline films [23]. There are two distinct ferromagnetic mechanisms in different conducting regimes. In the insulator regime, carriers are localized and prefer the formation of BMPs. In the metallic regime, free carriers mediated exchange interaction is dominant.

In the Mn:GaAs system, the magnetic and electronic dopings have the same origin: the ferromagnetic alignment of these spins is established by the spin polarization of free carriers and their interaction. Since the spin coherence depends strongly on the crystalline qualities associated with the spin-polarized current, epitaxial films are more desirable for forming III–V DMSs. Xu et al. demonstrated spin polarized in Co-doped ZnO based magnetic tunnel junctions. However, the roles of bound and free carriers on spin-transport are unclear in semiconducting regime for DMOs. [24] Therefore, distinguishing the effects of bound and itinerant carriers on ferromagnetism and the magneto-transport in DMOs is important in fundamental studies and application for spintronics devices.

The investigation examines the correlation of bound and itinerant carriers with the magnetic and magneto-transport properties using two different types of epitaxial semiconducting Co:ZnO films prepared on distinct substrates side by side in a single batch. We obtain single type domain (SD) structure and twin-type domain (TD) structure, the latter is textured with two rotational domains (rotated by 30°). The TD Co:ZnO films contain a higher defect density and show a larger saturation magnetization (M_s) than the SD ones. However, the itinerant carrier concentrations (n_i) of the TD films are lower than those of the SD films. The results reveal that the bound carriers that are produced by structural defects play a dominant role in the observed ferromagnetism. However, an examination of a slightly stronger AHE in the SD samples than in the TD samples shows that itinerant carriers of the TD samples are less polarized by the ferromagnetic domains than those of the SD samples. That is, both bound and free carriers are important for spin transport in semiconducting Co:ZnO films.

2. Experimental details

The samples in this work are grown in a molecular beam epitaxy system with a base pressure of 6.66×10^{-7} Pa. The SD and TD Co(5%):ZnO thin films with a thickness of 500 Å were prepared on Al_2O_3 (11-20) and Al_2O_3 (0001) substrates at 350 °C using the multilayer δ-doping technique. Multilayer δ-doping technique has been demonstrated as a useful method by theoretical calculation and experiment for enabling superior dopant control in magnetic semiconductors [25,26]. The δ-doping technique is established as an effective subsurfactant epitaxy method. For Co doping in ZnO, it is possible that the formation energy for the substitutional sites at the ZnO surface is lower than in the bulk. When the Co impurities deposit on ZnO surface, most of the Co react with the surface and replace Zn.

Pure (99.995%) ZnO and Co in a ratio of 20:1 were evaporated from two independent e-beam sources, with typical growth pressure below 6.66×10^{-7} Pa and film deposition rate of about 0.1 Å/s. The film structure and crystalline quality were determined by in situ high-energy electron diffraction. X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) were respectively carried out at the BL17B and wiggler C beamline of the Taiwan Light Source (TLS) in Hsinchu, Taiwan. The XAS at the Co and Zn *K*-edge was obtained to determine the valence state and local geometry of Co and Zn in ZnO lattice. Magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) in the temperature range of 5–350 K. Moreover, these films are photo patterned into Hall bars by photolithography with a channel 7000 μm long and 500 μm wide for AHE measurements at room temperature. The magnetic field was applied normal to the film plane by using a bipolar magnet providing a maximum field of 1 T.

3. Results and discussion

High-quality SD and TD (0002)-oriented Co:ZnO films were synthesized on Al_2O_3 (11-20) and Al_2O_3 (0001) substrates, respectively, under the same deposition conditions in a single batch. For example, the θ-2θ XRD scans of SD and TD Co:ZnO films show (0002) and (0004) diffraction peaks that correspond to the wurtzite structure of zinc oxide, as displayed in Fig. 1(a)–(b). The insets of Fig. 1(a) and (b) present the rocking curves of the SD and TD Co:ZnO films with full widths at half maxima of 0.215° and 0.334°, respectively. The average out of plane grain size of the SD and TD films estimated through the full width at half maximum of the (0002) diffraction peak is 41 nm and 26 nm, respectively. Fig. 1(c) and (d) shows the results of the in-plane azimuthal scans of SD and TD Co:ZnO films, indicating a six-fold and twelve-fold in-plane symmetry, respectively. Notably, the 12 reflection peaks in the TD Co:ZnO films [Fig. 1(d)] can be classified as a high intensity set and a low intensity set, each with a six-fold symmetry and separated by 30° from each other, suggesting the formation of twin domains in the TD Co:ZnO films. The XRD structural analyses demonstrate that the SD films exhibit a better crystalline quality and larger grains than the TD films. Clearly, the TD films have more domains and grain boundaries than the SD films. Neither the SD nor TD sample yields a secondary phase peaks in XRD. Since XRD results only indicate the volume-averaged difference in crystal quality, microstructure and local environments of SD and TD samples were also examined.

The average valence state and local structure of Co in the SD and TD Co:ZnO samples were studied by XAS. Because of the high sensitivity, X-ray absorption near-edge structure (XANES) is useful for determining the presence of TM metal clusters in host oxides. Fig. 2(a) shows the Co *K*-edge XANES spectra of the SD samples, TD samples and standard Co metal foil (Co^0) for comparison. In contrast with the marked shoulder around 7712 eV for the Co metal, the Co *K*-edge spectra of both SD and TD samples have a weak pre-edge peak. The pre-edge feature is a characteristic for some TM ion with partially filled 3*d* orbital due to 1*s*-3*d* transitions. The energy position and the shape of the pre-edge reflect the electronic structure and local environment of a specific element such as Co. In our case, the pre-edge peaks around 7709 eV are characteristic of Co^{2+} in tetrahedral coordination of oxygen atoms, indicating the Co^{2+} substitution for Zn^{2+} in ZnO [13]. An extended X-ray absorption fine structure (EXAFS) is also adopted to clarify the local structures around the Co atoms. Fig. 2(b) presents the radial distribution function (RDF), the Fourier-transformed amplitude of EXAFS, at the Co *K*-edge of the SD and TD samples. Notably, the RDFs at the Co *K*-edge of both samples are very similar to those of the Zn *K*-edge spectra especially in the first and second peaks, revealing that Co ions have similar local structures to those of Zn ions in ZnO. The minor peaks above the primary peaks are related to more outer shells of atoms. Notably, the variation of the minor peaks is related to the experimental resolution of EXAFS measurement due to the weak signal of the dilute doped Co(5%):ZnO films(500 Å). The quantitative local structural information is simulated (solid curves) using the ZnO model using the finite element fast Fourier (FEFF) program [27], which matches the experimental data with best fit [28]. The results suggest that most of the Co substitutes for Zn in both samples without detectable metallic Co or any secondary phase.