

## XPS and NEXAFS studies of C<sub>60</sub>-Co films with giant tunnel magnetoresistance

Seiji SAKAI\*<sup>1</sup>, Yoshihiro MATSUMOTO<sup>1</sup>, Hiroshi NARAMOTO<sup>1</sup>, Norie HIRAO<sup>2</sup>, Yuji BABA<sup>2</sup>,  
Toshihiro SHIMADA<sup>3</sup>, Yoshihito MAEDA<sup>1,4</sup>

<sup>1</sup>Advanced Science Research Center and <sup>2</sup>Synchrotron Radiation Center,

Japan Atomic Energy Agency, 2-4 Shirakata-Shirane, Tokai, Naka, Ibaraki 319-1195, Japan

<sup>3</sup>Department of Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-8654, Japan

<sup>4</sup>Department of Energy Science and Technology, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

In recent years, investigations on molecular spin electronics which control a transport of spin-polarized carrier through organic molecules including C<sub>60</sub>, carbon nanotubes (CNTs) and graphene have been performed intensively.[1] Very recently, we have found that C<sub>60</sub>-Co mixture films where Co nanoparticles are dispersed into a matrix of the C<sub>60</sub>-Co compound show the large tunnel MR effect of 80-90% at low temperature.[2,3] The observed MR ratios cannot be explained by the spin polarization of crystalline Co (~40%), and hence it is expected that the electronic and magnetic structures of the C<sub>60</sub>-Co compound play a significant role to the spin-dependent transport in the C<sub>60</sub>-Co films. In the present work, we studied about local electronic states of the C<sub>60</sub>-Co films by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. [4]

C<sub>60</sub>-Co mixture films were prepared by the co-deposition method under the UHV condition (10<sup>-7</sup>Pa). The experimental set-up for co-deposition consists of a Knudsen-cell for C<sub>60</sub> (99.99%, sublimated) and an electron beam evaporator for Co (99.99%). The C<sub>60</sub>-Co films with compositions of C<sub>60</sub>Co<sub>x</sub> (x: the number of Co atoms per a C<sub>60</sub> molecule), and thickness of 50 nm were deposited on Ag films on MgO (001). A pure C<sub>60</sub> film was prepared in a similar way. The prepared samples were transferred to an experimental chamber without breaking the UHV condition. XPS measurements were performed at Photon Factory BL-27A of High Energy Accelerator Research Organization (KEK-PF) employing Mg K<sub>α</sub> (hν=1253.6eV) and Y M<sub>ζ</sub> (hν=132.3eV) X-ray sources. NEXAFS measurements were performed at BL-7A of KEK-PF. The NEXAFS spectra were obtained by the total electron yield method.

Figure 1 and 2 show the XPS spectra in the valence region and the C1s NEXAFS spectra for the C<sub>60</sub> film and the C<sub>60</sub>-Co film (C<sub>60</sub>Co<sub>3</sub>) composed of the C<sub>60</sub>-Co compound.[5] In Figure 1, five peak components (A<sub>1</sub>-A<sub>5</sub>) associated with the molecular orbitals (MOs) of C<sub>60</sub> are confirmed in the C<sub>60</sub> film. In the C<sub>60</sub>-Co films, the A<sub>3</sub>-A<sub>5</sub> peaks lying in the range of E<sub>B</sub> = 5-9eV show comparable shifts from the positions in the C<sub>60</sub> film. Meanwhile, the structure close to the Fermi level (E<sub>B</sub><5eV) shows significant differences from the C<sub>60</sub> film, as represented by the peak components of B<sub>1</sub>-B<sub>5</sub>. The B<sub>2</sub> and B<sub>4</sub> peaks seem to be corresponding to the A<sub>1</sub> and A<sub>2</sub> peaks from the shifted quantities. Investigations on the C<sub>60</sub>-Ti and C<sub>60</sub>-Rb composites [6,7] have pointed out that, when metal atoms form covalent bonds with carbon atoms, new

peaks appear close to the Fermi level (E<sub>B</sub>~3-5eV) or close to the HOMO level of C<sub>60</sub> (A<sub>1</sub>). Judging from these reported results, the observed peaks of B<sub>1</sub>, B<sub>3</sub> and B<sub>5</sub> in the C<sub>60</sub>-Co film are reasonably ascribed to the hybridized states between the C<sub>60</sub> π and Co 3d orbitals. The comparable shifts of the A<sub>3</sub>-A<sub>5</sub> peaks in the C<sub>60</sub>-Co film indicate the cage distortion of C<sub>60</sub>, possibly by the hybridized bond formation. The π-d hybridization is confirmed in the absorption spectra. In Figure 2, the first peak of the C<sub>60</sub>-Co film is shifted toward the higher energy side and the peak width is wider than the LUMO peak of the C<sub>60</sub> film. This peak broadening and shift indicate the formation of the covalent bonds with the charge transfer (back donation) between C<sub>60</sub> π and Co 3d orbitals.

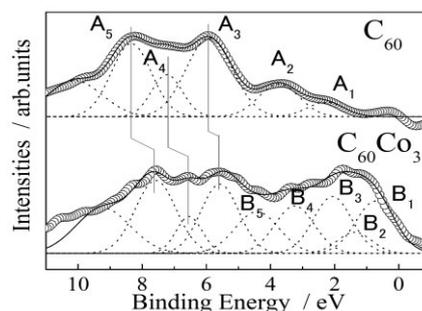


Figure 1 XPS spectra of the C<sub>60</sub> and C<sub>60</sub>-Co films (C<sub>60</sub>Co<sub>3</sub>) in the valence region

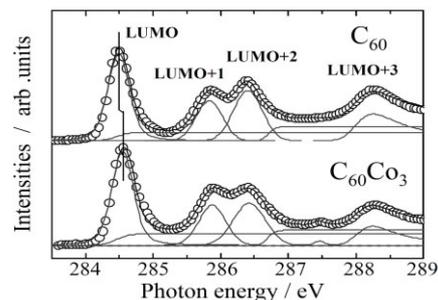


Figure 2 NEXAFS spectra of the C<sub>60</sub> and C<sub>60</sub>-Co films (C<sub>60</sub>Co<sub>3</sub>) by C1s core excitation.

- [1] W. J. M. Naber et al., J. Phys. D, **40** R205 (2007).
- [2] S. Sakai et al., Appl. Phys. Lett. **89** 113118 (2006).
- [3] S. Sakai et al., Appl. Phys. Lett. **90** 242104 (2007).
- [4] Y. Matsumoto et al., Mater. Res. Soc. Symp. Proc. *in press*.
- [5] S. Sakai et al., Thin Solid Films **515** 7758 (2007).
- [6] M. Nyberg et al., Phys Rev. B **63** 115117 (2001)
- [7] S. Satpathy et al., Phys. Rev. B **46** 1773 (1992).

\* sakai.seiji@jaea.go.jp