Tunable magnetic order of Co nanoparticles and magnetotransport in Co/ZnO nanocomposites

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We demonstrate tunable magnetic order of cobalt nanoparticles in Co/ZnO nanocomposites. High-density electronic states in ZnO formed during high vacuum annealing help generate bound and free charge carriers, which in turn enable the stable magnetic ordering of Co nanoparticles in the Co/ZnO nanocomposites in a tunable manner. This is demonstrated by the following experimental observations: (i) enhanced spontaneous magnetization and coercivity, (ii) transition from semiconducting to metallic electrical-transport, and (iii) transverse magnetotransport transition from negative magnetoresistance to the anomalous Hall effect. The work explores a route to manipulate the magnetic order of magnetic nanoparticles by means of intentionally generated defects in oxides. © 2008 American Institute of Physics. [DOI: 10.1063/1.2959081]

Nanocomposites (NCs) formed by dispersing electrically conducting nanoparticles (NPs) in a poor-conducting matrix are promising for optical, electrical, and magneto-optic applications. When magnetic NPs are applied, the composites are shown to exhibit novel phenomena such as the giant Hall effect, the magnetoelectric effect, and the tunnel magnetoresistance (MR) effect. Magnetic NCs possess excellent sensitivity for hard-disk read heads and magnetic sensors, high permeability for high-frequency shielding devices, and high coercivity for data storage. However, the size of the magnetic bits and, therefore, the magnetic NPs must decrease with an increasing density of the magnetic storage media. This eventually results in the anisotropy energy ($K_u$) per particle, i.e., the energy required to retain the magnetic moment along particular directions, being comparable to or even less than the thermal energy. Under this condition, the thermally driven flipping of magnetic moments of NPs rules out applications for reliable high-density data storage. Therefore, mechanisms for stabilizing the magnetic ordering of the magnetic NPs embedded in NCs are highly desirable.

Application of ferromagnetic (F) materials with high $K_u$ is the most direct way to maintain the magnetic order when the size of the magnetic bits decreases to the order of nanometers. Therefore, composites containing dispersed particles with perpendicular magnetic anisotropy, for example, $\text{L}_1\text{O}_2$-ordered FePt ($K_u\sim7\times10^5$ ergs/cm$^3$) in nonmagnetic oxides, have been extensively investigated for ultrahigh-density magnetic recording toward and beyond 1 Tbit/in$^2$. Besides the incorporation of high $K_u$ magnetic NPs in a composite, the possibility of maintaining magnetic ordering by incorporating specific separating layers is also being explored. For instance, antiferromagnetic (AF) oxides have been employed to provide an additional F/AF exchange coupling energy to overcome the thermal fluctuation and maintain the magnetic order among NPs that are dispersed in a composite. However, the Neel temperature of AF separating layers in a composite gives rise to a blocking temperature ($T_B$) that limits the magnetic order temperature.

In this paper, we report tunable magnetic order of cobalt NPs in Co/ZnO NCs. Annealing of the samples under high vacuum induces high-density defects in ZnO and helps generate bound and free charge carriers, which in turn enables the ferromagnetic ordering of Co NPs in the Co/ZnO NCs. We have fabricated the Co/ZnO NCs by an ion beam sputtering system with base pressure of $5\times10^{-7}$ Torr onto a 100 nm SiO$_2$/Si wafer at room temperature. Deposition of Co/ZnO NCs was executed in a process pressure of about $2.3\times10^{-4}$ Torr with an Ar ion beam acting alternatively on ZnO and Co targets for 40 cycles. The nominal thickness of the Co/ZnO NCs was about 40 nm. The as-deposited samples were further annealed at 250 °C for 1 and 3 h at $1.4\times10^{-9}$ Torr. Characterization of the magnetic properties was carried out by means of a superconducting quantum interference device magnetometer. The longitudinal ($R_\text{xx}$) and transverse ($R_\text{xy}$) resistances were measured in a four-point geometry with the current source parallel and perpendicular to the voltage probe, respectively. The current source was kept at 100 μA using a Keithley 2400 current source. The temperature-dependent electrical transport was measured by a physical property measurement system from 3 to 300 K.

Figure 1 shows the Z-contrast high resolution transmission electron microscopy (HRTEM) images of the as-deposited Co/ZnO NCs and those annealed at $10^{-9}$ Torr for 1 and 3 h. For the as-deposited samples, the contrast between Co and ZnO is weak and the interfaces of Co/ZnO are not clearly defined. For samples annealed for 1 and 3 h, the Co/ZnO interfaces become slightly sharper with the Co NPs diameter about 4–5 nm. It is noted that the size and distri-
bution of the Co NPs for the samples annealed for 1 and 3 h are quite similar.

Figure 2(a) shows traces of the magnetization (M) versus the applied magnetic field (H) at 300 K for the Co/ZnO NCs annealed at $10^{-9}$ Torr. The magnetic field was applied perpendicular to the film plane and the diamagnetic contribution of the substrates in the $M(H)$ traces was subtracted. As indicated in Fig. 2(a), the $M(H)$ loops of the as-deposited NCs reveal a weak hysteric property, where the coercivity ($H_c$) is only 14 Oe. However, for the Co/ZnO NCs annealed at $10^{-9}$ Torr for 1 and 3 h, apparent enhancement in $H_c$ (to 102 and 135 Oe, respectively) is shown in the insets of Fig. 2(a). The corresponding temperature dependence of magnetization $M(T)$ (not shown) reveals no blocking temperature below 300 K among all samples and enhanced spontaneous magnetization due to annealing. We have thus demonstrated that the magnetic order in the Co/ZnO NCs can be enhanced by annealing under high vacuum conditions.

We further investigated the transverse magnetotransport $R_{xy}$, i.e., resistance measured in a configuration with a current source perpendicular to a voltage probe, as a function of the magnetic field, as shown in Fig. 2(b). For granular composites, the negative MR behavior is commonly observed for longitudinal magnetotransport $R_{xx}$, where resistance is measured in a configuration with the current source in parallel with the voltage probe. For the as-deposited samples, the negative MR behavior appeared for both $R_{xx}(H)$ and $R_{xy}(H)$. The MR ratio for $R_{xy}(H)$ rapidly decreased from 5.04% (as-deposited) to 0.44% and 0.17% for the samples annealed for 1 and 3 h respectively at $10^{-9}$ Torr, as shown in Fig. 2(c). Fascinatingly, we discovered that for the Co/ZnO NCs annealed for 1 h, the negative MR deformed for the $R_{xy}(H)$. It is noticed that $R_{xy}$ in the positive saturation field ($H_{sat}$) was larger than that in the negative saturation field ($H_{sat}$). That is, the $R_{xy}(H)$ trace is asymmetric with the asymmetrical ratio defined by $[R_{xy}(H_{sat}) - R_{xy}(H_{sat})]/R_{xy}(H_{sat})$, being about 0.61%. With a further increase in annealing time to 3 h, $R_{xy}(H)$ made a complete transition to an anomalous Hall effect (AHE) instead of the negative MR behavior, and the asymmetrical ratio further increased to 1.23%. It should also be noted that $R_{xy}(H)$ corresponds well to the $M(H)$ loop [solid curves in Fig. 2(b)], as previously shown in Fig. 2(a). The transition from negative MR (scattering by disorder moments) to the AHE (asymmetric scattering by order moments) reflects the enhancement of the magnetization order of Co NPs, which is consistent with $M(H)$ and $M(T)$ data.

To further clarify the influence of vacuum annealing on the magnetic order and magnetotransport, we also studied the temperature-dependent electrical transport for the Co/ZnO NCs annealed at $10^{-9}$ Torr. Figure 3 shows the normalized resistance, $R_{xx}(T)/R_{xx}(300 \text{ K})$, as a function of temperature for NCs annealed at $10^{-9}$ Torr. For as-deposited samples, typical nondegenerate semiconductor behavior, i.e., electrical resistance decreases with increasing temperature, was observed. However, the Co/ZnO NCs annealed for 1 h showed a semiconductor to metal transition (SMT) with metalliclike (degenerate) conduction above ~44 K and nondegenerate semiconductor conduction below ~44 K, as shown in the inset of Fig. 3. The SMT temperature decreased to ~26 K when Co/ZnO NCs were further annealed for 3 h. These results revealed that the magnetic [$M(H)$ and $M(T)$], magnetotransport [$R_{xx}(H)$ and $R_{xy}(H)$], and temperature-dependent electrical properties [$R_{xx}(T)$] of the Co/ZnO NCs could be tuned by the vacuum annealing conditions.

Now, we show that the temperature-dependent resistivity transition due to vacuum annealing is most likely associated
with the formation of defects in ZnO, e.g., oxygen vacancies \(V_{0}\), Zn interstitials \(Z_{i}\), and other forms. According to band theory, the defects of ZnO may provide bound carrier orbits and the impurity band is formed from overlapping orbits. The impurity band due to \(V_{0}\) and \(Z_{i}\) has been reported to be near the bottom of conduction band. Based on the impurity band concept, we can interpret the observed SMT and MR to AHE transition in the \(10^{-9}\) Torr annealed Co/ZnO NCs. When the defect concentration is low, the defect-induced impurity band appears to be narrow and near the bottom of the conduction band of ZnO. In this situation, Co NPs themselves could simply interact by means of the weak dipole-dipole effect and correspond to the weak hysteresis of as-deposited Co/ZnO NCs. With increasing defect concentration, the impurity band becomes broader and closer to or even overlapping the minimum of the ZnO conduction band, which leads to high-density electronic states in the energy band gap of ZnO. The result brings about additional bound and free charge carriers, enhances the metalliclike conduction, and leads to SMT as well as the decrease of transition temperature with increased annealing time. Co NPs therefore can interact by assistance of defects-induced charge carriers and favor more stable magnetic order. We conclude that this work provides a route to manipulate the magnetic order of F-metal NPs in oxides by means of intentionally generated defects in oxides, which could be useful for magnetic recording media and spintronics.

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