SOFT X-RAY PHOTOELECTRON SPECTROSCOPY IN SILICON CLATHRATE SUPERCONDUCTORS

Silicon clathrate compounds consist of fullerene-like polyhedral Si-cages, which share their faces to form a three-dimensional Si-sp^3 covalent network. Guest elements such as an alkali atom or an alkali-earth one can be encapsulated in the cage. Recently, these compounds have attracted strong interest due to the discovery of superconductivity in a metal-doped silicon clathrate, $Ba_6Na_2Si_{46}$ [1], as well as the potential for thermoelectric applications.

Barium encapsulated type-I silicon clathrate, Ba_8Si_{46}, has been reported to show superconductivity below $T_c \sim 8$ K [2], which is the highest T_c observed in the silicon clathrate family. As schematically shown in Fig. 1, the crystal structure of Ba_8Si_{46} consists of two types of polyhedral cages, *i.e.* dodecahedral (Si_{20}) and tetrakaidecahedral (Si_{24}) cages. In an ideal-composition phase, Ba atoms occupy all of the cages resulting in the chemical formula of Ba_8Si_{46} per cubic unit cell. In Ba_8Si_{46}, we can substitute Ag atoms for Si atoms in 'Si (1)' sites shown in Fig. 1, where the chemical formula becomes $Ba_8Ag_xSi_{46-x}$ ($0 \leq x \leq 6$). The solid solution of Si and Ge clathrate, $Ba_8Ge_ySi_{46-y}$ ($0 \leq y \leq 40$), and pure germanium clathrate Ba_8Ge_{43} also have been synthesized. In both cases, the superconducting transition temperature T_c has been found to systematically decrease with increasing Ag or Ge concentration.

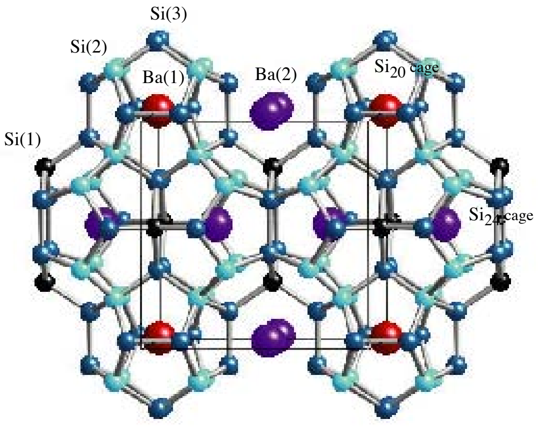

Fig. 1. Schematic illustration of crystal structure of silicon clathrate Ba_8Si_{46}. Two types of fullerene-like polyhedral cages, i.e. Si_{20} and Si_{24} cages, share their faces to form the sp^3 covalent network. A Ba atom is encapsulated in each cage.

Photoelectron spectroscopy (PES) allows us to directly observe the electronic structures in the valence band in addition to the core electrons in solid substances. Recently, it has been recognized that high-resolution PES using relatively high-energy soft X-ray is quite a powerful tool for investigating the bulk-states of solids. In the present study [3], PES was carried out by using a synchrotron radiation soft X-ray to investigate the electronic structure of silicon clathrate family. The relationship between the electronic structure and the systematic change of superconducting nature of silicon clathrate family is discussed.

Polycrystalline samples of clathrates $Ba_8Ag_xSi_{46-x}$ ($0 \leq x \leq 6$), $Ba_8Ge_ySi_{46-y}$ ($0 \leq y \leq 40$) and Ba_8Ge_{43} (pure germanium clathrate) were prepared by using a high-pressure synthesis technique as reported in previous works [1, 2]. Photoelectron spectra were measured at beamline **BL25SU** with various photon energies $h\nu$ between ~ 240 and ~ 1200 eV. The total energy resolution was ~ 150 meV at $h\nu \sim 800$ eV. Samples were cooled down to 20 K. obtain clean surfaces, samples were fractured under the ultrahigh vacuum of $\sim 1 \times 10^{-10}$ Torr just before the measurements were taken.

The valence-band photoelectron spectra of Ba_8Si_{46} are shown in Fig. 2. The horizontal axis indicates the binding energy E_B, where 0 eV corresponds to the Fermi energy E_F. Red and blue dots are measured by using excitation photon energy of $h\nu \sim 785$ and ~ 776 eV, respectively. The former corresponds to the Ba 3*d* to 4*f* transition energy, called ‘on resonance,’ and the latter is below the Ba 3*d* to 4*f* transition energy, called ‘off resonance.’ The letters A-D indicate four prominent structures. The overall spectral shape is similar to the density of states (DOS) calculated by using local density approximation (LDA) [4]. The structures A-C are assigned to the *s* -, *sp* - and *p*-like bands characteristics to the sp^3 bonded Si_{46} network. The extremely narrow band D, with the width of ~ 0.3 eV, is seen beside the *p* -band with a gap of ~ 1.2 eV. In a previous work [5], however, ultraviolet photoelectron spectra (UPS) showed a broad extra peak in the gap between C and D. It was proposed that the discrepancy between the UPS and the calculated DOS were caused by electron-correlation effects. The UPS, however, may include surface-state components due to a short photoelectron mean free path.

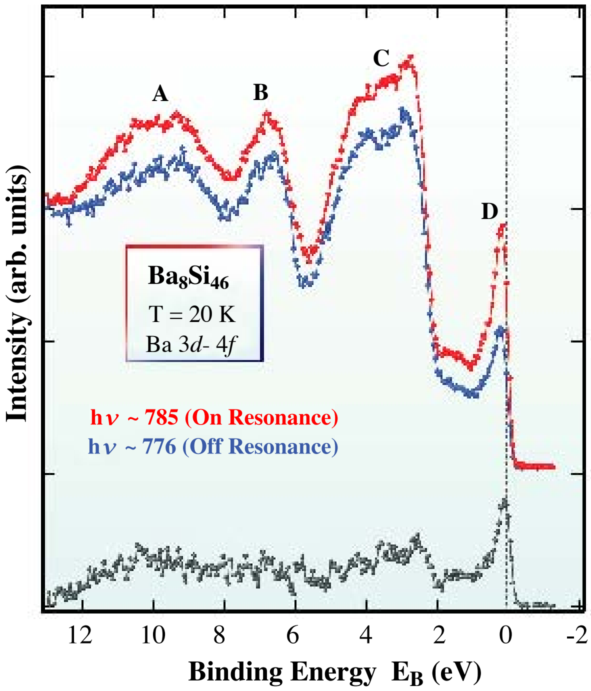

Fig. 2. Valence-band photoelectron spectra of silicon clathrate Ba_8Si_{46}. Red and blue dots are measured by using excitation photon energy of hν~ 785 and ~ 776 eV, respectively. The former corresponds to the Ba 3d to 4f transition energy, called ‘on resonance,’ and the latter is below the Ba 3d to 4f transition energy, so called ‘off resonance.’ The black dots show the difference spectrum between the ‘on resonance’ and the ‘off resonance’ spectra.

The present results, which are more bulk-sensitive spectra, basically support the LDA calculation, indicating that the electron-correlation effects are not so strong in Ba_8Si_{46}. It is noticed that the Fermi level E_F is located at the band D, resulting in the high DOS at E_F. The black dots in Fig. 2 show the difference spectrum between the ‘on resonance’ and the ‘off resonance’ spectra. Generally speaking, this spectrum corresponds to the Ba related partial DOS in the valence band. The band D is obviously enhanced by the Ba 3*d* - 4*f* resonance excitation; therefore, it is confirmed that the Ba orbital strongly contributes to the band D. The LDA calculation has predicted the narrow band at E_F, constructed by a hybridization of Ba 5*d* orbital and the conduction band of the Si_{46} network. The high DOS at E_F is expected to be responsible for the relatively high T_c in terms of the Bardeen-Cooper-Schrieffer (BCS) theory for phonon-mediated superconductivity. Furthermore, Ba-related states seem to spread widely over in the valence band, as seen in the difference spectrum in Fig. 2. It may originate from the hybridization between *s*-like state of Ba and valence band of the Si_{46} network.

The valence-band photoelectron spectra of $Ba_8Ag_xSi_{46-x}$, $Ba_8Ge_ySi_{46-y}$ and Ba_8Ge_{43} are shown in Fig. 3. The intensity of the band D systematically decreases with increasing Ag concentration in $Ba_8Ag_xSi_{46-x}$, as seen in the lower half of Fig. 3. Simultaneously, new states appear between the C and D bands at E_B = 0.5 ~ 2 eV, whose intensity increases with the Ag concentration. Similar phenomena are also observed in the solid solution of Si and Ge clathrate as shown in the upper half of Fig. 3. In Fig. 4, the superconducting transition temperature T_c of clathrates is plotted as a function of the integrated intensity of the band D. It is clear that the sample with higher T_c has a band D with higher intensity. The decrease in the intensity of the band D means the decrease in DOS at E_F. This must be responsible for the decrease in T_c in the clathrates, $Ba_8Ag_xSi_{46-x}$ and $Ba_8Ge_ySi_{46-y}$, in terms of the BCS theory.

The core level spectra of Si 2*p*, Ag 3*d* and Ba 4*d* show systematic change with increasing x in $Ba_8Ag_xSi_{46-x}$. From the analysis of the chemical shift of core level spectra, it is found that there is systematic electron transfer from Ba atoms to the Ag + Si network with increasing x. This may weaken the hybridization between Ba and the Si network, resulting in the decrease of the band D. The new state at E_B = 0.5 ~ 2 eV may be constructed by acceptor states originating from the Ag and Si hybridization in $Ba_8Ag_xSi_{46-x}$. On the other hand, in $Ba_8Ge_ySi_{46-y}$ and Ba_8Ge_{43}, the core level spectra of Ge 3*d* and Ba 4*d* show systematic change with increasing the Ge concentration. The Si 2*p* spectra, however, does not show any change. The new states at E_B = 0.5 ~ 2 eV may be constructed by the Ge and Ba hybridization, in $Ba_8Ge_ySi_{46-y}$ and Ba_8Ge_{43}. Consequently, the weakened hybridization between Ba and Si network results in the decrease in the band D.

In conclusion, we have investigated the electronic structure of silicon clathrate superconductors by using the bulk-sensitive PES. We have clarified the relationship between the electronic structure and the systematic change of superconducting nature of the silicon clathrate family.

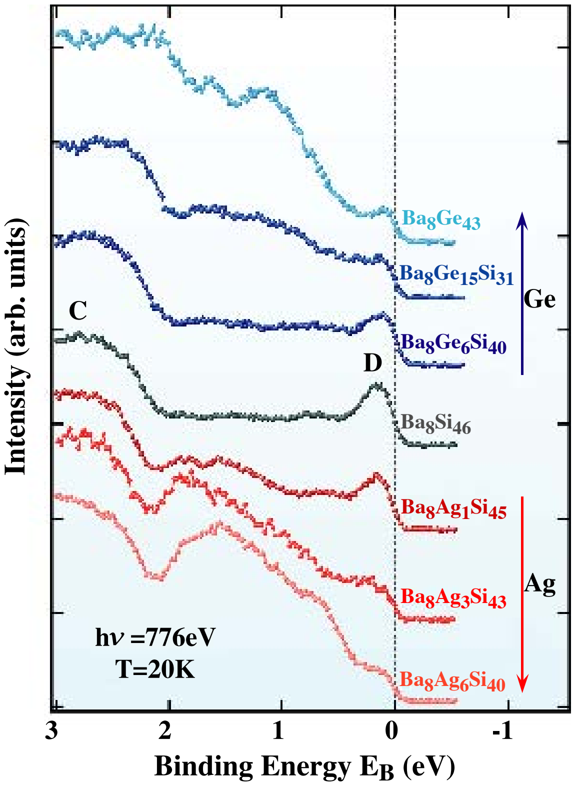

Fig. 3. Valence-band photoelectron spectra of silicon clathrates $Ba_8Ag_xSi_{46-x}$, $Ba_8Ge_ySi_{46-y}$ and Ba_8Ge_{43} measured by using excitation photon energy of hν ~ 776 eV.

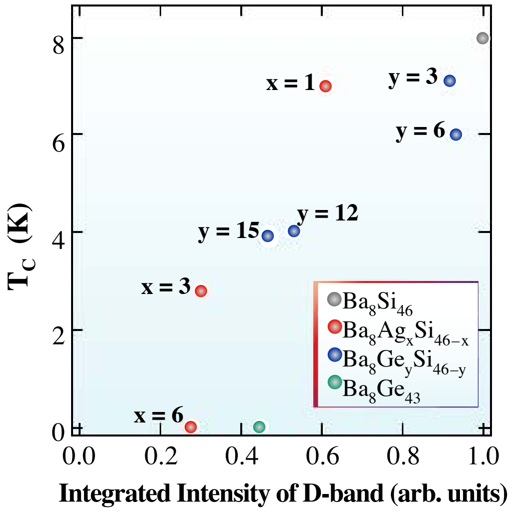

Fig. 4. Relationship between the superconducing transition temperature T_C and the intensity of the band D (see Fig. 2 and 3) in valence-band photoelectron spectra of silicon clathrates $Ba_8Ag_xSi_{46-x}$, $Ba_8Ge_ySi_{46-y}$ and Ba_8Ge_{43}.

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