

Reversible Subsurface Diffusion and Redox Reactions of 2D Copper Boride

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Boron exhibits exceptional chemical stability, making it an attractive material for applications in catalysis and energy storage [1]. This stability arises from its strong covalent bonding, which makes elemental boron highly resistant to oxidation. When oxidized to boron oxide (B_2O_3), it is thermodynamically stable and difficult to reduce, even in reducing environments such as CO or hydrogen. 2D boron, which is characterized as borophene or a transition metal boride, depending on the substrate, is often grown on Cu(111) [2]. There is limited knowledge in the current literature regarding the chemistry of 2D boron. However, partially oxidized 2D copper oxide species are considerably more reactive and can be reduced more readily than fully oxidized 2D copper oxide [3]. This same concept can be applied to partially oxidized 2D boron. Despite the importance of these oxidation states, their formation and evolution have received little attention for 2D boron surfaces. Understanding the oxidation process is therefore critical for controlling the chemical stability, reversibility, and performance of 2D boron, motivating the investigation of early-stage oxidation presented herein.

2D B/Cu(111) synthesis was first optimized by post annealing while recording in-situ low energy electron microscopy (LEEM) and low energy electron diffraction (LEED) data. The results were confirmed with scanning tunneling microscopy (STM) (Fig. 1) and auger electron spectroscopy (AES). Boron deposition on Cu(111) produced a clean 2D copper boride film through reversible diffusion between the surface and subsurface. Oxidation experiments revealed the reaction pathway in which copper boride first forms partially oxidized boron oxide (Fig. 2), reacts preferentially with water at elevated temperature to produce boric acid, and subsequently dehydrates into stable B_2O_3 upon reduction with CO.

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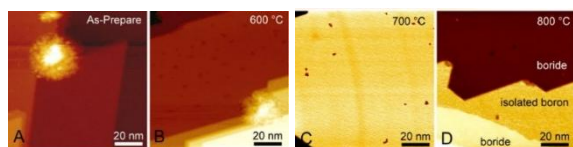


Figure 1. Large-scale room temperature STM images of the B/Cu(111) surface of (A) as-prepared condition; and after being flash annealed once to (B) 600 °C, (C) 700 °C, and (D) 800 °C. Image size: $100 \times 100 \text{ nm}^2$. $I_t = 0.2 \text{ nA}$ or 0.3 nA ; $V_{\text{gap}} = 0.7$ or 1.5 V .

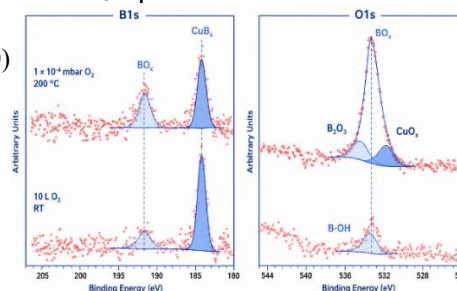


Figure 2. B1s and O1s XPS spectra collected before and after exposure of the boride-covered Cu(111) surface to $1 \times 10^{-4} \text{ mbar O}_2$. The spectra demonstrate that thermal activation is necessary to promote significant oxidation of boron species on the surface. Elevated temperature (200 °C) is required to oxidize boron at $1 \times 10^{-4} \text{ mbar O}_2$.