Structure of the Boron Atomic Wire on Cu(111) and its Unique Relationships to the Carbon Chain Molecules

We investigated atomic structure and electron states of 2D ordered phase, √73 ×√39-B/Cu(111) by a concerting usage of positron diffraction and photoemission spectroscopy. The surface overlayer is 2D copper boride with a periodic arrangement of the boron atomic chains that are isoelectronic to cumulene. The unique chemical character of the 1D boron molecule may allow us to call it *Bumulene*. Though it has been known that the B and Cu phases are completely separated in three-dimensional (3D) materials, the present study intriguingly revealed that a compound is formed in two-dimension (2D) at the surface. The 2D Cu-B compound on Cu(111) likely becomes an ideal B/Cu interface to develop surface science and boron chemistry.

Recently, there have been growing interests in chemistry and physics of boron polymorphs or metal borides on surfaces due to unique multi-center bonding between boron atoms [1]. On the well-known Cu(111) substrate, the 2D ordered phase, √73 ×√39, is prepared by boron deposition where the surface structure has not been known. In the present research, we made the structure analysis by total-reflection high-energy positron diffraction (TRHEPD) experiment at SPF, with a measurement setup illustrated in **Fig. 1(a)**. The positron beam is totally reflected at a glancing angle (θ) below the critical angle and the probe has the highest surface sensitivity among the surface analysis method. There have been arguments on the two structure models of monolayer boron (borophene) [2] and a 2D boride, [3-5] that are drawn in **Fig. 1(b)** and **(c)**, respectively.

Figure 1(d-f) compares rocking curves of the TRHEPD experiments and theoretical simulations. One can find that the experimental curve matches not with a simulated curve of the model **(b)** but with that of the model **(c)**. The surface structure is described by the 2D Cu boride model with the alternate arrangement of Cu and boron atomic chains.

Evaluations of the chemical states were made by measurements of the Cu and B core-level spectra as shown in **Fig. 2(a, b)**. In the 2D Cu boride, there appear two Cu components that can be ascribed to the surface layer (L) and in the bulk (Bu), while the B 1s spectrum has only a single component. The B 1s binding energy at 187.8 eV means that the boron atoms were negatively charged, and the electrons are likely transferred to the boron atoms from the surrounding copper atoms.

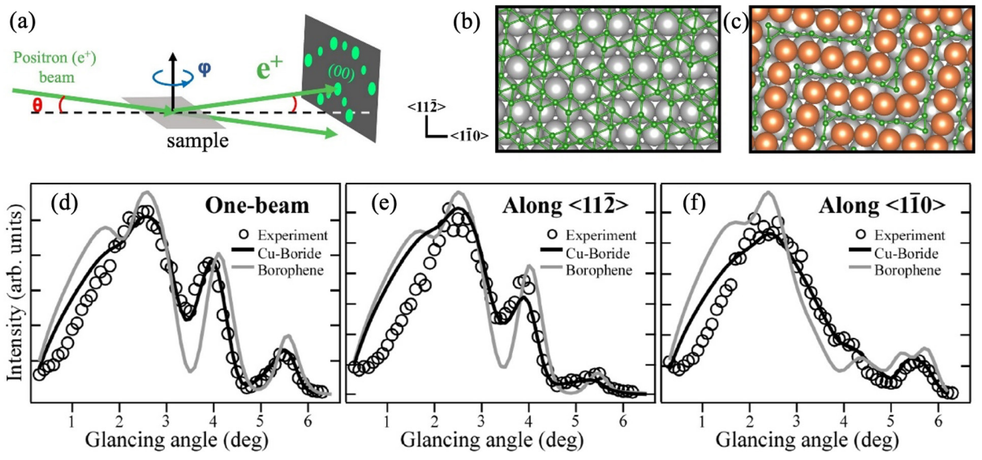

Figure 1: (a) A schematic drawing of the total-reflection high-energy positron diffraction (TRHEPD). The positron beam is incident to a sample surface at a glancing angle θ with the in-plane orientation fixed in azimuthal angle ϕ. **(b, c)** Structure models of **(b)** borophene and **(c)** 2D Cu boride. In the figure, boron and copper atoms are colored in green and brown (gray). **(d-f)** Experimental TRHEPD rocking curves (open circles) taken with the beam intensity at the (00) spot taken at 10 keV under the **(d)** one-beam and **(e, f)** many-beam conditions. Simulated curves for the 2D Cu boride (black) and borophene (gray) models are also shown [4].

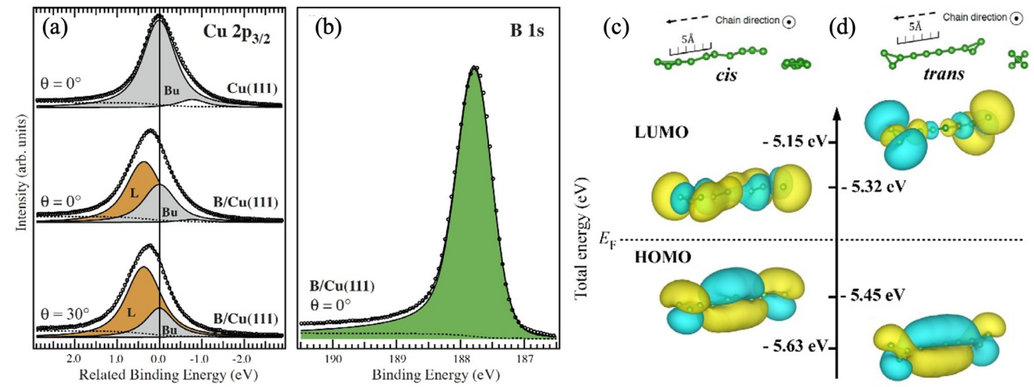

Figure 2: The experimental XPS spectra of the **(a)** Cu 2p$_{3/2}$ and **(b)** B 1s core-levels taken at various emission angles θ with photon energies of hν = 1050 eV and hν =285 eV, respectively. The curve-fitted spectra were also shown in the figures [4]. **(c, d)** Building blocks of the B chain along with the associated molecular orbitals. A **(c)** *cis*-type or **(d)** *trans*-type 1D boron molecule, *Bumulene*, with triangle edges. The atomic arrangement is shown from the side and front views with the LUMO and HOMO. Each energy is given with reference to the vacuum level [4].

A combination of TRHEPD and XPS results evidences a correlation between the surface structure and the negative charge at the boron atom. Taking the building blocks of the boron atom chain as linear molecules with two triangular terminals, **Figures 2 (c, d)** show the **(c)** *cis*- and **(d)** *trans*-configurations, respectively. In the *cis*-type (*trans*-type), the LUMO and HOMO energy levels were -5.15eV (-5.32 eV) and -5.63eV (-5.45 eV) with reference to the vacuum level, respectively. In a free space, an optimized structure of the molecule takes the *trans*-configuration. On the other hand, the 2D Cu boride model (**Fig. 1(c)**) has the triangle groups lying on the surface, taking the *cis*- configuration. The difference can be understood by considering the charge state between the two structures. We first recall that boron atoms are negatively charged, as unveiled by XPS in **Fig. 2**. The following discussion deals with electron-doping into these molecular orbitals of the boron chains. As shown in figure, the highest occupied molecular orbital (HOMO) of the molecules has a character of the π-type bonding for both the *trans*- and *cis*-types. On the other hand, concerning the lowest unoccupied molecular orbital (LUMO), the *trans*-type molecule has that of the σ*-type antibonding, while the *cis*-type molecule has of the π-type bonding. Thus, the electron addition to the LUMO makes the *trans*-type unstable, indicating the *cis*-type are energetically favored when the molecule is negatively charged. The chemical stability, thus, can be attributed to these molecules having the same electronically π-type configuration as a carbon chain. The boron chain is electronically similar to an unsaturated chain of carbon atoms, such as cumulene. The boron atom chain can therefore be regarded as a cumulene-type boron that may be referred to as *Bumulene* [4].

The present study unveiled that a 2D Cu-B compound is formed at the surface. This is sharply contrast to the 3D materials that have allowed only a complete separation of the B and Cu phases. Intriguingly, the surface structure was also found to be made of atomic chains of boron. Boron-adsorbed surfaces of the Cu crystals likely become an ideal system to investigate the 1D boron and to explore novel B/Cu interface structure.

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