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Magnetic and magnetotransport properties of pyromellitic dianhydride-4,4′-oxydianiline polyimide-Co granular thin films prepared by vapor deposition polymerization are investigated. The prepared sample is composed of Co particles with diameters of 2–3 nm homogeneously dispersed in a denatured polyimide matrix. The temperature dependence of the resistivity closely follows the $T^{-1/2}$ law, suggesting that the dominant conduction mechanism is tunneling between metallic granules embedded in the insulating polyimide matrix. The magnetoresistances at 300 and 90 K are 2.6% and 3.0%, respectively. The results indicate that polyimide is a promising material for organic spintronics. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4768783]

Recently, in the field of spintronics, organic materials have started to attract considerable attention as a mediator for spin dependent transport.[1] The reasons for this are, first, organic materials are superior at conserving the spin information during transport because their small spin-orbit interactions lead to a long spin relaxation time, and the spin diffusion length becomes extremely large. Second, from the view point of device applications, their unique physical property of plasticity enables the development of highly functional spintronic devices with flexibility, arbitrary shape, shock resistance, biocompatibility, etc. Since the pioneering work introducing organic semiconductors into spintronics,[2] various organic materials have been investigated.[1] The observation of large magnetoresistance in LSMO/Alq$_3$/Co sandwich structures,[3] in particular, has contributed to the rapid growth of the research field of *organic spintronics* spread rapidly. However, the number of investigations of organic spintronics is still much lower than that expected for such a diverse range of organic materials, and further extensive and efficient exploration of organic materials for spintronics is needed. Recently, we focused on pyromellitic dianhydride-4,4′-oxydianiline polyimide (PI) as a spin mediator. PI is well known as one of the *super engineering plastics* because of its exceptional properties such as thermal stability, chemical resistance, and high electrical insulation performance. If PI were well suited to spin transport, one could easily adapt it to practical spintronic devices because of its excellent performance and reliability.

Magnetic granular film, wherein magnetic nanoparticles are dispersed in an organic matrix, is a simple and reliable system for evaluating the suitability of an organic material for spin-dependent transport since it shows either giant magnetoresistance (GMR)[4] or tunneling magnetoresistance (TMR) effects,[5,6] depending on the electrical properties of the matrix. Various organic materials with granular systems have been examined in the literature, including tris(8-hydrixyquinoline) aluminum (Alq$_3$),[7] copper-phthalocyanine (CuPc),[8] rubrene,[9]

poly(3-hexylthiophene,2,5-diyl) (P3HT),[10] and polytetrafluoroethylene (PTFE).[11] Regarding granular systems with a PI matrix, however, to date, there has only been one report, by Popok *et al.*[12] They prepared PI-Co composite films by ion-implantation and showed a MR of less than 0.1%. Although their films had a granular structure,[13] the mechanism of electron transport in the films was not clear. In addition, the performance of the PI matrix as a spin mediator is completely hidden by the very small MR that probably results from the fabrication technique. In these circumstances, it is necessary to establish a fabrication process for PI-based granular systems with a fine structure.

We believe that the key to a well-defined PI-based granular film is to adopt the vapor deposition polymerization (VDP) technique[14] for the synthesis of the PI matrix. VDP is a completely dry process with co-evaporation of monomers in vacuum. Wet processes such as the Langmuir–Blodgett (LB) method,[15] and spin coating[16] are commonly used for the production of high-quality PI film. However, the VDP technique has the following important advantages over these wet processes: (i) magnetic metal particles do not suffer from contamination and oxidation because of the solvent-free process in vacuum, (ii) the film thickness can be precisely controlled by using quartz monitors, and (iii) a hybrid heterostructure can be created without breaking the vacuum in order to execute the next stage of the process. In this letter, we report the structural, electrical, magnetic, and magneto-transport properties of VDP-grown PI-Co granular films.

For the preparation of PI-Co granular films with the VDP technique, we built a high vacuum evaporation system equipped with two effusion cells to evaporate the monomers of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA), and three resistive heating boats for metal sources. The base pressure is on the order of 10^{-7} Torr. Cover glasses were employed for the substrates, on which a pair of 3000 μm-wide Cr/Au electrodes with a gap of 50 μm was evaporated beforehand. PI-Co granular films were then formed by the co-evaporation of the three sources Co, PMDA, and ODA at a substrate temperature of 60 °C. The

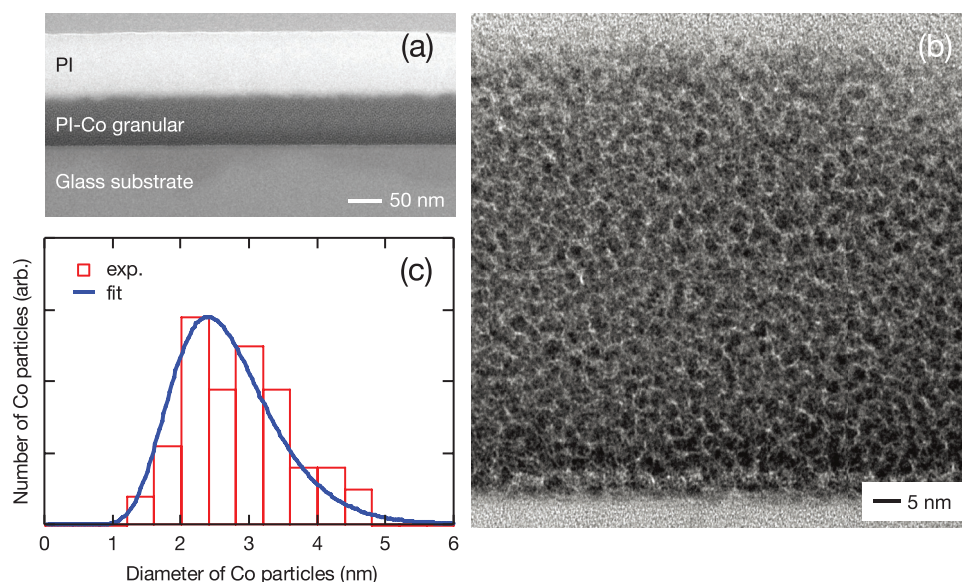a)Electronic mail: kita@bk.tsukuba.ac.jp.

FIG. 1. (a) Cross-sectional TEM image of the glass substrate/PI-Co granular/PI layers. (b) Magnified image of the PI-Co granular layer. (c) Histogram of the diameter of Co particles and the result of LNDF fitting.

deposition rates of the polyamic acid (PAA) and Co were 0.03–0.04 nm/s and 0.03 nm/s, respectively, where PAA is produced by the reaction of PMDA and ODA on the substrate. A 100 nm-thick PAA layer was successively deposited on the granular film for capping. After deposition, the samples were annealed in-situ at 200 °C for 1 h in order to polymerize the PAA into PI. The total designed thickness of the film was 58 ± 5 nm. Magnetization (M) was measured by using a SQUID magnetometer (Quantum Design's MPMS). The magnetotransport properties were evaluated with the standard dc four-probe method, with applied fields up to 90 kOe by using Quantum Design's PPMS. The molecular structure was determined by an attenuated total reflection infrared spectroscopy (ATR-IR) using a 500 nm-thick PI-Co granular film in order to increase the weak signals from polyimide or other organic species.

Figure 1(a) shows a cross-sectional TEM image of our sample. The interface between the PI-Co granular layer and the PI capping layer is well defined, indicating that there is no significant intermixing of the granular and the PI layers. Figure 1(b) is a magnified TEM image of the granular region. Co particles with diameters in the range of about 2–3 nm are homogeneously dispersed in the PI matrix. The particle-size distribution and the fit to the log-normal distribution function (LNDF) are plotted in Fig. 1(c). The average size of the Co particles is estimated to be 2.8 nm from the result of the fit.

Figure 2 shows the results of the ATR-IR measurements for the substrate, the 500 nm thick VDP-PI film (PI film fabricated with a conventional VDP technique), and the PI-Co granular film (the annealed co-evaporation film of monomers and Co). The five vertical dashed lines correspond to the vibration modes for the imide ring. The numbers above the lines indicate the correspondence to the vibration modes as follows: #1: C-N stretching mode or C-H rocking mode, #2: $(OC)_2$ symmetric stretching mode (Imide III), #3: C-N stretching mode (Imide II), and #4 and #5: out-of-phase C=O stretching mode and in-phase C=O stretching mode.[17,18] The spectrum of VDP-PI shows the existence of imide bonding, indicating that the PI film was properly synthesized with

co-evaporation of the monomers. On the other hand, in the spectrum of the PI-Co granular film, the #3 band corresponding to the C-N stretch mode in an imide ring was also clearly observed in the same manner as that of the VDP-PI film, indicating that polymerization by imidization occurred even with co-evaporation of monomers and Co.[19] The disappearance of C=O stretching modes from the carboxylic acid anhydride of PMDA at 1790 and 1850 cm^{-1} is consistent with this reaction.[14] However, there are three distinctive differences between the spectra of the VDP-PI and PI-Co granular films. First, bands #4 and #5 were not observed in the spectrum of the PI-Co granular film. Second, a broad structure was observed around 1500–1700 cm^{-1}, which is a superposition of amide groups (C=O stretching at 1650 cm^{-1} and N-H bending at 1550 cm^{-1} as determined from our PAA film) and an ionized carboxyl vibration mode of carboxyl groups complexes with metal ions (1500–1600 cm^{-1}), though, the absorbance of the C=O bonds of the amide groups is reduced.[20,21] Thus, it seems reasonable from these changes in the bands to presume that the PAA-Co complexes[20,21] and the C-O-Co complexes were created by replacing the original C=O bonds of PI[18,22] due mainly to the chemical reaction at the Co/PI
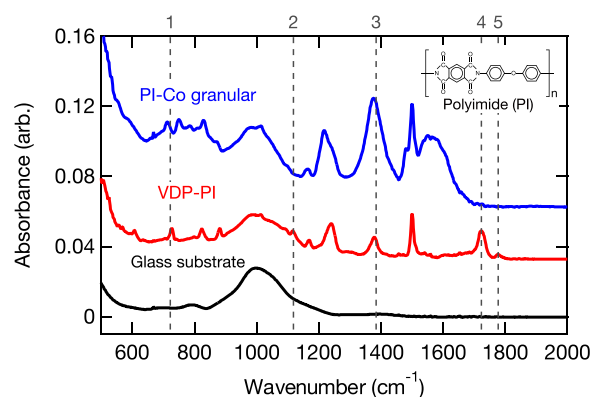

FIG. 2. ATR-IR spectra for the glass substrate (lower), glass/PI film (middle), and glass/PI-Co granular film (upper). The vertical dotted lines indicate bands corresponding to imide bonding in PI. The inset shows the molecular structure of PI.

interface.[23] Furthermore, new vibration modes at around 800 cm^{-1} and 1480 cm^{-1} were observed in the spectrum of the PI-Co granular film. These bands may be new chemical species resulting from the chemical reaction either between Co and PI or between Co and PAA.[19,23] Therefore, a matrix is believe to be formed in our granular film from denatured PIs which have Co-PI bonds and PAA-Co bonds.

Figure 3(a) shows magnetization curves plotted against the reduced fields of H/T, where temperature (T) and magnetic fields (H) were varied from 70 to 300 K and from 0 to 40 kOe, respectively. All data points seem to be on a single curve that follows the Langevin function. This fact indicates that Co particles are superparamagnetic, implying no significant interaction between the particles. The particle size estimated by the Langevin analysis is approximately 2.2 nm, which is consistent with that determined from the TEM image. The blocking temperature (T_B) obtained from the peak temperature in the zero-field-cooled (ZFC) M-T curve is about 20 K. Assuming that cobalt particles have a spherical shape and a diameter of 2.8 nm, one can estimate the magnetic anisotropy constant (K) from the relation[24] of $KV = 25k_BT_B$. The K was estimated to be 6.0×10^6 erg/cm^3 which is comparable to that of hcp-Co.

Figure 3(b) shows the temperature dependence of the resistivity in the PI-Co granular film. The resistivity increases exponentially with decreasing temperature. According to the tunneling conduction model for a granular film with an insulating matrix,[25] the temperature dependence of the resistivity (ρ) is expressed as

$$\ln \rho = 2\sqrt{\frac{T_0}{T}} + \text{const.} \qquad (1)$$

Here, T_0 is proportional to the charging energy of a metallic particle in the granular film (E_c) and is written as

$$T_0 = \frac{sE_c}{k_B}\sqrt{\frac{2m^*\phi}{\hbar^2}}, \qquad (2)$$

where s, ϕ, k_B, $\hbar$, and m^* stand for the inter-particle spacing, the barrier height, Boltzmann's constant, Planck's constant, and the effective mass of the electron, respectively. The inset in Fig. 3(b) shows a plot of $\ln\rho$ versus $T^{-1/2}$. A linear relationship between $\ln\rho$ and $T^{-1/2}$ is clearly observed, indicating that the dominant mechanism of electron conduction in the granular film is tunneling between Co particles. From the slope of the fitted line, T_0 is estimated to be 2200 K, which corresponds to an E_c of 6.7 meV, where $s = 3.0$ nm,[26] $\phi = 3.5$ eV,[15] and $m^* = 9.1 \times 10^{-31}$ kg (the mass of the free electron) are assumed. According to the spherical capacitor model, E_c is represented as

$$E_c = \frac{e^2}{4\pi\epsilon d}\frac{(s/d)}{1/2 + (s/d)}, \qquad (3)$$

where ϵ denotes the dielectric constant for PI. If one assumes $\epsilon/\epsilon_0 = 3.4$ ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m),[14] $d = 2.2$ nm (obtained from Langevin analysis), and $s = 3.0$ nm, E_c is calculated to be 141 meV, which is 21 times the value obtained from Eq. (2). This discrepancy partly results from the overestimation of E_c by Eq. (3), since, unlike in the spherical capacitor model, an actual particle in the granular film is not completely surrounded by a conductor. In addition, the values of ϕ and ϵ may be much smaller than those used for the estimation and the calculation, respectively, because the PI matrix of our granular film is denatured. By taking into account these factors, one may interpret the factor of 21 as being a reasonable estimate.

Figure 4(a) shows the MR curves measured at 90, 150, and 300 K. Here, the MR ratio is defined as $[R(H) - R(0)]/R(0)$. The MR ratios are 3.0% at 90 K, 3.2% at 150 K, and 2.6% at 300 K, respectively. If the granules are in the superparamagnetic state and have a small size distribution, the MR curve and the total magnetization process follow the simple relationship of $R(H)/R(0) \propto 1 - [M(H)/M_s]^2$, where M_s denotes the saturation magnetization.[27] Figure 4(b) shows a plot of $R(H)/R(0)$ against $[M(H)/M_s]^2$. $M(H)$ and M_s are obtained by fitting the magnetization curves in Fig. 3(a) with the Langevin function. At 90 K, the MR is nearly proportional to $[M(H)/M_s]^2$, meaning that the MR behavior corresponds to the magnetization process of the Co particles. Above 90 K, however, $R(H)/R(0)$ deviates from a straight line as the temperature increases, suggesting that the conduction paths via the Co particles with smaller size (larger E_c)
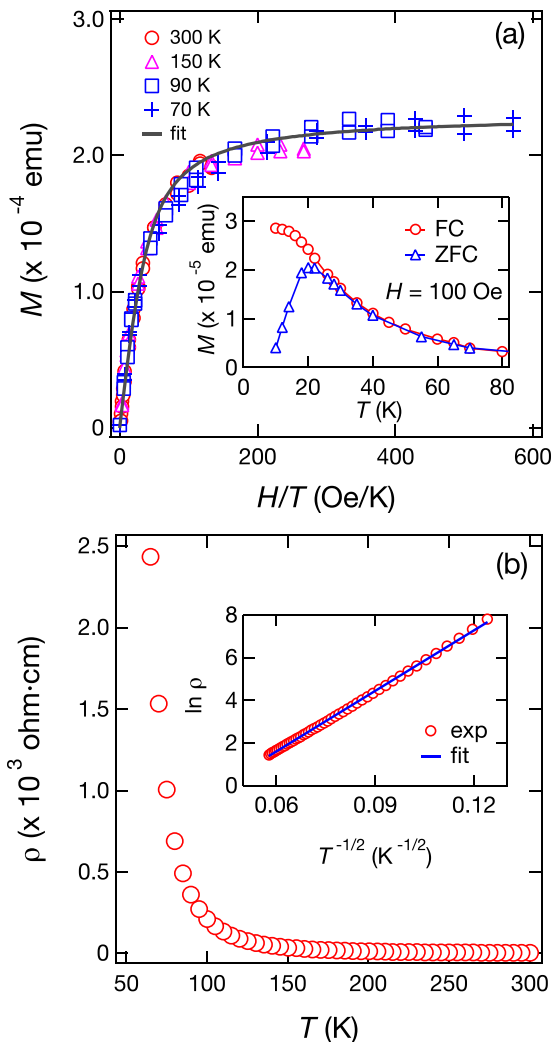

FIG. 3. (a) Magnetization curves plotted against the reduced field. The blue line indicates a fit to the Langevin function. The inset is a plot of FC and ZFC curves under a magnetic field of 100 Oe. (b) Temperature dependence of the resistivity.
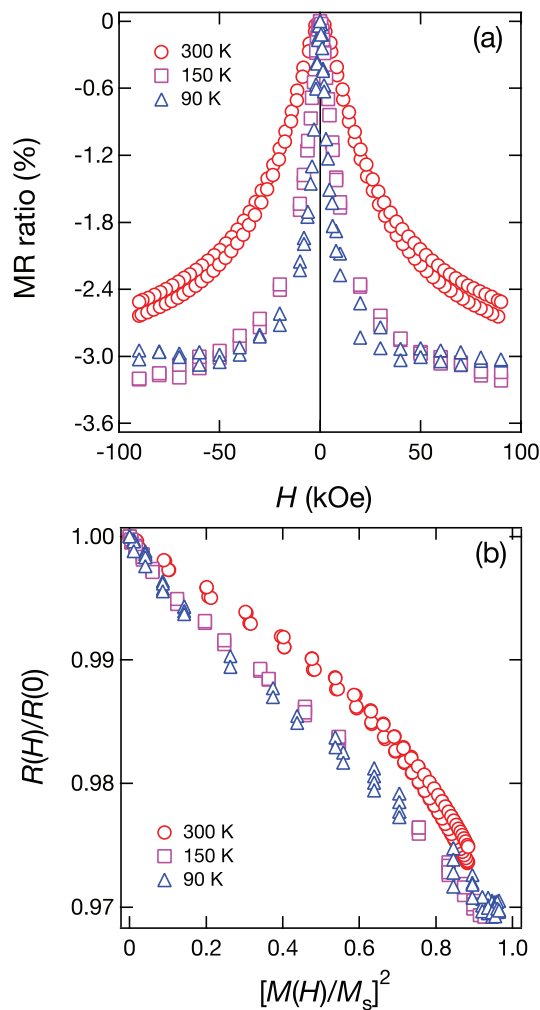
FIG. 4. (a) Magnetoresistance curves at temperatures ranging from 90 to 300 K. (b) $R(H)/R(0)$ versus $[M(H)/M_s]^2$ plots. Here, the M_s and $M(H)$ were obtained by fitting magnetization curves with a Langevin function at each temperature.

open with increasing temperature. Therefore, it is concluded that the observed magnetoresistance results from the spin-polarized tunneling of electrons between the Co particles through the matrix of the denatured PI. Although one might expect a maximum MR ratio of 12% from Julliere's model[28] ($MR = P^2$) using the spin polarization of the Co particles ($P = 0.34$),[29] the obtained MR ratio is 3% at room temperature even under a high field at which the magnetization is nearly saturated. This unexpectedly low MR ratio can be attributed to magnetic impurities existing in the matrix, in the same manner as a system of Al-O rich Co-Al-O granular films.[27,30] Since magnetically disordered Co atoms and/or particles may exist between the ferromagnetic particles, they may work as scattering centers causing spin-flip tunneling.

In conclusion, we have fabricated PI-Co granular films by a VDP technique and achieved a room-temperature MR of 2.6% at magnetic fields of 90 kOe. TEM observation and IR absorption spectra indicate that the Co particles were dispersed in the denatured PI. The electrical transport in the prepared sample was found to be governed by a tunneling process. The MR behavior is consistent with the magnetization processes when temperature-dependent channels between the small particles are considered. This indicates that the origin of the MR observed in our granular film is spin-polarized tunneling through the denatured PI. Although the observed MR ratio is smaller than that of a conventional inorganic matrix system at present (cf. 7.8% at RT for Co-Al-O[27]), room-temperature TMR in a well-defined PI-granular structure was achieved. Considering the excellent properties of bulk PI, the proposed VDP-synthesized PI film is a very promising tunneling barrier for organic spintronics.

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