XPS and NEXAFS studies of C_{60}-Co films with giant tunnel magnetoresistance

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In recent years, investigations on molecular spin electronics which control a transport of spin-polarized carrier through organic molecules including C_{60}, carbon nanotubes (CNTs) and graphene have been performed intensively.[1] Very recently, we have found that C_{60}-Co mixture films where Co nanoparticles are dispersed into a matrix of the C_{60}-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_{60}-Co compound play a significant role to the spin-dependent transport in the C_{60}-Co films. In the present work, we studied about local electronic states of the C_{60}-Co films by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.[4]

C_{60}-Co mixture films were prepared by the co-deposition method under the UHV condition (10^-10 Pa). The experimental set-up for co-deposition consists of a Knudsen-cell for C_{60} (99.99%, sublimated) and an electron beam evaporator for Co (99.99%). The C_{60}-Co films with compositions of C_{60}Co_y (x: the number of Co atoms per a C_{60} molecule), and thickness of 50 nm were deposited on Ag films on MgO (001). A pure C_{60} 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 Kα (hv=1253.6eV) and Y M₄ (hv=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_{60} film and the C_{60}-Co film (C_{60}Co_y) composed of the C_{60}-Co compound.[5] In Figure 1, five peak components (A₋₅) associated with the molecular orbitals (MOs) of C_{60} are confirmed in the C_{60} film. In the C_{60}-Co films, the A₋₅ peaks lying in the range of E_B≈5-9eV show comparable shifts from the positions in the C_{60} film. Meanwhile, the structure close to the Fermi level (E_B<5eV) shows significant differences from the C_{60} film, as represented by the peak components of B₋₅. The B₋₅ peaks seem to be corresponding to the A₋₅ peaks from the shifted quantities. Investigations on the C_{60}-Ti and C_{60}-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_B≈3-5eV) or close to the HOMO level of C_{60} (A₋₅). Judging from these reported results, the observed peaks of B₋₅, B₋₅ in the C_{60}-Co film are reasonably ascribed to the hybridized states between the C₋₅ π and Co 3d orbitals. The comparable shifts of the A₋₅ peaks in the C_{60}-Co film indicate the cage distortion of C_{60}, possibly by the hybridized bond formation. The π₋₅ hybridization is confirmed in the absorption spectra. In Figure 2, the first peak of the C_{60}-Co film is shifted toward the higher energy side and the peak width is wider than the LUMO peak of the C_{60} film. This peak broadening and shift indicate the formation of the covalent bonds with the charge transfer (back donation) between C₋₅ π and Co 3d orbitals.

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