Atomic visualization of cleaved bimetal-intercalated graphite superconductor by photoelectron holography

Graphite intercalation compounds (GICs are old and new superconducting materials. The highest transition temperature (T_c) value for the GIC superconductors at ambient pressure is currently 11.5 K for CaC_6 [1]. Other than the confirmation of T_c at 65 mK for BaC_6 in 2015, the members of the GIC superconductor family have remained unchanged for many years. Recently, a new series of bimetal-intercalated graphite superconductors, $Ca_xK_{1-x}C_y$, has been successfully fabricated by a group at Okayama University [2]. As K and Ca atoms intercalated, a graphite flake became a golden superconducting compound (Fig. 1). The T_c of KC_8 was only 136 mK, but the introduction of a very small amount of Ca drastically increased this value. T_c for $Ca_xK_{1-x}C_y$ continuously increased to 11.5 K ($x = 1$; CaC_6) as x increased [2].

The direct visualization of three-dimensional (3D) atomic arrangements around intercalant atoms is essential to clarify the superconducting mechanism. X-ray diffraction is a standard method of determining bulk crystal structures, but it is not suitable for the local structure analysis of nonperiodic alloy compounds. Moreover, the cleaved surface of GICs is readily degraded by moisture and oxygen in the atmosphere. The local structure around the intercalant atoms of bimetal GIC superconductors has remained unclear.

Optical holograms are widely used in our daily lives as security devices on credit cards, for example. 3D structure information can be recorded in an optical hologram based on the wavelike nature of light. Similarly, the 3D atomic arrangement can be recorded using an electron wave [3]. A photoelectron wave emitted from an atom by X-ray excitation is partially scattered by the surrounding atoms. As a result, an interference pattern between direct and e waves, a *photoelectron hologram*, is formed. Photoelectron holography (PEH) is a powerful method for studying surface and subsurface atomic structures in 3D owing to the short probing depth of photoelectrons. Recently, we have developed a new holography algorithm, the scattering pattern-extraction algorithm (SPEA)-maximum entropy method (MEM) for reconstructing atomic arrangements [4]. In this method, the 3D images of atomic arrangements around a photoelectron emitter atom are directly obtained from element-specific holograms.

Photoelectron spectrum and hologram measurements were carried out [5] using a two-dimensional display-type analyzer installed at the circularly polarized soft X-ray beamline **BL25SU**, SPring-8. A superconducting $Ca_{0.11}K_{0.89}C_{7.1}$ sample ($T_c = 9.9$ K) has recently been prepared by Kubozono's group. We made a vacuum sample transfer system for transfer between Okayama and SPring-8 in order to prevent the degradation of the samples cleaved at the laboratory in inert Ar gas. The photoelectron spectra of this cleaved surface showed only C 1*s* and K 2*p* peaks, and the Ca 2*p* peak intensity was less than a few hundredths of that of the K 2*p* peak. The observation of the K dominant structure at the cleaved surface implies that Ca atoms are dispersed in the bulk and likely form high T_c domains.

Figures 2(a) and 2(b) show full-hemisphere C 1*s* and K 2*p* photoelectron holograms obtained at a kinetic energy of 600 eV. The incidence direction of the soft X-ray was aligned along the surface normal. From these holograms, we directly reconstructed atomic images from the few-layer region of the cleaved surface. Atomic images of the graphene were collected

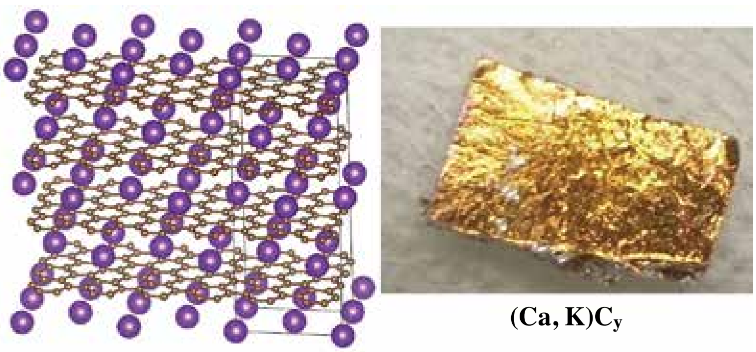

Fig. 1. **(a)** KC_8 crystal structure. **(b)** Photograph of (Ca,K)C_y sample.

in the in-plane cross sections of the layers 3.3 Å and 5.7 Å above the photoelectron emitter C atom and the stacking structures were determined as *AB*- and *AA*-type, respectively. An intercalant metal atom layer was found between two *AA*-stacked graphenes. The K atomic image revealing 2×2 periodicity, occupying every second center site of C hexagonal columns, was reconstructed as shown in Figs. 2(c) and 2(d).

These observations revealed that the cleavage preferentially occurs at the K atom intercalated layers containing no Ca atoms, which are likely the most fragile part of the crystal sample. The most important result of the present study is that the cleaved surface does not always represent the average bulk structure. The structure and composition of the surface and the bulk can be substantially different, especially in a layered system. Special attention must therefore be paid when using surface-sensitive methods, such as photoelectron spectroscopy and scanning probe microscopy.

A surface phonon is often softened by bulk truncation, structure modification, and interaction with adsorbates. Recently, the superconductivity of In and Pb monoatomic layers and GIC and FeSe ultrathin films on surfaces has been discovered and has attracted substantial fundamental interest. The crystal sizes of newly developed functional materials are often very small and the densities of impurity atoms playing important roles are low. As mentioned above, PEH is one of the most effective methods for studying surface and subsurface atomic structures in 3D. Our technique for directly visualizing atomic arrangements by element-selective PEH is expected to be a powerful tool for developing new superconducting materials.

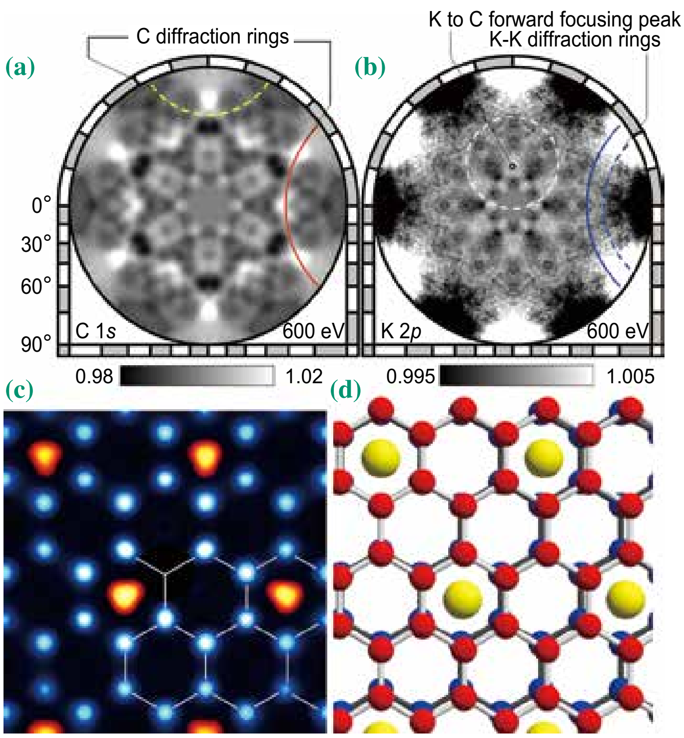

Fig. 2. **(a)** C 1*s* and **(b)** K 2*p* photoelectron intensity angular distributions (holograms) obtained from (Ca,K)C_y. Diffraction contrasts are indicated by gray scale. **(c)** Images showing atomic arrangements of C (blue) and K (orange) layers. **(d)** Structure model of the cleaved surface region of (Ca,K)C_y.

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