VIII-Z Syntheses of Fullerene-Based New Materials with Novel Physical Properties and Their Application toward New-Generation Electronic Devices

Fullerene-based new materials are synthesized and their structures and electronic properties are studied in solid, thin film and nanometer scale. The crystal structures of metallofullerene solids are determined by Rietveld refinements for X-ray diffraction patterns with synchrotron radiation. The resistivity and field effect transistor (FET) characteristics are studied with thin films of metallofullerens and higher-fullerenes. Furthermore, the scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of metallofullerenes deposited onto the well-defined semiconducting surfaces are studied under ultrahigh vacuum.

VIII-Z-1 Crystal Structure and Electronic Transport of Dy@C_{82}

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The crystal structure of Dy@C_{82} isomer I at 298 K has been determined by Rietveld refinement for x-ray powder diffraction with synchrotron radiation. Isomer I shows a simple cubic structure (sc: $Pa\bar{3}$) with a lattice constant a of 15.78(1) Å. The C_2 axis of a C_{2v}-C_{82} cage aligns along the [111] direction of this crystal lattice. The C_{82} cage is orientationally disordered to satisfy a $\bar{3}$ symmetry along [111], which is requested in this space group. The large thermal parameter for the Dy atom estimated from the x-ray diffraction probably reflects a large disorder caused by a floating motion of the Dy atom inside the C_{82} cage as well as a ratchet-type motion of the Dy@C_{82} molecule. The electronic transport of thin film of Dy@C_{82} shows a semiconducting behavior. The energy gap E_g is estimated to be 0.2 eV. Further, the variation of valence from Dy^{3+} to Dy^{2+} is found by metal doping into the Dy@C_{82} crystals.

VIII-Z-2 Synthesis, Structure, and Magnetic Properties of the Fullerene-Based Ferromagnets, Eu_3C_{70} and Eu_9C_{70}

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Intercalation of C_{70} with europium affords two kinds of magnetic compounds, a canted antiferromagnet Eu_xC_{70}($x \approx 3$) and a ferromagnet Eu_xC_{70}($x \approx 9$) with transition temperatures (T_c) of 5 and 38 K, respectively. The Curie constants in the paramagnetic phase and the saturation moment in the ferromagnetic phase are both understood by the full moment of Eu^{2+} for both systems. The structure of $Eu_{3-\delta}C_{70}$ ($\delta \approx 0.27$) is pseudo-monoclinic, derived by a simple deformation of the parent face-centered cubic (*fcc*) structure. $Eu_{9-\delta}C_{70}$ ($\delta \approx 0.2$) forms an *fcc* structure, in which cuboctahedral clustering of Eu^{2+} ions is observed in the enhanced size octahedral holes. The observed T_c of the $Eu_{9-\delta}C_{70}$ ferromagnet is comparable to or larger than those of simple binary Eu-based ferromagnets, such as Eu chalcogenides or carbides, despite the low atomic ratio of Eu in the chemical formulas. This can be understood by the short Eu^{2+}–Eu^{2+} distances and high coordination numbers permitted by the multiple occupation by Eu^{2+} ions of the expanded octahedral interstitial sites in higher fullerene-based solids.

VIII-Z-3 Pressure-Induced Structural Phase Transition in Fullerides Doped with Rare Earth Metals

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[*Phys. Rev. B* **67**, 94101 (2003)]

Rare-earth-metal-doped fullerides with nominal composition of R_3C_{70} (R = Sm, Eu) adopt a pseudo-monoclinic structure in which C_{70} dimers glued with rare-earth ions are involved. High-pressure powder x-ray diffraction experiments revealed that these compounds undergo a reversible first-order structural phase transition at 1.5 GPa, associated with 2.7%–2.9% reduction of the unit cell volume. Structural analyses showed that the rare-earth ions, which are located close to the edge of tetrahedral sites at ambient pressure, move back to the center of the tetrahedral sites. Simultaneously, C_{70} molecules are realigned so that the fivefold (long) axes are perpendicular to the $(10\bar{1})$ or $(11\bar{1})_{fcc}$ plane at high pressure. The derived charge density map indicates that the transition is regarded as a structural change from dimers to three-dimensional polymers of fullerenes. These features are ascribed to the unique bonding nature in rare-earth C_{70} compounds.

VIII-Z-4 Molecular- and Atomic-Like Photoionization of C_{60} in the Extreme Ultaviolet

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[*Chem. Phys. Lett.* **374**, 1 (2003)]

Photoion yield spectra of C_{60} in the gas phase were measured from 23 to 180 eV by synchrotron radiation. Two peaks at 26 and 34 eV and a flat area ranging 40–50 eV are newly observed in the high-energy side of the giant resonance at ~ 20 eV. These features are assigned to the shape resonance on photoionization of the valence electrons of C_{60}; the ionized electron is temporarily trapped inside a centrifugal barrier. Above ~ 50 eV the yield curve shows a steady decrease with increasing photon energy like the photoabsorption cross section of atomic carbon. Thus, the spectrum is interpreted as essentially determined by photoionization of the 2*s* orbitals of carbon atoms.

VIII-Z-5 A Complex Fulleride Superstructure-Decoupling Cation Vacancy and Anion Orientational Ordering in $Ca_{3+x}C_{60}$ with Maximum Entropy Methods

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[*Chem. Mater.* **15**, 1830 (2003)]

The structure of the alkaline-earth fulleride $Ca_{3.01}C_{60}$ is refined using maximum entropy data analysis of synchrotron powder diffraction data. Despite the size and complexity of the structural problem, the fulleride anion orientations and the details of multiple occupancy of the octahedral interstitial sites in the fcc anion array are determined. The power of the maximum entropy technique in solving underdetermined problems in powder crystallography is thus demonstrated.

VIII-Z-6 Development of a Photoionizaion Spectrometer for Gaseous Fullerenes in the Extreme Ultraviolet

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[*Rev. Sci. Instrum.* **74**, 3769 (2003)]

A photoionization spectrometer has been developed for measuring the ion yields for fullerenes in the photon energy range of 23–200 eV. Gaseous fullerenes were supplied from a high-temperature oven, ionized by irradiation of monochromatized synchrotron radiation, and detected after analysis with a time-of-flight mass spectrometer. The fluxes of the synchrotron radiation and fullerene beams were monitored concurrently with the acquisition of the ion signal counts in order to obtain reliable photoionization efficiency curves. The performance of the apparatus was examined by measuring the efficiency curve of C_{60}^+ produced from C_{60}. The spectrum demonstrated better statistics than the previous results in the same photon energy region. Three distinct features were newly observed in the higher-energy side of the prominent resonance at ~ 20 eV.

VIII-Z-7 Structural and Electronic Properties of Ce@C_{82}

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[*Phys. Rev. B* **68**, 94104 (2003)]

X-ray diffraction patterns for a solid sample of Ce@C_{82} that contains a mixture of two isomers, I and II, can be indexed in a face-centered cubic lattice with a lattice constant of 15.88(5) Å, while x-ray diffraction patterns for Ce@C_{82} isomer I alone indicate a simple cubic lattice with a lattice constant of 15.78(1) Å. Rietveld refinement for the x-ray diffraction pattern of the latter, Ce@C_{82} isomer I, has been carried out with a space group of $Pa\bar{3}$. Thin films of Ce@C_{82} were first prepared by thermal deposition under ~ 10^{-7} Torr. The Raman spectra for these thin films show a peak ascribable to a Ce-C_{82} cage-stretching mode at ~ 160 cm^{-1}, implying that the valence of Ce in this structure is +3. This valence of +3 is supported by Ce L_{III}-edge XANES for a thin film of Ce@C_{82}. Furthermore, the local structure around the Ce ion could be determined by Ce L_{III}-edge EXAFS for a thin-film. Transport properties of a thin film of Ce@C_{82} have been studied by a four-probe method, and these demonstrate a semiconducting behavior with a small gap of 0.4 eV.

VIII-Z-8 N-Channel Field Effect Transistors with Fullerene Thin Films and Their Application to a Logic Gate Circuit

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[*Chem. Phys. Lett.* **379**, 223 (2003)]

N-channel field effect transistors (FETs) were fabricated with thin films of C_{60} and Dy@C_{82}. A typical enhancement-type FET property was observed in C_{60} FET above 220 K. The mobility of C_{60} FET increased with increasing temperature. This fact suggests hopping transport as the conduction mechanism, with the activation energy of 0.29 eV. The Dy@C_{82} FET was found to be a normally-on type FET, which has a property different from that for C_{60} and C_{70} FETs. A complementary metal oxide semiconductor (CMOS) logic gate circuit was first fabricated with C_{60} and pentacene thin-film FETs.

VIII-Z-9 Scanning Tunneling Microscopy of Dy@C_{82} and Dy@C_{60} Adsorbed on Si(111)-(7x7) Surfaces

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[*Phys. Rev. B* in press]

Dy@C_{82} and Dy@C_{60} adsorbed on Si(111)-(7×7) surface are investigated by scanning tunneling microscopy (STM) at 295 K. The Dy@C_{82} molecules in the first layer are adsorbed on Si(111)-(7×7) surface without formation of islands and nucleation, and the internal structure of the Dy@C_{82} molecule is first observed on the surface at 295 K. The average heights of the Dy@C_{82} molecule in the first and second layers are estimated to be 7.2 and 10.8 Å, respectively, by STM. These results suggest strong interactions between the Si atoms and the Dy@C_{82} molecules in the first layer. The STM image reveals that Dy@C_{60} molecule is nearly spherical, showing that the metal endohedral C_{60} possesses a cage-form structure.

VIII-Z-10 Preferred Locations of Metal Ions in Two M@C_{82} Isomers

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[submitted]

Location of metal ion in the minor isomer of M@C_{82} (M: metal ion with valence of +3) was determined for the first time by Dy L_{III}-edge EXAFS of Dy@C_{82}. The Dy ion lied near the fused bond between two hexagon rings. On the other hand, the EXAFS showed that the Dy ion in the major isomer of Dy@C_{82} lied near the center of a hexagon ring. The locations found in the minor and major isomers were consistent with those predicted theoretically for the respective isomers.

VIII-Z-11 Fabrication and Characterization of a New Type of Carbon Cluster Field Effect Transistor

SHIBATA, Kana[1]; KUBOZONO, Yoshihiro[2]; KANBARA, Takayoshi[1]; HOSOKAWA, Tomoko[1]; FUJIWARA, Akihiko[3]; SHINOHARA, Hisanori[4]; ITO, Yasuhiro[4]
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[submitted]

A new type of carbon cluster field effect transistor (FET) was fabricated with thin film of C_{84}, and *n*-channel normally-on depletion-type FET characteristics were found in this FET device. The C_{84} FET device exhibited the highest mobility, μ, of 1.3×10^{-3} $cm^2V^{-1}s^{-1}$ among normally-on carbon cluster FETs. The carrier transport of this FET device suggested a thermally-activated hopping transport. Carrier type (*n*-channel) and transport mechanism (hopping) reflect the electronic properties of the C_{84} molecule. This is the first report of the FET with higher-fullerene thin-film.

VIII-Z-12 Structural and Electronic Characterizations of Two Ce@C_{82} Isomers

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[submitted]

X-ray diffraction patterns for the Ce@C_{82} isomers I and II, which refer to major and minor isomers, respectively, are studied in a wide temperature region. The diffraction patterns observed at 295 K can be indexed based on a simple cubic (sc) structures with the lattice constants, *a*'s of 15.78(1) Å for the isomer I and 15.74(4) Å for the isomer II. Rietveld analyses are achieved for these X-ray diffraction patterns with a space group of $Pa\overline{3}$. Temperature dependence of *a* for the isomer I shows a drastic change around 150 K which implies an existence of structural phase transition. The structural phase transition above 300 K cannot be detected for the Ce@C_{82} isomer I in contrast with the fact that the phase transition at 400 K was previously reported for La@C_{82} isomer I by a differential scanning calorimetry and dielectric constant measurements. Temperature dependence of *a* for the isomer II indicates no structural phase transition from 100 to 300 K. Pressure dependence of *a* for the isomer I exhibits a monotonous decrease with an increase in pressure. This result implies no pressure-induced structural phase transition for the isomer I.