

Characteristic tunnel-type conductivity and magnetoresistance in a CoO-coated monodispersive Co cluster assembly

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We have studied electrical conductivity, σ , and magnetoresistance in a CoO-coated monodispersive Co cluster assembly fabricated by a plasma-gas-aggregation-type cluster beam deposition technique. The temperature dependence of σ is described in the form of $\log \sigma$ vs $1/T$ for $7 < T < 80$ K. The magnetoresistance ratio $(\rho_0 - \rho_{3T})/\rho_0$ increases sharply with decreasing temperature below 25 K: from 3.5% at 25 K to 20.5% at 4.2 K. This marked increase (by a factor of 6) is much larger than those observed for conventional metal-insulator granular systems. These results are ascribed to the Coulomb blockade effect in the monodispersed cluster assemblies. © 1999 American Institute of Physics. [S0003-6951(99)01901-4]

Giant magnetoresistance (GMR) has been observed in a structure of two ferromagnetic layers separated by a thin insulator (FM/I/FM).¹ Such GMR arises from a spin-dependent tunneling effect. Electron tunneling between two ferromagnetic electrodes through an insulating layer depends on the relative orientation of the magnetizations of the electrodes. When the relative orientation of the magnetization is changed by applying a magnetic field, tunnel-type magnetoresistance (TMR) is expected to occur. Although this effect was discovered by Julliere² in 1975 and subsequently in several other FM/I/FM junctions,^{3,4} large and reproducible TMR ratios have been found only very recently.^{5,6}

In FM-I granular systems, where the magnetic metal granules or clusters are embedded in an insulator matrix, the TMR effect has also been detected⁷ and a marked TMR effect has been reported recently in FM-I granular systems.⁸ For these materials, when the metal cluster concentration is just below the percolation threshold, the electrical conduction is dominated by tunneling between metallic clusters, with a tunnel resistance enhanced by the Coulomb blockade at low temperatures and also dependent on the relative orientation of the magnetization in the two clusters. The tunnel current between randomly oriented magnetic granules is smaller than that between the magnetically aligned ones. Since conventional granular materials have been produced by codeposition of a metal and an oxide and subsequent precipitation of magnetic granules on the substrate, there is normally wide distribution of the cluster size and intercluster distance (namely the tunnel-barrier thickness). In such heterogeneous granular systems, the temperature dependence of the low-field conductivity is expressed in the form of $\propto \exp(-b/T^\alpha)$ with $\alpha = 1/2$ for a wide temperature range.^{9,10}

In this study, we have measured the electrical conductivity and TMR in oxide-coated monodispersive Co cluster assemblies. Cobalt (II) oxide, CoO, is an antiferromagnetic semiconductor with a Néel temperature of 293 K. The room-temperature resistivities of CoO single crystals are $10^8 - 10^{15} \Omega \text{ cm}$, and the activation energies are 0.73–1.35 eV.¹¹ This letter discusses the transport properties, spin-dependent tunneling and Coulomb blockade effect in the CoO-coated Co cluster assembly. In particular, we emphasize that the monodispersed Co cluster size distribution and a nearly uniform thickness of the CoO shells give rise to the characteristic features in their electrical conductivity and TMR. Our samples are fabricated with a plasma-gas-aggregation (PGA) type cluster beam deposition apparatus.¹² It is a combination of sputtering and gas-aggregation techniques. The PGA type cluster beam deposition apparatus is mainly composed of three parts: a sputtering chamber, a cluster growth room and a deposition chamber. The vaporized atoms in the sputtering chamber are decelerated by collisions with a large amount of Ar gas (the Ar gas flow rate: $R_{\text{Ar}} = 250 - 500$ (sccm) injected continuously into the sputtering chamber, and are swept into the cluster growth room, which is cooled by liquid nitrogen. The clusters formed in this room are ejected from a small nozzle by differential pumping and a part of the cluster beam is intercepted by a skimmer, and then deposited onto a sample holder in the deposition chamber ($10^{-5} - 10^{-4}$ Torr). Using this system, we obtained monodispersed transition metal clusters of 6–14 nm in size.¹² In this study, we introduced oxygen gas into the deposition chamber during the depositing to form CoO shells covering the Co clusters, as schematically shown in the inset of Fig. 1. For a constant R_{Ar} , the gas pressure in the deposition chamber can be adjusted by changing the flow rate of oxygen gas (R_{O_2}). The initial stage of clusters deposited on the mi-

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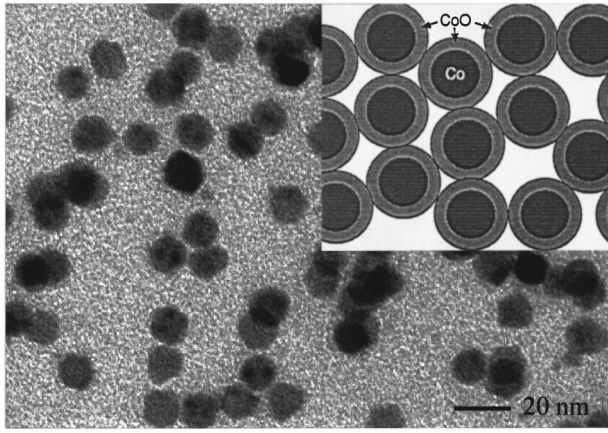


FIG. 1. TEM image of the clusters (with mean cluster diameter=13 nm) prepared on a carbon-coated microgrid at $R_{Ar}=500$ sccm and $R_{O_2}=1$ sccm. The inset shows schematic drawing of the CoO-coated monodispersed Co cluster assembly, showing Co cores (dark shaded) and surrounding CoO shells.

crogrids were observed by a Hitachi HF-2000 transmission electron microscope (TEM) operating at 200 kV. Figure 1 shows a TEM image of the clusters produced at $R_{Ar}=500$ sccm and $R_{O_2}=1$ sccm. As shown here, the clusters are almost monodispersed, with the mean diameter of about 13 nm. The cluster size was found to be insensitive to the deposition time and R_{O_2} . The electron diffraction pattern clearly indicated the coexistence of Co and CoO phases, while the high resolution image displayed Co clusters covered with CoO.¹³ The cluster assemblies were formed on a polyimide film at room temperature with a thickness of about 100 nm, as measured by a quartz thickness monitor. Using a conventional four-probe method, the electrical resistivity was measured at a constant voltage because the ohmic law ceased to hold at low temperatures. The MR was measured in the applied field parallel to the electrical current direction.

Figure 2(a) shows the temperature dependence of the electrical resistivity $\rho(T)$ for the sample prepared at $R_{Ar}=500$ sccm and $R_{O_2}=1$ sccm. In the CoO-coated Co cluster assembly, the temperature coefficient of resistivity (TCR) is negative below room temperature, and $\rho(T)$ decreases dramatically with decreasing temperature below 10 K. As seen from the inset of Fig. 2(a), the resistivity at 4.2 K is four orders of magnitude larger than that at room temperature. In the pure Co cluster assemblies, on the other hand, TCR is positive in the range of $20 < T < 300$ K and becomes slightly negative below 20 K. At 4.2 K, the resistivity of the CoO-coated Co cluster assemblies is about ten orders of magnitude larger than that of the pure Co cluster assemblies. Such a huge resistivity value and negative TCR in the cluster assemblies are attributable to the tunnel-type conduction between metallic Co clusters via CoO shell layers.

The low-field tunnel-type electrical conduction of granular materials was discussed by Neugebauer and Webb.¹⁴ Most simply, the conductivity is expressed as follows:

$$\sigma \propto \exp(-2\kappa s - E_c/2k_B T), \quad (1)$$

where s is the tunnel-barrier thickness between the two clusters, κ is the tunneling exponent of electron wave functions in the insulator, $\kappa = [2m^*(\phi + E_F - E)/\hbar^2]^{1/2}$; m^* is the ef-

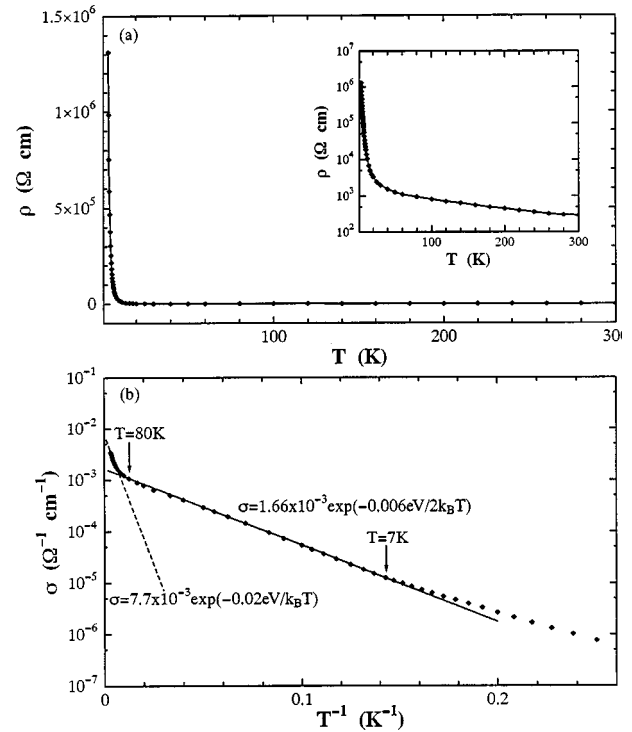


FIG. 2. (a) Temperature dependence of the electrical resistivity ρ at zero magnetic field for the CoO-coated Co cluster assembly prepared at $R_{Ar}=500$ sccm and $R_{O_2}=1$ sccm and $\log \rho$ vs T in the inset. (b) The logarithmic conductivity $\log \sigma$ as a function of T^{-1} .

fective electron mass, ϕ is the barrier height, E is the electron energy, E_F is the Fermi level and \hbar is Planck's constant. E_c is the electrostatic energy required to create a positive-negative charged pair in two clusters by tunneling, and gives rise to the Coulomb blockade effect at a low temperature. When the applied voltage and thermal energy are much smaller than E_c , electrons or holes cannot tunnel from one neutral cluster to another without exciting their states from the Fermi level to the levels higher than E_c . When clusters are monodispersed with a uniform intercluster distance (namely the same barrier thickness), Eq. (1) predicts a simple hopping type temperature dependence for the low-field conductivity: $\sigma(T) \propto \exp(-E_c/2k_B T)$.¹⁴ As shown in Fig. 2(b), a linear dependence of $\log \sigma$ vs $1/T$ is observed in the range of $7 < T < 80$ K for the present CoO-coated Co cluster assemblies. This temperature dependence of $\sigma(T)$ is different from the form of $\log \sigma$ vs $1/T^{1/2}$ commonly observed in conventional granular systems. The charging energy estimated from the plot of $\log \sigma$ vs $1/T$ is $E_c = 6$ meV, corresponding to the thermal energy of $k_B T$ with $T \approx 70$ K. This implies that when $T > 70$ K, normal activation type conduction is restored because the charging energy is overcome by the thermal energy. In addition, as seen from Fig. 2(b), the conductivity abruptly increases with increasing temperature above 80 K: the estimated activation energy is 0.02 eV at $T > 150$ K. This behavior is ascribable to the small and/or large polaron band-hopping conduction in the CoO semiconductor layer because there are usually a large number of defects and excess carriers in the transition metal oxides.

Figure 3 shows the temperature dependence of the MR ratio $[\rho_{H=0} - \rho_{3T}]/\rho_{H=0}$ for the CoO-coated Co cluster assembly prepared at $R_{Ar}=500$ sccm and $R_{O_2}=1$ sccm. The

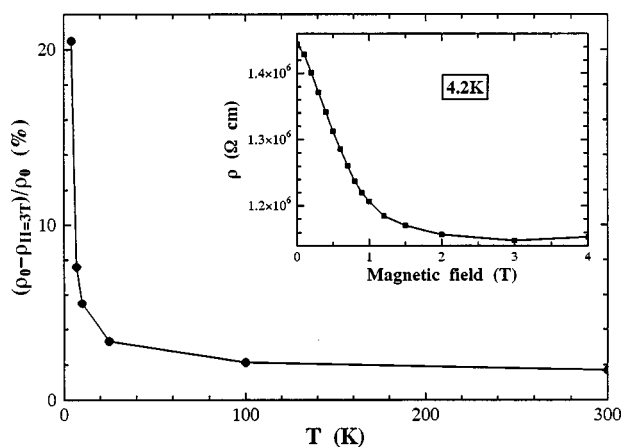


FIG. 3. Temperature dependence of the MR ratio at $H=3$ T for the CoO-coated Co cluster assembly prepared at $R_{Ar}=500$ sccm and $R_{O_2}=1$ sccm. The inset shows the field dependence of the MR ratio at 4.2 K.

inset of Fig. 3 shows the magnetic field dependence of the MR at 4.2 K for this sample. The MR gradually decreases with the increase in magnetic field up to $H=3$ T and saturates at $H>3$ T. This result is well correlated with the magnetization curve (not shown here). Because of the exchange interaction between the antiferromagnetic CoO shell and the ferromagnetic Co core, the magnetization curve of the CoO-coated Co cluster assembly hardly saturates, in contrast to the behavior of the pure Co cluster assembly. As seen in Fig. 3, the MR ratio increases slightly with decreasing temperature in the range of $25<T<300$ K, while below 25 K it increases markedly with decreasing temperature, i.e., from 3.5% at 25 K to 20.5% at 4.2 K. Comparing Fig. 2(a) with Fig. 3, there is a good correlation between the MR ratio and the resistivity at low temperatures: both the resistivity and the MR ratio increase drastically with decreasing temperature. Such remarkable enhancement of the MR ratio at low temperatures was also observed in micrometer-sized ferromagnetic tunnel junctions,¹⁵ single-electron transistors consisting of ferromagnetic metals (Ni/NiO/Co/NiO/Ni)¹⁶ and double ferromagnetic tunnel junctions with small ferromagnetic islands (Co/Al₂O₃/Co).¹⁷ Moreover, it should be noted that, as shown in Fig. 3, the MR ratio increases by a factor of 6 from 25 to 4.2 K in the present CoO-coated Co cluster assembly. This increase is predicted by Takahashi and Maekawa¹⁸ and is much larger than the reported ones for the ferromagnetic junction with the Coulomb blockade effect¹⁶ and the FM-I granular systems with broad distributions of size and intergranule distance.¹⁹ Thus, the enhanced MR effect is attributed to the monodispersiveness of the cluster size in the Co-coated Co cluster assembly, which led to the more distinct Coulomb blockade effect.

Figure 4 shows the bias voltage dependence of the resistivity and the MR ratio at 4.2 K for the CoO-coated Co cluster assembly prepared at $R_{Ar}=500$ sccm and $R_{O_2}=0.44$ sccm. As one can see in Fig. 4, the resistivity is huge. It decreases more than 1 order of magnitude with increasing bias voltage V_B at $V_B < 10$ V. On the other hand, the MR ratio decreases by a factor of 2 with the increase in bias voltage below 40 V and is found to be insensitive to V_B above 40 V. The decrease of the MR ratio with V_B is not as marked as that observed in ferromagnetic tunnel junctions.^{5,6}

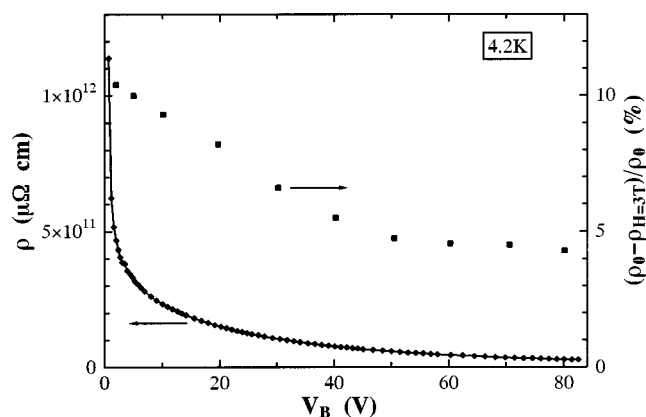


FIG. 4. Bias voltage dependence of the resistivity ρ and the MR ratio at 4.2 K for the CoO-coated Co cluster assembly prepared at $R_{Ar}=500$ sccm and $R_{O_2}=0.44$ sccm.

Since the present MR measurement is on many junctions in the series, such V_B dependence of the MR ratio is attributable to the following aspects: (1) the fine structure in the spin polarized density of states, which is related to the rapid decrease of the MR with V_B in classical junctions, is blurred by the Coulomb blockade effect; or/and (2) the spin polarized electrons are affected by spin flip scattering through multi-step tunneling.

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