Studies of two- and three-dimensional ZnO:Co structures through different synthetic routes

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Multilayers of Co and ZnO, with nominal layer thicknesses on the atomic scale with up to 25 bilayers, were deposited by ion beam sputtering on silicon and glass substrates at ambient temperature. Thick epitaxial $Co_xZn_{1-x}O$ films on $Al_2O_3(012)$ substrates were grown by metalorganic chemical vapor deposition using a liquid precursor delivery system. All were co-doped with Al. Comparative analysis of magnetization, resistivity, and magnetoresistance measurements, performed in the temperature range 2.5–300 K, is presented. At small thickness of Co layers in the multilayer samples, these structures are diluted magnetic semiconductor (DMS) superlattices, with properties close to the epitaxial films. A crossover from DMS to discontinuous magnetic metal/semiconductor multilayers is observed with increasing metal content in the multilayers. This leads to changes in conduction mechanisms, with increasing contribution of quasithree-dimensional or quasitwo-dimensional intergranular hopping, and superparamagnetism. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1669224]

Room temperature ferromagnetism has been recently demonstrated in transition metal-doped, wide band gap diluted magnetic semiconductor (DMS) films based on TiO_2,[1–3] ZnO,[4–8] GaN,[9,10] AlN,[11–13] and SnO_2[14] using a variety of deposition techniques. Theoretical work has predicted hole-mediated room temperature ferromagnetism in ZnO doped either with Mn[15] or Co.[16] A ferromagnetic state has been confirmed experimentally in both materials. ZnO-based materials have been prepared previously via pulsed laser deposition[4,8] and rf sputtering[5] from oxide targets. Recently we have reported the preparation of Al-co-doped ZnO:Co by both multilayer ion beam sputtering (IBS) deposition on Si and glass substrates,[6] and plasma-enhanced metalorganic chemical vapor deposition (MOCVD) of epitaxial films of Al-doped $Co_xZn_{1-x}O(110)$ on $Al_2O_3(012)$ using a liquid precursor delivery system.[7] The IBS-grown multilayers are weakly ferromagnetic above room temperature at small ratios of Co/ZnO nominal thicknesses in the 25-bilayer stack, but turn superparamagnetic with increasing relative Co content. The MOCVD-grown thick single crystal films also show weak ferromagnetism with a Curie temperature of at least 350 K. In this work we present a comparative analysis of the properties of the materials with a variety of morphologies and differing dimensionalities. It appears that magnetic properties in the ferromagnetic state are weakly dependent on the method of preparation. Even though ferromagnetism in these systems is carrier mediated, it cannot be enhanced beyond certain limits simply by increasing conductivity. Our measurements of magnetotransport have not revealed clearly anomalous (spin-dependent) effects, except for the granular samples.

Superlattices of Co/ZnO doped with Al, with varying nominal thickness of metal (2–10 Å) and semiconductor (2–20 Å), were prepared by IBS at ambient temperature and Ar pressure of 1.1×10^{-4} Torr.[6] X-ray diffraction (XRD) patterns are shown in Fig. 1(a) for two samples 1 and 6, with the nominal compositions $(ZnO_{20Å}Co_{2Å})_{25}$ and $(ZnO_{20Å}Co_{10Å})_{15}$ respectively. XRD for sample 1 shows only nanocrystalline ZnO peaks, while diffuse peaks of metallic Co appear in sample 6. Three MOCVD-grown samples [thicknesses 430 nm (A), 280 nm (B), 330 nm (C); Co substitution of Zn~10%] were vacuum annealed to achieve variable conductivities due to oxygen vacancies. Sample A

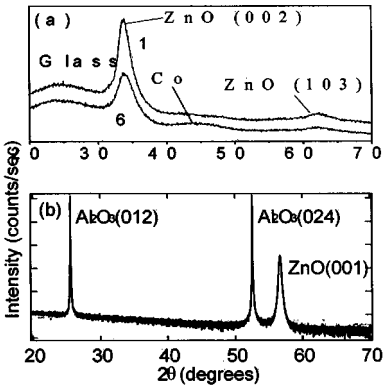

FIG. 1. X-ray diffraction pattern on: (a) IBS multilayer samples (1) $(ZnO_{20Å}Co_{2Å})_{25}$ and (6) $(ZnO_{20Å}Co_{10Å})_{15}$, and (b) MOCVD film.

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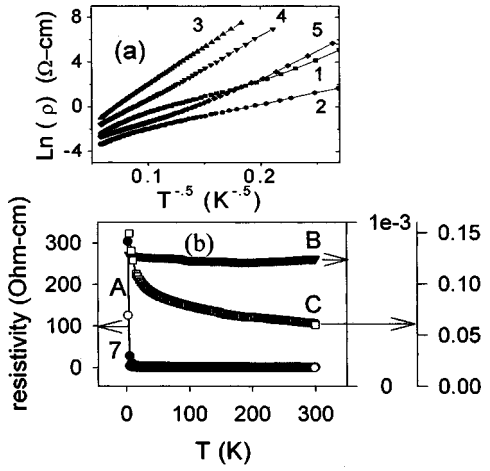

FIG. 2. (a) Fits to the VRH relation for resistivity of multilayer IBS samples 1–5 and (b) resistivity vs temperature in bulk MOCVD samples A, B, C, and a standard ZnO sample 7.

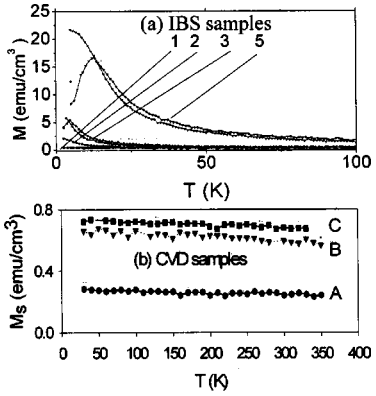

FIG. 3. (a) Zero field cooled and field cooled magnetization measurements at $H=20$ Oe for IBS samples with varying nominal thickness of ZnO layers x and Co layers y $(\mathrm{ZnO}_{x\text{Å}}\mathrm{Co}_{y\text{Å}})_n$ and (b) spontaneous magnetization for MOCVD samples A–C.

was almost insulating, B metallic, and C of intermediate conductivity (see below). A typical XRD pattern for an epitaxial sample on sapphire is shown in Fig. 1(b). These samples show good crystallinity and epitaxial quality (see Ref. 7 for more structural characterization details). Concentrations of elements in all samples discussed in this work were verified by Rutherford backscattering.

Magnetic, transport, and magnetotransport measurements were carried out over a temperature range of 2.5–300 K on a Quantum Design MPMS-5 system. Magnetization was measured with the Reciprocating Sample Option (RSO) option, and contacts for transport measurements were made by pressed indium. Based on the theory of Ref. 15, one would expect a correlation between conductivity and ferromagnetism, so we studied conduction mechanisms in detail. Figure 2(b) shows temperature dependences of resistivity for samples of MOCVD series A, B, and C. For comparison the data for a standard ZnO film without Co doping (made by IBS) are shown. Sample A has high resistivity, increasing dramatically with decreasing temperature. At low temperatures the dependence is activational $\ln\rho(T_0/T)^n+\text{constant}$, with $n=1$ and the activation energy $k_BT_0\sim 1$ meV. We notice that this behavior is close to that of the undoped standard sample 7 made by IBS. Sample B is metallic with an almost temperature-independent resistivity of less than 1 $\mathrm{m}\Omega\,\mathrm{cm}$, while sample C is intermediate with resistivity $\sim 0.1\ \Omega$ cm. Resistivities of the multilayered samples: (1) $(\mathrm{ZnO}_{20\text{Å}}\mathrm{Co}_{2\text{Å}})_{25}$, (2) $(\mathrm{ZnO}_{20\text{Å}}\mathrm{Co}_{4\text{Å}})_{20}$, (3) $(\mathrm{ZnO}_{10\text{Å}}\mathrm{Co}_{4\text{Å}})_{20}$, (4) $(\mathrm{ZnO}_{5\text{Å}}\mathrm{Co}_{4\text{Å}})_{20}$, and (5) $(\mathrm{ZnO}_{2\text{Å}}\mathrm{Co}_{4\text{Å}})_{20}$ are shown on a logarithmic scale as a function of $1/T^{1/2}$, to underline that the dependence $\ln\rho\sim(T_0/T)^n+\text{constant}$ holds for some of these samples, with n varying close to 1/2. This shows that they can be described by the variable range hopping (VRH) conduction mechanism.[17–19] However, the behavior of samples 1 and 2, with the nominally thinnest Co layers and the thickest ZnO layers, does not follow the VRH law with a single exponent. Rather, it is qualitatively similar to the behavior of the undoped sample 7 and the most resistive MOCVD sample A, though with a higher rate of low-T resistivity divergence than in A and 7. In the IBS films, conduction undergoes a crossover from the semiconductor type to one that is determined by hopping between metallic granules, as more such granules nucleate at increasing relative amounts of Co. The actual best fit exponent n for granular multilayer samples increases with increasing nominal thickness ratio $t_{\mathrm{Co}}/t_{\mathrm{ZnO}}$, from ~ 0.4 in (3) $(\mathrm{ZnO}_{10\text{Å}}\mathrm{Co}_{4\text{Å}})_{20}$, to ~ 0.7 in (5) $(\mathrm{ZnO}_{2\text{Å}}\mathrm{Co}_{4\text{Å}})_{20}$. The value of n close to 0.4 is often observed in three-dimensional cosputtered metal–insulator films.[17] The increase of n with decreasing ZnO layer thickness is consistent with the VRH theory[18] and reflects the decreasing dimensionality of the system. Hopping conduction becomes quasitwo-dimensional when the ZnO thickness is reduced and the Co granules appear to arrange effectively in one plane.

Figures 3(a) and 3(b) show the temperature dependencies of magnetization for the two sets of samples. For multilayered IBS samples we plot both zero-field-cooled and field-cooled magnetization measured in a field of 20 Oe [Fig. 3(a)]. Sample 1 (the smallest ratio of Co to ZnO thickness) is ferromagnetic and has a constant magnetization up to room temperature, while sample 2 with greater relative Co is paramagnetic. Other samples with increasing relative Co concentration, which are granular multilayers, show superparamagnetism and magnetic blocking. We notice a considerable increase of the blocking temperature with decreasing distance between magnetic layers. We assume that it is due not only to an increase in the Co particle size, but also reflects the effect of increasing dipole–dipole interactions as the magnetic particles get closer.[20] In the bulk MOCVD samples Co^{2+} ions substitute for Zn sites and do not form granules.[7] For these samples we plot spontaneous magnetization as a function of temperature in Fig. 3(b), which remains nearly constant up to and above room temperature. Considerable difference in saturation magnetization is observed between samples A (dielectric) and C (intermediate). However further increase of conductivity does not have a positive effect on spontaneous magnetization. The largest coercive fields among ferromagnetic samples, both at 10 and at 300 K, were

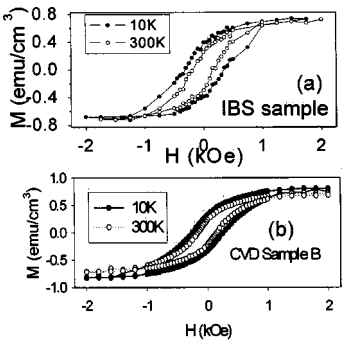

FIG. 4. Magnetic hysteresis loops measured in: (a) IBS multilayer film 1 and (b) MOCVD film B at 10 and 300 K.

observed in sample B (metallic bulk) and sample 1 (superlattice), as seen in Fig. 4.

In order to further clarify the correlation of carriers with magnetism, we investigated magnetoresistance in all samples, and Hall effect where feasible. No appreciable anomalous Hall contribution was found. Magnetoresistance had a complex temperature and field dependence, however we had to conclude that no anomalous effects were observed in the DMS samples, neither bulk nor superlattice. Figure 5(b) shows magnetoresistance of the three bulk MOCVD films (notice a log scale of resistivity for the insulating sample A). At least three different behaviors are observed with positive and negative signs of magnetoresistance, depending on the temperature and field range. A very sharp square peak in fields of $\sim$200 Oe and low temperatures is seen in measurements on the metallic sample. We have certain reservations about this as it may be due to the indium contacts becoming superconducting at low temperature. The high-field behavior is qualitatively similar to previous observations in TM-doped ZnO.[21] We do *not* consider these effects to be related to the presence of Co ions in the structure as the standard undoped ZnO sample shows similar behavior [Fig. 5(a) on the left]. Examples of magnetoresistance of granular multilayers at $T=30$ K are also shown in this figure. This behavior is generally typical of tunneling magnetoresistance in superparamagnetic granular systems,[22] as it scales roughly with the square of magnetization and confirms once again the dominance of intergranular tunneling in the conduction of these samples.

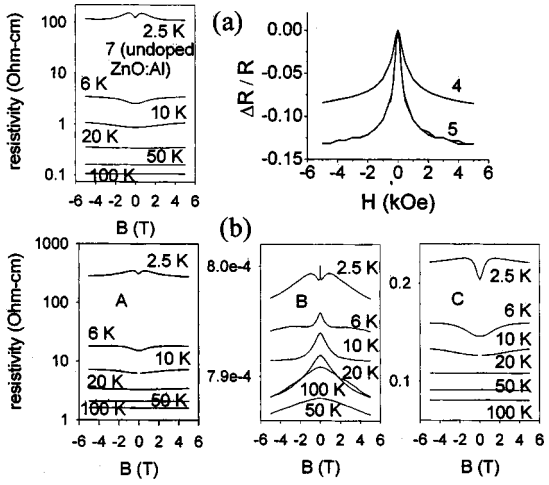

FIG. 5. Magnetoresistance measurements (a) on the standard ZnO film 7 and granular multilayers 4 and 5 and (b) on MOCVD samples A, B, and C.

In conclusion, we have prepared Al codoped ZnO:Co DMS bulk films by MOCVD, and DMS superlattices by IBS, with the Curie temperature higher than room temperature. Overdoping with cobalt leads to the suppression of high temperature ferromagnetism in the multilayers, and a crossover to superparamagnetism with varied dimensionality. This crossover is even more evident in VRH. Ferromagnetic properties of samples made by both techniques are comparable. We have not observed effects of Co on the magnetotransport of DMS samples made by either of these methods.

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