Transition from granular to dilute magnetic semiconducting multilayers in ion-beam-deposited ZnO/Co

A. B. Pakhomov, Bradley K. Roberts, and Kannan M. Krishnan[a)]
Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195-2120

(Received 24 June 2003; accepted 29 September 2003)

Multilayers of Co/ZnO, with varying nominal thickness of metal (2–10 Å) and semiconductor (2–20 Å), were prepared by ion-beam sputtering. Magnetic, transport, and magnetotransport measurements were carried out over a temperature range of 2.5 to 300 K. Upon decreasing Co thickness and increasing ZnO thickness in the multilayer stack, the properties of the samples undergo a crossover from those of granular metallic Co/semiconductor multilayers to a dilute magnetic semiconductor superlattice. We interpret ferromagnetism in the latter case as due to ordering in the Co-rich layers, mediated by carriers from lightly doped, high carrier concentration layers. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1629369]

Development of room-temperature ferromagnetic (FM) semiconductors and their nanostructures for spin electronics[1] has been attracting increasing effort since the discovery of ferromagnetism, with a relatively high Curie temperature of 110 K, in Mn-doped GaAs diluted magnetic semiconductors (DMSs).[2] Room-temperature FM has been recently demonstrated in Co-doped oxide semiconductor films, such as anatase TiO_2[3,4] and wurtzite ZnO,[5,6] in GaN doped with Cr[7] or Mn,[8,9] and Cr-doped AlN,[10,11] deposited by various techniques. However, superb magnetic properties have been associated with the presence of clusters of concentrated phase in a more diluted matrix for some room-temperature FM samples.[12–14] On the theoretical side, discussion continues in the literature on the mechanisms of FM in room-temperature DMSs, including the role of carriers in magnetism.[11,15–18]

In this letter, we report a study of magnetic and transport properties of multilayers made by alternating deposition of atomic-scale layers of ZnO and Co, with aluminum doping. At relatively low Co content, this method results in a superlattice with alternating layers of heavily magnetically doped, low carrier concentration material, and a lightly magnetically doped, but more conductive, semiconductor. Increasing the relative nominal thicknesses of the Co layers leads to a crossover from a DMS superlattice, with the Curie temperature higher than 300 K, to superparamagnetic granular multilayers with zero remanence and zero coercivity at room temperature. This change is associated with a crossover from conduction of the type similar to Al-doped ZnO to variable range hopping (VRH), with varying dimensionality, between metal granules.

Superlattices of Co/ZnO doped with Al, with varying nominal thickness of metal (2–10 Å) and semiconductor (2–20 Å), were prepared by ion-beam sputtering on silicon and glass substrates at room (ambient) temperature, at a base pressure of 10^{-7} Torr and deposition Ar pressure of 1.1×10^{-4} Torr. The number of double layers varied between 15 and 25. The deposition rate was calibrated to achieve uniform values of 0.22 Å/s for ZnO, and 0.25 Å/s for Co. The films were characterized by x-ray diffraction (XRD) and Rutherford backscattering (RBS). Magnetic, transport, and magnetotransport measurements were carried out over a temperature range of 2.5 to 300 K on a Quantum Design MPMS-5 system.

RBS studies showed the Co/Zn atomic ratios in the range from 0.1 to 1.25, consistent with the expected values, an excess of oxygen compared to Zn in stoichiometric ZnO, and about 5% of aluminum (donor dopant). Figure 1 shows the XRD pattern for a $(ZnO_{20\ Å}Co_{2\ Å})_{25}$ sample on a glass substrate, which reveals the nanocrystalline structure of ZnO and no peaks of metallic Co. Samples with larger relative Co content indicated diffuse metallic Co reflections. Figures 2(a)–2(d) show the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements as a function of temperature in a field of 20 Oe for samples with fixed nominal thickness of 2 Å of Co layers and varying (2–20 Å) ZnO thickness. Magnetization is normalized to the nominal total volume of Co, which is the same for all these samples. Higher relative content of Co results in a granular multilayer structure, which demonstrates magnetic blocking phenomena and superparamagnetism. Blocking is seen from splitting of

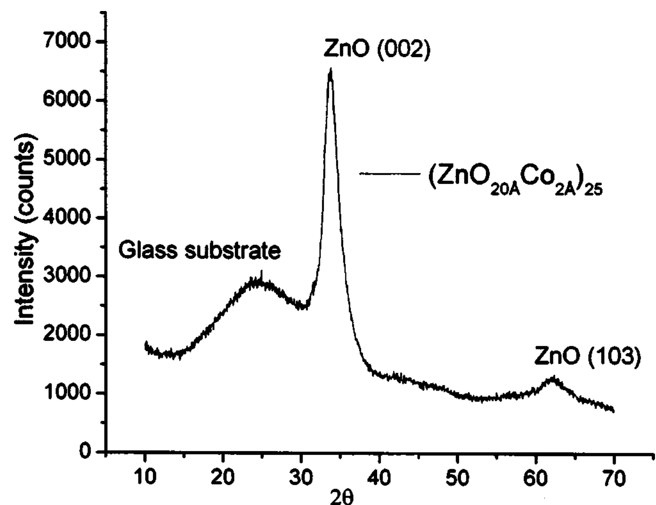

FIG. 1. XRD pattern on sample $(ZnO_{20\ Å}Co_{2\ Å})_{25}$.

a)Electronic mail: kannanmk@u.washington.edu

 © 2003 American Institute of Physics
Downloaded 19 Nov 2003 to 128.95.118.93. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

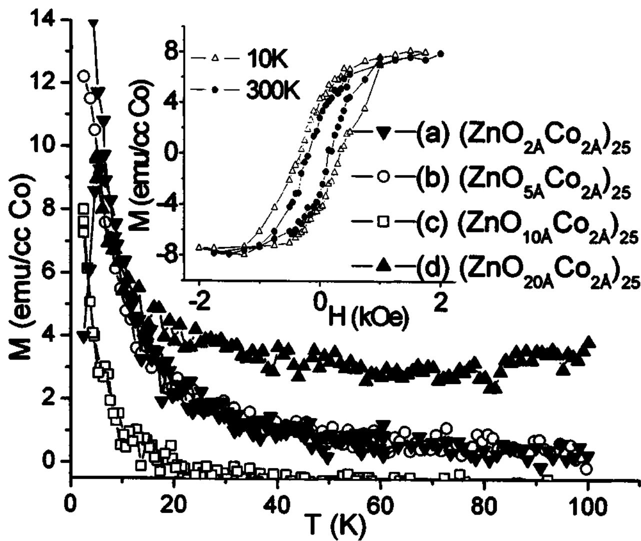

FIG. 2. ZFC and FC magnetization measurements at $H=20$ Oe for samples with varying nominal thickness of ZnO layers x $(ZnO_{x\ Å}Co_{2\ Å})_{25}$, normalized to the total nominal volume of Co metal. Inset: Magnetic hysteresis loops measured on sample $(ZnO_{20\ Å}Co_{2\ Å})_{25}$ at 10 and 300 K.

the ZFC and FC curves, and, for the sample with the thinnest ZnO layers $[(ZnO_{2\ Å}Co_{2\ Å})_{25}]$, a maximum in the ZFC susceptibility near the blocking temperature [Figs. 2(a) and 2(b)]. The sample with the thickest ZnO layers $[(ZnO_{20\ Å}Co_{2\ Å})_{25}]$ behaves as a DMS; that is, it does not show any sign of blocking phenomena down to 2.5 K, and its magnetization does not go to zero at high T and remains approximately constant in the temperature range of 40 to 300 K [Fig. 2(d)]. M versus H dependences for this sample are hysteretic both at 10 and 300 K, as shown in the inset of Fig. 2, where the background signal of the substrate has been subtracted. Small values of spontaneous moment mean that only a minority of Co atoms are magnetically ordered. Loops with no hysteresis typical of superparamagnetic materials are observed in samples a–c (ZnO thickness 2–10 Å) above the blocking temperature (not shown here).

Figures 3(a)–3(d) show the logarithm of resistivity as a function of $1/T^{1/2}$ for samples with increasing ZnO thickness. The dependence for a standard ZnO:Al film without Co doping is shown in Fig. 3(e) for comparison. For granular samples with the thinnest ZnO layers, resistivity follows a VRH law ($\ln\rho\sim(T_0/T)^n+$constant) with n close to 1/2, typical of hopping between metal granules in an insulator at intermediate temperatures.[19] Detailed analyses of these data show[20] that a crossover from the dominating quasi-two-dimensional ($n\gtrsim 1/2$) to three-dimensional ($n\lesssim 1/2$) VRH occurs as the ZnO nominal thickness increases from 2 to 5 Å. A dependence with $n=1$ is observed at low temperatures, both in the sample with 20 Å ZnO layers and in the Al-doped ZnO film with no Co added. We conclude that the dominating conduction mechanisms in this sample are similar to those in ZnO:Al. Figures 4(a)–4(d) show the magnetoresistance of these samples, measured with the magnetic field perpendicular to the film plane, at 48 K, a minimum temperature at which resistances for all samples were measurable within the limitations of our instruments. We assume that the negative tunneling magnetoresistance[21] is dominating in the superparamagnetic state [Figs. 4(a) and 4(b)]. A small positive magnetoresistance in samples with thicker ZnO layers [Fig. 4(d)] is typical of doped semiconductors.[20,22] This positive component increases greatly at low temperatures, as shown by the curve (e) for the sample with 20 Å ZnO layers.

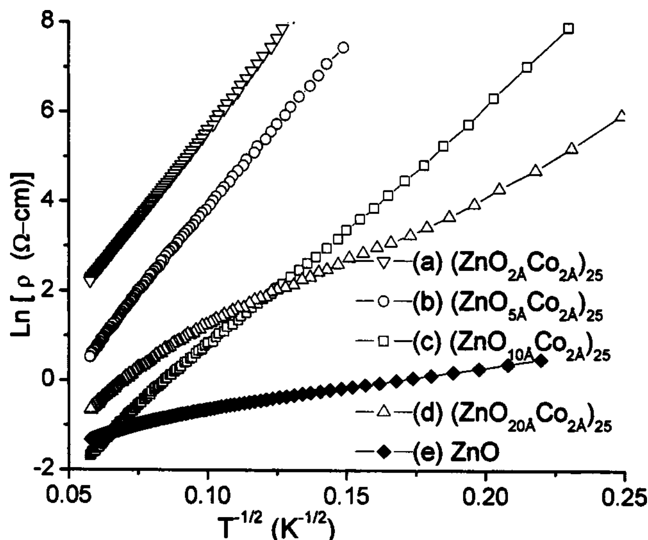

FIG. 3. Logarithm of resistivity as a function of $1/T^{1/2}$.

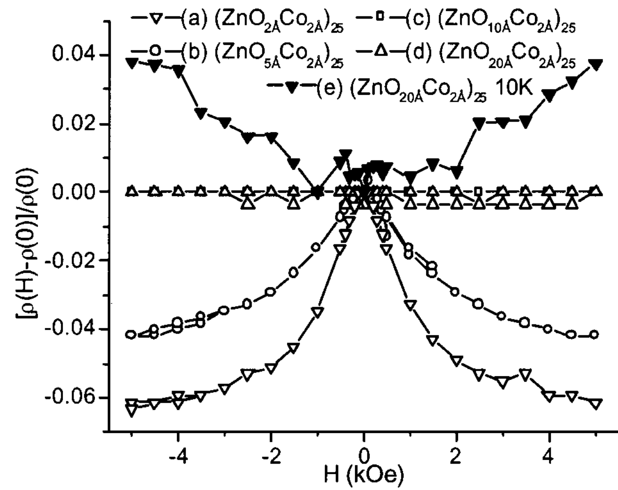

FIG. 4. Magnetoresistance of the four samples at $T=48$ K (open symbols), and magnetoresistance of the $(ZnO_{20\ Å}Co_{2\ Å})_{25}$ structure at $T=10$ K (filled triangles).

There are two competing channels of conduction in the system, which differ in the temperature dependence of resistivity. Increasing the total relative amount of Co in the films, at a fixed Al doping level, increases the resistivity of the semiconductor [compare Figs. 3(d) and 3(e)]. Hence, cobalt impurities, while necessary for the presence of magnetic moments, provide traps for carriers that mediate magnetic order. Upon further decreasing ZnO layer thickness, the number of Co metal inclusions grows, which leads to increasing conductivity via intergranular tunneling (hopping) channel. At the same time, the number of carriers in the semiconductor matrix, needed for mediating FM in DMS, decreases sharply, and high-temperature FM disappears. Now let us consider the FM structure $(ZnO_{20\ Å}Co_{2\ Å})_{25}$. This sample contains no metal inclusions, based on both magnetic and structural results. We assume that, due to limited diffusion length at

Downloaded 19 Nov 2003 to 128.95.118.93. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

given ambient deposition conditions, the semiconductor superlattice consists of cobalt-rich, low carrier-concentration layers, alternating with layers lightly doped with Co, and hence having higher carrier concentration. We hypothesize that the presence of lightly doped layers can play an important role in FM by mediating exchange in the Co-rich layers. A uniform increase of the concentration of transition metal in DMS eventually leads to the deterioration of FM properties above a certain doping level. On the other hand, clusters of very heavily doped anatase $(TiCo)O_2$ in almost depleted anatase matrix have been shown to have very high spontaneous moment per Co atom.[14] Our hypothesis of the "proximity effect" of the conducting matrix on heavily doped regions, if correct, may not only be useful in resolving this controversy, but also pave a new path in engineering of high-moment DMS nanostructures.

In summary, we have prepared (Zn,Co)O:Al DMS superlattices, with the Curie temperature higher than room temperature, by alternating deposition of ZnO and Co as multilayers on the atomic scale. Over-doping with cobalt leads to a suppression of high-temperature ferromagnetism. At the same time, Co granules are formed at decreasing thickness of ZnO layers, leading both to superparamagnetism and a crossover of conduction to hopping between metal granules.

The authors are grateful to V. Shutthanandan, David E. McCready, and S. Thevuthasan at Pacific North-West National Laboratory, WA, for RBS and XRD measurements. We appreciate helpful discussions with S. Chambers, M. Olmstead, and D. Gamelin. The work was supported by NSF/ECS 0203069. One of the authors (A.B.P.) acknowledges partial support from the UW-PNNL Joint Institute of Nanotechnology.

[1] H. Ohno, Science **281**, 951 (1998); G. A. Prinz, *ibid.* **282**, 1660 (1998).
[2] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996); B. Beschoten, P. A. Crowell, I. Malajovich, D. D. Awschalom, F. Matsukura, A. Shen, and H. Ohno, Phys. Rev. Lett. **83**, 3073 (1999).
[3] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, Science **291**, 854 (2001).
[4] S. A. Chambers, S. Thevuthasan, R. F. C. Farrow, R. F. Marks, J. U. Thiele, L. Folks, M. G. Samant, A. J. Kellock, N. Ruzycki, D. L. Ederer, and U. Diebold, Appl. Phys. Lett. **79**, 3467 (2001).
[5] K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. **79**, 988 (2001).
[6] S. G. Yang, A. B. Pakhomov, S. T. Hung, and C. Y. Wong, IEEE Trans. Magn. **38**, 2877 (2002).
[7] S. E. Park, H. J. Lee, Y. C. Cho, S. Y. Jeong, C. R. Cho, and S. Cho, Appl. Phys. Lett. **80**, 4187 (2002).
[8] M. L. Reed, N. A. El-Masry, H. H. Stadelmaier, M. K. Ritums, M. J. Reed, C. A. Parker, J. C. Roberts, and S. M. Bedair, Appl. Phys. Lett. **79**, 3473 (2001).
[9] G. T. Thaler, M. E. Overberg, B. Gila, R. Frazier, C. R. Abernathy, S. J. Pearton, J. S. Lee, S. Y. Lee, Y. D. Park, Z. G. Khim, J. Kim, and F. Ren, Appl. Phys. Lett. **80**, 3964 (2002).
[10] S. G. Yang, A. B. Pakhomov, S. T. Hung, and C. Y. Wong, Appl. Phys. Lett. **81**, 2418 (2002).
[11] S. Y. Wu, H. X. Liu, L. Gu, R. K. Singh, L. Budd, M. van Schilfgaarde, M. R. McCartney, D. J. Smith, and N. Newman, Appl. Phys. Lett. **82**, 3047 (2003).
[12] K. Ando, Appl. Phys. Lett. **82**, 100 (2003).
[13] J.-Y. Kim, J.-H. Park, B.-G. Park, H.-J. Noh, S.-J. Oh, J. S. Yang, D.-H. Kim, S. D. Bu, T.-W. Noh, H.-J. Lin, H.-H. Hsieh, and C. T. Chen, Phys. Rev. Lett. **90**, 017401 (2003).
[14] S. A. Chambers, T. Droubay, C. M. Wang, A. S. Lea, R. F. C. Farrow, L. Folks, V. Deline, and S. Anders, Appl. Phys. Lett. **82**, 1257 (2003).
[15] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
[16] M. Berciu and R. N. Bhatt, Phys. Rev. Lett. **87**, 107203 (2001).
[17] K. Sato and H. Katayama-Yoshida, Semicond. Sci. Technol. **17**, 367 (2002).
[18] A. Kaminski and S. Das Sarma, Phys. Rev. Lett. **88**, 247202 (2002).
[19] P. Sheng, Philos. Mag. B **65**, 357 (1992).
[20] A. B. Pakhomov, B. K. Roberts, V. Shutthanandan, D. McCready, S. Thevuthasan, A. Tuan, S. A. Chambers, and K. M. Krishnan, 9th Joint MMM-Intermag Conference, Anaheim, CA, January 5–9, 2004.
[21] J. I. Gittleman, Y. Goldstein, and S. Bozowski, Phys. Rev. B **5**, 3609 (1972).
[22] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984).

Downloaded 19 Nov 2003 to 128.95.118.93. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp