

Microstructure evolution of a Cu and θ -Al₂O₃ composite observed by aberration corrected HAADF-STEM

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Delafossite-structured CuAlO₂ is a p-type transparent semiconductor that is of interest for optoelectronic applications [1]. The stability of thick film [2] and bulk [3] CuAlO₂ has been examined in varying atmospheres where novel metal-ceramic composite microstructures were observed to form during reduction. These composite microstructures, consisting of nano-scale metallic copper and θ -alumina are expected to provide interesting combinations of mechanical and electrical properties. The object of this work was to understand the microstructural evolution of the nano Cu/ θ -Al₂O₃ composite during the reduction of delafossite CuAlO₂. Bulk samples of CuAlO₂ were prepared using the methods described in ref. 3. The samples were then subjected to a reduction anneal of 3 h at 1000 °C (pO₂ < 10⁻²⁰). Focused ion beam milling (FIB) was used to extract thin foil samples from regions at the reduction front that contained both reduced and unreduced CuAlO₂. TEM characterization was conducted using an aberration corrected STEM (JEOL 200CF), enabling sub-angstrom imaging of the structure before, during, and after reduction.

Figure 1 shows the microstructure of the reduced CuAlO₂ at different length scales. Figure 1 (a) depicts the region of the sample containing the reduction front. At low magnification, coarse bands of metallic Cu are clearly visible within the microstructure of the reduced CuAlO₂. Observation at higher magnification reveals a nano-scale two-phase structure of θ -Al₂O₃ and Cu (Figure 1(c-d)). Note that under BSE (back-scattered electron) imaging, the Cu exhibits brighter contrast relative to the θ -Al₂O₃. SEM examination of the partially reduced samples revealed that the transformation nucleates at the CuAlO₂ grain boundaries/edges, with copper/ θ -Al₂O₃ laths growing inwards and consuming the grain body (Figure 1 (b), Figure 2(a)).

The CuAlO₂ structure consists of planar arrays of Cu⁺ ions alternating with layers of edge-sharing AlO₆ octahedra; the plane normal is [0001] [4]. For the atomic resolution images depicted in Figure 2 (c), the CuAlO₂ phase is oriented to a [10 $\bar{1}$ 0] direction; hence the (0003) Cu⁺ atomic planes are aligned edge-on and are readily distinguishable in HAADF imaging due to their bright contrast. At the phase boundary of the CuAlO₂, these planes terminate in a series of ledges. It was consistently observed that for the copper atomic planes, there was a gradual reduction in contrast in the ledge region, which indicates a lower concentration of copper within the atomic columns (see Figure 2 (b-c)). There was no discernable contrast variation, however, in the adjacent Al-O layers. These observations strongly suggest that during the reduction transformation, the copper atomic planes retract by the sequential outward diffusion of copper atoms, with detachment occurring at the plane edges. It is suggested that the remnant Al-O layers undergo a slight rearrangement to form θ -Al₂O₃. Clearly there must also be concurrent outward diffusion of oxygen, but unfortunately, imaging of the oxygen ions at the requisite concentration levels is beyond the capability of the microscope. Careful study also revealed that an epitaxial orientation relationship exists between the θ -Al₂O₃ and the parent CuAlO₂ phase, as well as between the nano-copper regions and the parent CuAlO₂ phase. In summary, aberration corrected HAADF imaging has provided valuable insight into the mechanism by which delafossite CuAlO₂

transforms to Cu and θ -Al₂O₃ during reduction. Characterization of the mechanical and electrical properties of the composite is ongoing.

References:

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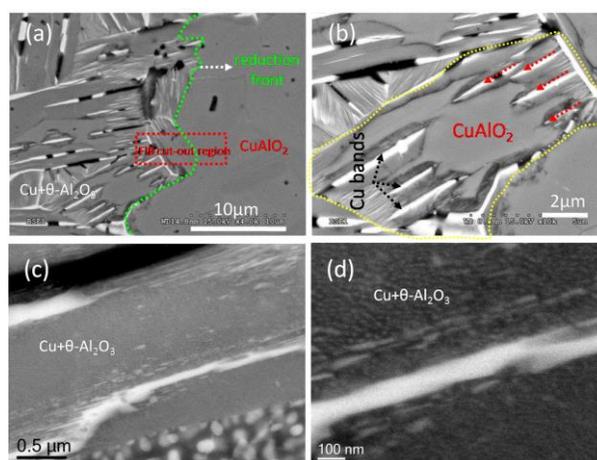


Figure 1. (a-d) Microstructure of the Cu/ θ -Al₂O₃ composite at different scales. (a) The position where the FIB sample was extracted is marked. (b) The dotted lines delineate the boundaries of the grain of interest. (SEM, BSE)

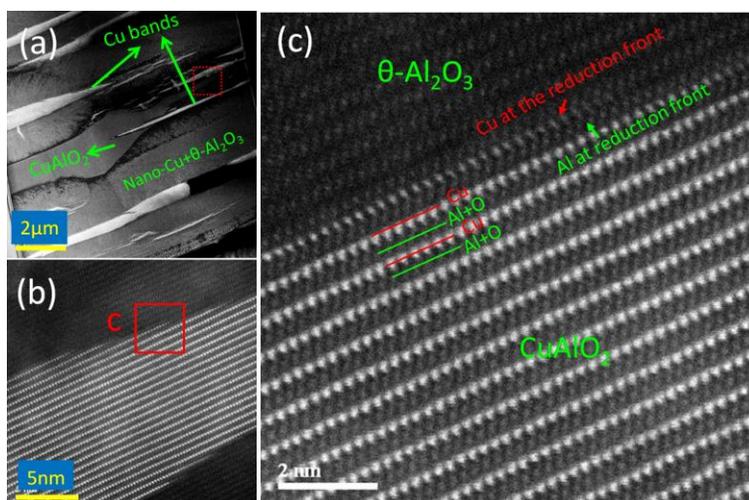


Figure 2. (a-b) The reduction front of delafossite CuAlO₂ at different magnifications. (c) High resolution HAADF images clearly showing the decrease in copper concentration in the vicinity of the plane ledges.