

## Visualization of Band Structure in a Powdered Crystal by Micro-Focused ARPES

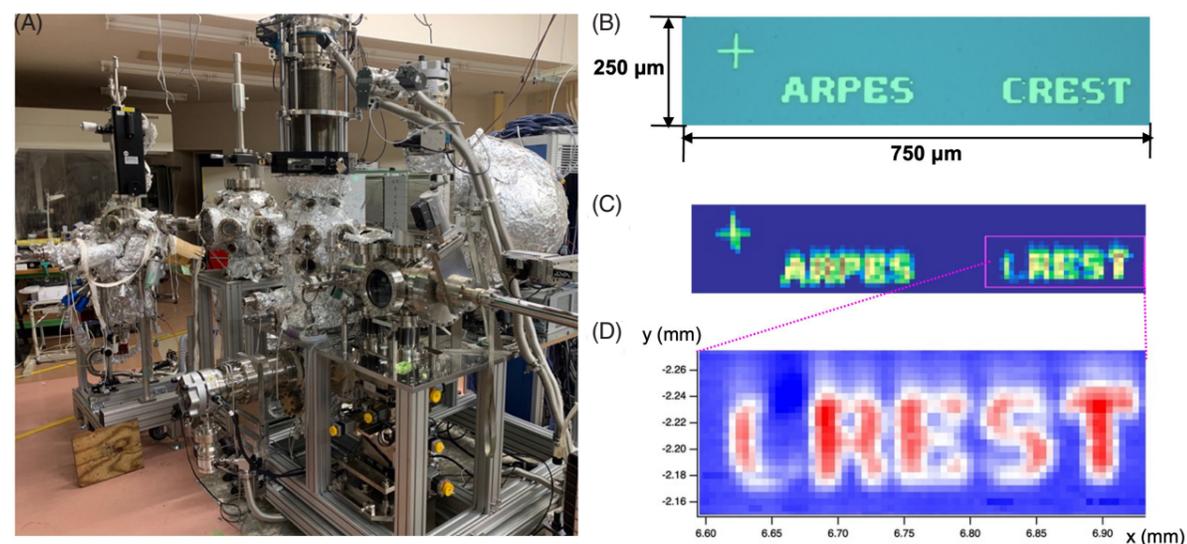
We demonstrate that angle-resolved photoemission spectroscopy using a micro-focused synchrotron beam spot (micro-ARPES) is a powerful tool to elucidate the band structure in tiny powdered samples. By utilizing the state-of-the-art micro-ARPES system developed at BL-28A, we demonstrate a direct imaging of the band structure in a powdered tiny ( $\sim 20 \times 20 \mu\text{m}^2$ ) semiconductor rhombohedral boron monosulfide, r-BS. We found that r-BS is a  $p$ -type semiconductor characterized by quasi-two-dimensional band structure with a band gap exceeding 0.5 eV. The present result shows the high applicability of micro-ARPES to tiny powder crystals, and expands an opportunity for revealing the electronic states of various tiny materials.

Development of boron-based two-dimensional (2D) materials is a current challenge in materials science since they are expected to show novel quantum properties such as superconductivity and massless Dirac fermions. Recently, r-BS is attracting great deal of attention as a new type of layered boride [1]. r-BS crystal has  $R\bar{3}m$  symmetry and consists of periodically stacked 2D sheets of B and S atoms. It has been theoretically predicted that the 2D BS sheet exhibits various functional properties such as high hydrogen storage, high thermal conduction, and efficient photocatalysis. On the other hand, there exist no experimental outputs on the band structure even for bulk r-BS because the obtained bulk single crystals are very small and powder-like (grain size of less than 30 nm), hindering an access by spectroscopy techniques such as photoemission spectroscopy. Although the determination of band structure for such a tiny powder crystal with conventional ARPES is almost impossible, we have overcome this difficulty by utilizing a micro-focused photon-beam [2].

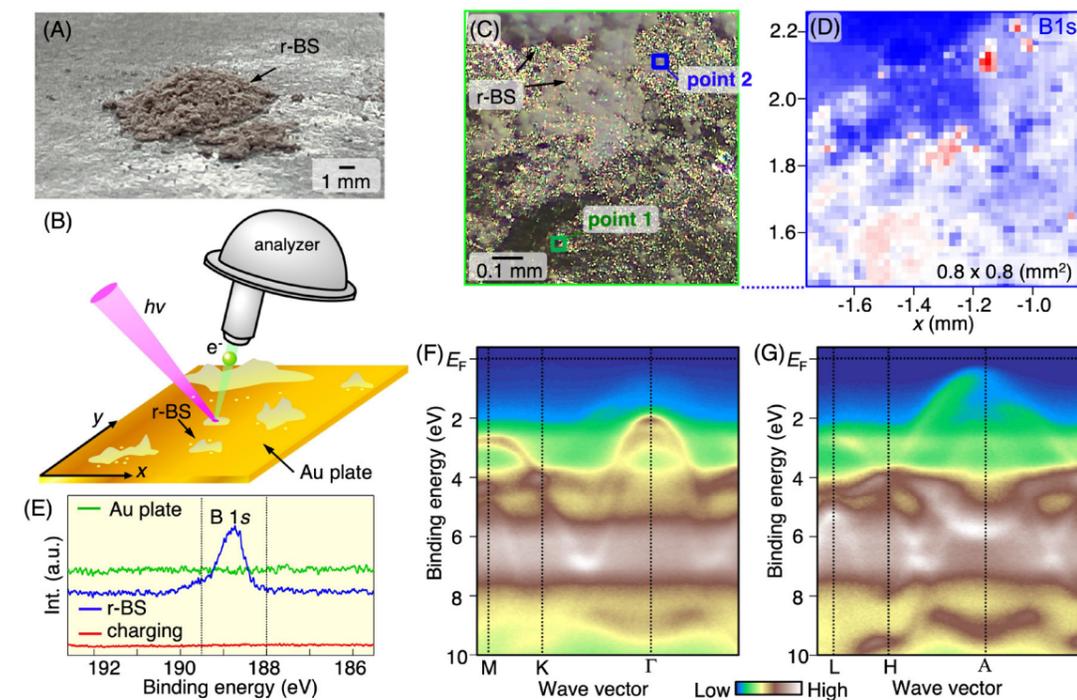
First, we briefly explain the state-of-the-art micro-ARPES system for observing the electronic states of tiny samples [2]. **Figure 1(A)** shows a photograph of micro-ARPES

system constructed at the BL-28A beamline. By placing the K-B mirror chamber next to the ARPES measurement chamber, the focused beam size was achieved to be  $10 \mu\text{m}$  (horizontal)  $\times$   $12 \mu\text{m}$  (vertical) at the photon energy of 200 eV. We have carried out photoemission measurements on a Au photolithography pattern on Si with the letter pattern “ARPES” and “CREST” (**Fig. 1(B)**). The spatial mapping for the photoelectron intensity of Au 4f7/2 peak is shown in **Fig. 1(C)** and **(D)** in which one can clearly recognize individual characters. This result indicates that the photoelectron spatial mapping with a spatial resolution of the order of  $10 \mu\text{m}$  can be achieved using this micro-ARPES system.

To perform micro-ARPES measurements on a tiny r-BS crystal (**Fig. 2(A)** and **(B)**), we at first dispersed r-BS powders on a polycrystalline Au substrate attached to the sample holder in the atmosphere and exfoliated *in-situ* by Kapton tape under ultrahigh vacuum better than  $2 \times 10^{-10}$  Torr (see ref. [3] for the detailed procedure to obtaining a clean surface for the tiny sample). To distinguish cleaved r-BS crystals from the Au substrate, we performed scanning  $\mu$ -PES measurements (**Fig. 2(D)**) with a finer step of 20 nm and mapped out the spatial distribution of



**Figure 1:** (A) A photograph of the micro-ARPES system developed at BL-28A. (B) An optical microscope image of Au photolithography pattern on Si. (C) Photoelectron spatial mapping of the Au 4f core-level intensity of (B). (D) Same as (C) but expanded in the purple rectangle area of (C).



**Figure 2:** (A) A photograph of r-BS powder crystals. (B) Schematic view of micro-ARPES measurements for powdered r-BS on Au film. (C) Optical microscope image of r-BS powder crystals on a Au substrate after exfoliation by a Kapton tape. (D) Spatial mapping of photoemission intensity integrated over the  $E_B$  range of 185.5–192.5 eV around B1s core level, measured with  $h\nu = 250$  eV in the same spatial region as the microscopy image of (C). (E) Representative PES spectra around the B-1s core level at three representative sample positions where the B-1s core-level peak is clearly recognized (point 2; blue curve), the strong signal from the Au substrate dominates (point 1; green curve), and the strong charging effect is seen (on white colored r-BS clusters) (red curve). (F, G) ARPES intensity plot measured along the  $\Gamma$ KM cut ( $k_z = 0$  plane) and the AHL cut ( $k_z = \pi$  plane) with  $h\nu = 105$  eV and 125 eV, respectively.

photoelectron intensity integrated at the binding-energy ( $E_B$ ) of 185.5–192.5 eV where the B-1s core-level peak is expected to appear (blue curve in **Fig. 2(E)**). Also, to compare with the ARPES spatial mapping, we show in **Fig. 2(C)** optical microscope image obtained in the same area as in **Fig. 2(D)**. One can identify overall similarity of the optical image and the strongest photoelectron intensity appearing in a single pixel of  $20 \times 20 \mu\text{m}^2$  marked as point 2. We were able to obtain high-quality ARPES data at point 2 as shown in **Fig. 2(F)**. These results indicate that it is essential to carry out a high-spatial-resolution mapping with a pixel size comparable to that of powder crystals to efficiently find an appropriate sample position for the ARPES measurements [3].

Next, to clarify three-dimensional (3D) band structure of r-BS, we have performed ARPES measurements at point 2 by varying photon energy, and compared the result with the first-principles band-structure calculations [3]. We found that the band structure measured with  $h\nu = 105$  and 125 eV corresponds to the  $\Gamma$ KM cut at  $k_z \sim 0$  plane and AHL cut at the  $k_z \sim \pi$  plane (**Fig. 2(F)** and **(G)**), respectively. As seen in **Fig. 2(G)**, the uppermost valence band moves upward and shows a hole-like dispersion topped at 0.5 eV, corresponding to the valence-band maximum. Also, the absence of  $E_F$  crossing of bands signifies the semiconducting nature with a band gap exceeding 0.5 eV [3].

In conclusion, we have succeeded in directly visual-

izing the 3D band structure of r-BS powder crystal by utilizing scanning micro-ARPES. The present study opens a pathway toward investigating the band structure of a wide variety of powder crystals for which application of electron spectroscopy techniques has been limited.

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### BEAMLINE

BL-28A

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