Magnetic and Magnetotransport Properties in Nanogranular Co/C$_{60}$-Co Film with High Magnetoresistance

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Magnetic properties were investigated for the alternately deposited film of C$_{60}$ and Co which has found to exhibit tunnel magnetoresistance (MR) of 10–80%. Magnetic field and temperature dependences of magnetization showed typical superparamagnetic behaviors with the blocking temperature of 40 K. The magnetization curve at 300 K was well fitted by the Langevin function with the size distribution of Co particles, and the mean diameter and size distribution were evaluated to be 3.1 nm and ~1 nm, respectively. Based on the magnetic properties, the structure and magnetotransport properties are discussed in details. [doi:10.2320/matertrans.48.754]

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1. Introduction

Much interest has been paid for the spin-dependent transport in inorganic systems like tunnel junctions of magnetic metal-metal oxide. On the other hand, the spin-transport in organic molecule-based systems has remained unclarified in spite of the recent development of organic electronics. The hybrid systems between organic molecules involving carbon nanotubes (CNTs) and transition metals (TMs) has recently attracted attention as a new class of materials systems for spintronics following the theoretical predictions for high spin-polarization.$^{1-4}$ In particular, magnetotransport properties in ferromagnetically contacted CNTs have been investigated.$^{5-7}$ The reported magnetoresistance (MR) in such CNT-TM systems, however, is as small as less than 10% different from the theoretical predications. C$_{60}$ is also an attractive organic molecule, and recently the tunnel magnetoresistance (TMR) of about 10–30% has been reported for the nanogranular Co/pure-C$_{60}$ films in which Co nanoparticles are embedded in a matrix of pure-C$_{60}$.$^{8,9}$ C$_{60}$-TM hybrid systems make up possibly for the drawbacks of the CNT-TM systems (e.g., difficulty in fabrication of specific structure and poor reproducibility). In the previous studies, we have evidenced that the C$_{60}$-Co compounds with C$_{60}$Co$_{x}$ (x ≤ 5) are formed in the co-deposited mixture films and that the nanogranular films of Co nanoparticles and a matrix of the C$_{60}$-Co compound (C$_{60}$Co$_{5}$) are generated under the Co-rich conditions.$^{10-15}$ Very recently, we have shown that the alternately (alt-) deposited C$_{60}$-Co film exhibits the remarkable TMR ranging from 10% to 80%.$^{16,17}$

In the present paper, magnetic properties of the alt-deposited Co/C$_{60}$-Co film are described, and the structure and the magnetic field/bias voltage dependent magnetotransport behaviors$^{16,17}$ are discussed based on them.

2. Experimental

Co/C$_{60}$-Co films were prepared by the alternate (alt-) deposition under the ultra high vacuum condition of 10$^{-7}$ Pa. C$_{60}$ and Co with purities of 99.99% were evaporated by using a Knudsen cell and an electron beam evaporator, respective-ly. The relevant materials were deposited alternately onto mirror-polished MgO(001) substrates heated at 200°C. The distances between the evaporation sources and the substrate were kept larger than 20 cm to avoid the influence of thermal radiation from the evaporation sources. For the electrical conduction measurements, a pair of Ag electrodes (71 nm thick) separated by 250 μm in distance was deposited on the MgO substrate in advance. The alt-deposition was conducted repeatedly with the unit layer thicknesses of 1.8 nm for C$_{60}$ and 0.42 nm for Co, resulting in the total film thickness of 91 nm. The surface of the deposited film was capped with a SiO layer (160 nm thick) to avoid the easy oxidation of the C$_{60}$-Co compound.$^{10,12}$ Raman spectroscopic analysis was performed by using a micro-Raman system (NANO-FINDER, Tokyo Instruments) with an Ar ion laser (488 nm), where the probing laser (50 W/cm$^2$) was guided through the backside of the MgO substrate. Any spectral changes during the illumination were not detected under the present condition. The magnetic properties and the electrical conduction were measured by using a SQUID magnetometer. The current (I)-bias voltage (V) characteristics and the V-dependent magnetoresistance (MR) behaviors were measured at the temperatures (T) of 2–300 K in a two-terminal geometry with the electrical current. Magnetic fields up to 10 and 50 kOe were applied in the in-plane direction in the electrical and magnetic measurements. MR was defined as the resistance (R) decrease divided by the maximum resistance (R$_{max}$); MR = ΔR/R$_{max}$. 

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3. Results and Discussion

Figure 1 shows the Raman spectrum for the Co/C$_{60}$-Co film together with the spectra for pure polycrystalline C$_{60}$ (pure-C$_{60}$) and the C$_{60}$-Co compound with a composition of C$_{60}$Co$_5$ (C$_{60}$Co$_5$) which was prepared by the co-deposition method.$^{10,12}$ The influences coming from the MgO substrate are approximately subtracted from the respective spectra in this figure. In the pure-C$_{60}$, there appear the 10 Raman-active peaks of C$_{60}$ with icosahedral ($I_h$) symmetry.$^{18}$ Meanwhile, in the Co/C$_{60}$-Co film, one can recognize about 20 peaks (some peaks are overlapping) in addition to the 10 Raman-active peaks. The 300 cm$^{-1}$ peak can be assigned to the split component of the H$_g$(1) mode known as a fingerprint which indicates symmetry lowering from $I_h$-symmetry.$^{19-21}$ It is also noticeable that the $A_g(n)$ ($n = 1, 2$) peaks are strongly damped as compared to pure-C$_{60}$. These spectral features are fully consistent with those for the C$_{60}$-Co compounds$^{10,12}$ in which the formation of the covalent C-Co bonds with a bond length (0.201 nm) similar to the $\pi$-complexes of transition metals was revealed.$^{13}$ This clearly suggests the formation of the similar compound even in the alt-deposited Co/C$_{60}$-Co films. The composition of the C$_{60}$-Co compound in the present film is estimated to be close to C$_{60}$Co$_5$ judging from the peak positions of the $A_g(2)$ and $H_g(8)$ peaks (1450 cm$^{-1}$ and 1562 cm$^{-1}$), which were indicated to shift by $-4.2$ cm$^{-1}$/Co atom and $-3.6$ cm$^{-1}$/Co atom from the peak positions for pure-C$_{60}$ (1468 cm$^{-1}$ and 1574 cm$^{-1}$).$^{10,12,14}$ The extent of charge transfer from the bonded Co atom to C$_{60}$ molecules is estimated to be as small as about 0.2 electrons per a Co atom from the H$_g(8)$ peak position which was indicated to shift by $-15$ cm$^{-1}$ per a single electron transferred electron to a C$_{60}$ molecule.$^{22,23}$

Figure 2 shows magnetization ($M$)-applied magnetic field ($H$) curves at 4.2 K and 300 K. The components coming from the MgO substrate are subtracted experimentally. The $M$-$H$ curve at 4.2 K exhibits magnetic remanence at zero field and a coercive field ($H_C$) of 450 Oe, and saturated up to $H = 10$ kOe. Meanwhile, the $M$-$H$ curve at 300 K shows no remanence and $H \sim 20$ kOe is required to attain saturation.

The diameter distribution of Co nanoparticles is estimated from the fitting of the $M$-$H$ curve at 300 K with the Langevin function assuming the log-normal diameter distribution (the details of the procedure is described elsewhere$^{24}$). Figure 3 shows the diameter distribution calculated for the fitted curve (broken line) shown in the inset. The average diameter ($D$) of Co nanoparticles is evaluated to be 3.1 nm with narrow size dispersion ($\sigma \sim 1$ nm). The average interparticle distance ($S$) is evaluated to be about 3 nm by considering the volume fraction of the particles ($\sim 12\%$) estimated from the saturation magnetization ($M_s$) of 7 kemu/mol Co.

Figure 4 shows $M$-$T$ curves obtained under field-cooled (FC) and zero-field-cooled (ZFC) conditions at $H = 100$ Oe. The splitting between the FC and ZFC curves is observed at the lower temperature than the blocking temperature ($T_B$) of 40 K and the curves at the higher temperature are in agreement with the Curie-Weiss (C-W) law with a low C-W
temperature (θ) of −2 K. These behaviors are reasonably attributed to the superparamagnetism in small Co nanoparticles, and the C-W temperature relatively close to zero indicates negligible magnetic interactions between the individual Co nanoparticles.25)

The formation of the similar C_{60}-Co compound to the co-deposited one even by the alt-deposition is an interesting finding because this evidently suggests the formation of the C_{60}-Co compound through the spontaneous migration of the deposited Co atoms into C_{60} layer regardless of the large cohesive energy of Co (4.39 eV). The analogous mixing phenomena have been reported for the other organic molecule-metal systems also.26,27) Our recent theoretical calculation predicted that such atomic migration occurs due to the on-cage diffusion of the bonded Co atoms on C_{60} molecules.28) The evaluated small size/narrow size dispersion of Co nanoparticles (D = 3.1 nm/σ ~ 1 nm) and the negligible interparticle magnetic interactions indicate that the secondary growth of the precipitated Co nanoparticles is inhibited regardless of the elevated deposition temperature of 200°C. This stability against the particle growth might be attributed to the spontaneous migration of Co atoms into C_{60} layer, which plausibly causes particle precipitation in the inside of the layer accompanied with the C_{60}-Co compound formation, and the efficiency of the C_{60}-Co compound matrix as a growth barrier.

Figure 5 shows I–V curve at 4.2 K with a plot of logarithmic plot of resistivity (ρ) vs T^{−1/2} characterized under the small bias voltage of 7–1 V at 4.2–6.2 K and 0.2 V at 6.5–300 K (inset). The sample shows the strong nonlinear I–V characteristics which can be classified into two regions; lower and higher bias regions (LB and HB regions, hereafter) than a certain threshold bias voltage (V_T) of 50 V at 4.2 K. Here, the average voltage drop between Co nanoparticles is estimated to be a few meV at V = V_T from the particle number (n) of ~5 × 10^4 to the direction along to the applied bias between the electrodes, that is roughly estimated from the gap length of 250 μm, S ~ 3 nm and D = 3.1 nm. In the LB region, the V-dependent current increase is well describ-
magnetoresistance (MR) \( H \) curves in the LB and HB regions measured at \( V = 35 \) V and 67 V\(^{16} \) for comparison. In contrast to the saturated \( (M/M_s)^2 H \) curve, the MR-\( H \) curves exhibit non-saturating behaviors up to \( H = 10 \) kOe irrespective of the applied voltage. It is notable that the maximum of the both MR-\( H \) curves takes place at the magnetic field of 250 Oe that is smaller than \( H_C \) of 450 Oe. This suggests that the smaller Co nanoparticles in average than the magnetically characterized \( D \) are dominating the electrical conductivity. The dominated conductivity by the smaller Co nanoparticles might be associated with the non-saturating MR-\( H \) curves at high field.

Figure 6 shows examples of the MR(10 kOe) measured at 2 K, 4.2 K and 8 K\(^{16} \) respectively. The MR(10 kOe) at 4.2 K shows a decreasing tendency from 24% to the minimum value of 17% with increasing \( V \) in the LB region. The similar behavior is confirmed at the lower temperature (e.g., 2 K) also but disappears at the higher temperature (e.g., 8 K). On the contrary, the MR(10 kOe) increases monotonically up to the magnitude above 60% with increasing \( V \) in the HB region.

According to the Julliere’s model\(^{35} \), tunnel magnetoresistance in granular systems is given by \( MR = P^2/(1 + P^2) \), where \( P \) is spin-polarization at the Fermi level, for sequential tunneling.\(^{36} \) By considering the MR enhancement of less than 2 times by cotunneling process\(^{31,37} \) as suggested from the \( T^{-1/2} \) dependence of MR in the LB region,\(^{16} \) the model gives \( P \) larger than 50% for the MR(10 kOe) of 30% under the smallest \( V \) at 2 K. The magnitude of \( P \) is rather close to the reported one for Co crystal (~40%)\(^{38} \) and it is, therefore, reasonable to say that the spin-dependent transport in the LB region is basically attributed to the conduction electrons in Co nanoparticles.

The MR decrease with \( V \) in the LB region seems to be a similar behavior reported in the tunneling junctions of magnetic metal and metal oxide\(^{32,33} \) while the voltage drop between Co nanoparticles in the present case is two orders smaller than the reported voltage drops of 100’s of meV reported for the inorganic systems. The MR decrease with \( V \) might be interpreted by the \( V \)-dependent variations of the spin densities of states for the conduction electrons at the Fermi level in the metal.\(^{34} \) It can be surmised the larger MR decrease with \( V \) than inorganic systems to be relevant to the modification of electronic structure on the particle surface through the \( \pi-d \) hybridization with \( C_{60} \)\(^{39} \) in the \( C_{60}-Co \) compound.

The MR increase with \( V \) in the HB region is the peculiar behavior to the Co/\( C_{60}-Co \) film. The magnitude of MR in the HB region has reported to attain 50–80% at the low temperatures than 10 K\(^{16} \) as shown in Fig. 7 as examples. These values are anomalously high in granular systems and the MR(10 kOe) exceeds the upper-limit of MR = 50% under the condition of complete spin-polarization \( (P = \)
100%) in the sequential tunneling regime. The MR(10 kOe) of 50–80% gives anomalously high P roughly above 60–80% assuming the enhancement by cotunneling. The increase in conductivity in the HB region deviated from the relationship in the LB region (see Fig. 5) implies some change in the tunneling process above \( V = V_T \). The spin-dependent transport in the HB region might be associated with the highly spin-polarized molecular-like states generated in the \( C_{60}\)-Co compound as theoretically predicted for various organic molecule-TM systems\(^1\–^4\). As for the existence of such shallow mid-gap states, the \( C_{60}\)-Co compounds exhibit a small conductivity explained by the activated transport from the midgap states at less than one \( -10' \)s meV from the Fermi level\(^10\,\,12\) which is nearly equivalent to the interparticle voltage drop above a few meV (at \( V = V_T \)) in the HB region. Analytical and theoretical approaches to the electronic structure of the \( C_{60}\)-Co compounds itself and at the interface with Co crystal are indispensable to make obvious the electronic origin of the observed TMR effect, and are in progress.

4. Summary

A systematic study was performed for the alternately (alt-) deposited film of \( C_{60} \) and Co exhibiting high tunnel magnetoresistance (MR) of 10–80% at low temperature. The characterization of Raman spectral features, magnetic properties and electrical resistivity confirmed that the nano-\( C_{60}\)-Co film composed of well-dispersed Co nanoparticles with the average diameter of 3.1 nm and narrow size dispersion (\( \sigma \approx 1 \) nm) and a matrix of \( C_{60}\)-Co compound (\( C_{60}\)-Co\(_x\)) were synthesized by the alternate deposition of relevant materials. The bias voltage dependent MR showed an absence of the well-known proportional relationship between MR and squared magnetization. By evaluating the electrical charging energy from the temperature and bias voltage dependences of conductivity, it was suggested that the \( C_{60}\)-Co compound has a band gap much smaller than that in \( C_{60}\). The spin-dependent transport in the HB region might be associated with the highly spin-polarized molecular-like states generated in the \( C_{60}\)-Co compound.

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REFERENCES