Physical Properties of Metallofullerenes in Solid, Thin Film and Nanometer Scale

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The structures and physical properties of metallofullerenes are studied in solid, thin film and nanometer scale. The crystal structures of isomers I and II of M@C_{82} (M: Ba, Ce and Dy) have been determined by X-ray diffraction at ambient and high pressures. The crystals of isomers I of Ce@C_{82} and Dy@C_{82} take a simple cubic (sc) structure with the space group of $Pa\bar{3}$ at 290 K under ambient pressure. The Dy atom lies at the off-center position on the C_2 axis of the Dy@C_{82} molecule. The C_2 axis aligns along [111] of this crystal lattice. The thin films of M@C_{82} and Dy@C_{60} have been formed in order to study the electrical and optical properties. The thin films are characterized by XANES, EXAFS and Raman. The XANES and Raman show that the valence of the metal atoms is +3 in Ce@C_{82} and Dy@C_{82}. The EXAFS shows the same structural parameters for the thin films of Ce@C_{82} and Dy@C_{82} as those for the powder samples. This implies that the meatallofullerenes are not damaged by thermal deposition in forming the thin films. The resisitivity, ρ, of Dy@C_{82} and Ce@C_{82} shows a semiconductor-like temperature dependence; the temperature dependence of ρ for Dy@C_{82} is shown in Fig. 1. The energy gap, E_g's , of Ce@C_{82} and Dy@C_{82} have been estimated to be 0.4 and 0.2 eV, respectively. The E_g's are consistent with that, ~0.3 eV, determined by UPS and electronic absorption for La@C_{82}.[1,2] This implies that these metallofullerenes are narrow gap semiconductors. The field-effect transistors (FET's) have been fabricated with the thin films of metallofullerenes. The Dy@C_{82} thin-film FET shows an *n*-channel normally-on type property (Fig. 2). The electrical and optical properties of Dy@C_{60} have also been studied with the thin film.

The STM images of M@C_{82} and Dy@C_{60} adsorbed on Si(111)-(7X7) surface have been observed at 290 and 100 K. The STM shows a clear image of single molecule of these metallofullerenes. The height of Dy@C_{82} molecule determined by STM is 11.3 Å where the molecule is adsorbed on the first layer of Dy@C_{82}. The value is close to the van der Waals diameters along the C_2 axis and the another long axis of the Dy@C_{82} molecule. The van der Waals diameters of these axes are 11.3 – 11.4 Å, while the distance is ~10.8 Å for the short axis. Consequently, it has been concluded that either of the long axes in Dy@C_{82} is oriented along the direction perpendicular to the surface. This molecule has a dipole moment because the Dy is displaced from the center of the C_{82} cage. The dipole moment should affect the orientation of the molecule. The STS has been measured to determine the local electronic structures of metallofullerenes. The STS shows the E_g of 0.1 eV for Dy@C_{82} which is consistent with that, 0.2 eV, estimated from the ρ. The STS of metallofullerenes adsorbed on SiO_2/Si by applying the gate voltage is tried to realize the nanoscale FET.

1) B. Kessler et al., *Phys. Rev. Lett.* 79, 2289 (1997).
2) C. J. Nuttall et al., *Adv. Mater.* 14, 293 (2002).

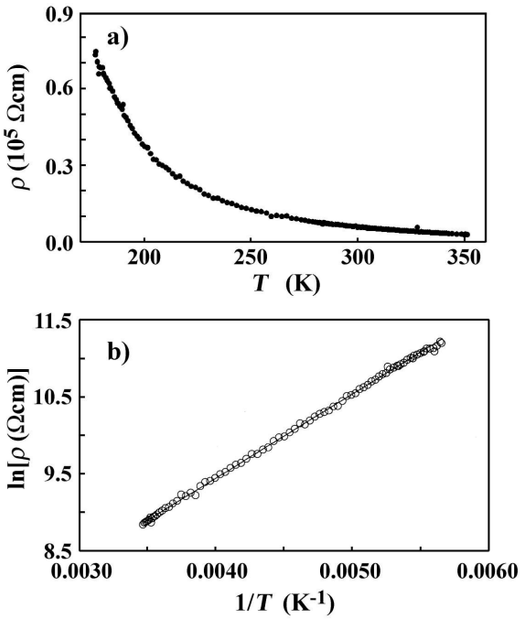

Fig. 1. (a) Temperature dependence of ρ in thin film of Dy@C_{82}, and (b) temperature dependence of lnρ.

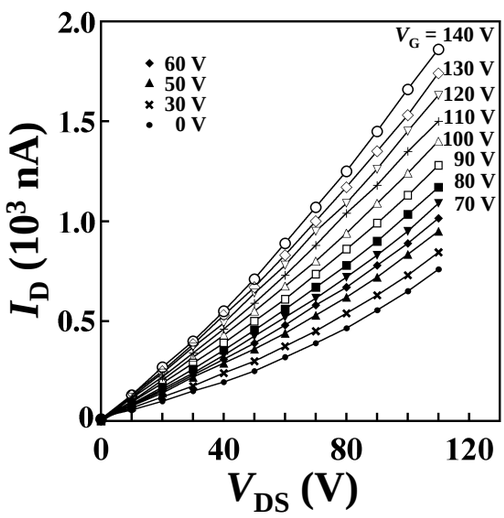

Fig. 2. I_D-V_{DS} plots of Dy@C_{82} thin-fIlm FET at 290 K.