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Microstructure evolution of a Cu and θ-Al_2O_3 composite observed by aberration corrected HAADF-STEM

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Delafossite-structured $CuAlO_2$ is a p-type transparent semiconductor that is of interest for opto-electronic applications [1]. The stability of thick film [2] and bulk [3] $CuAlO_2$ 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-Al_2O_3 composite during the reduction of delafossite $CuAlO_2$. Bulk samples of $CuAlO_2$ were prepared using the methods described in ref. 3. The samples were then subjected to a reduction anneal of 3 h at 1000 ºC ($pO_2 < 10^{-20}$). Focused ion beam milling (FIB) was used to extract thin foil samples from regions at the reduction front that contained both reduced and unreduced $CuAlO_2$. 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 $CuAlO_2$ 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 $CuAlO_2$. Observation at higher magnification reveals a nano-scale two-phase structure of θ-Al_2O_3 and Cu (Figure 1(c-d)). Note that under BSE (back-scattered electron) imaging, the Cu exhibits brighter contrast relative to the θ-Al_2O_3. SEM examination of the partially reduced samples revealed that the transformation nucleates at the $CuAlO_2$ grain boundaries/edges, with copper/ θ-Al_2O_3 laths growing inwards and consuming the grain body (Figure 1 (b), Figure 2(a)).

The $CuAlO_2$ structure consists of planar arrays of Cu^+ ions alternating with layers of edge-sharing AlO_6 octahedra; the plane normal is [0001] [4]. For the atomic resolution images depicted in Figure 2 (c), the $CuAlO_2$ 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 $CuAlO_2$, 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-Al_2O_3. 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-Al_2O_3 and the parent $CuAlO_2$ phase, as well as between the nano-copper regions and the parent $CuAlO_2$ phase. In summary, aberration corrected HAADF imaging has provided valuable insight into the mechanism by which delafossite $CuAlO_2$

transforms to Cu and θ-Al_2O_3 during reduction. Characterization of the mechanical and electrical properties of the composite is ongoing.

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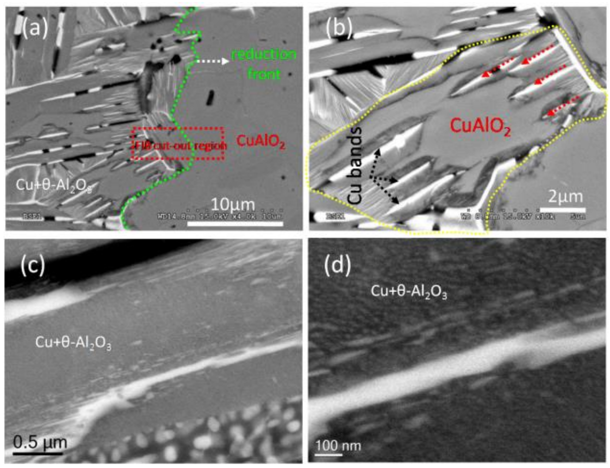

Figure 1. (a-d) Microstructure of the Cu/θ-Al_2O_3 composite at different scales. (a) The position where the FIB sample was extracted is marked. (b) The dotted lines delineate the boundaries of the grain of interest. (SEM, BSE)

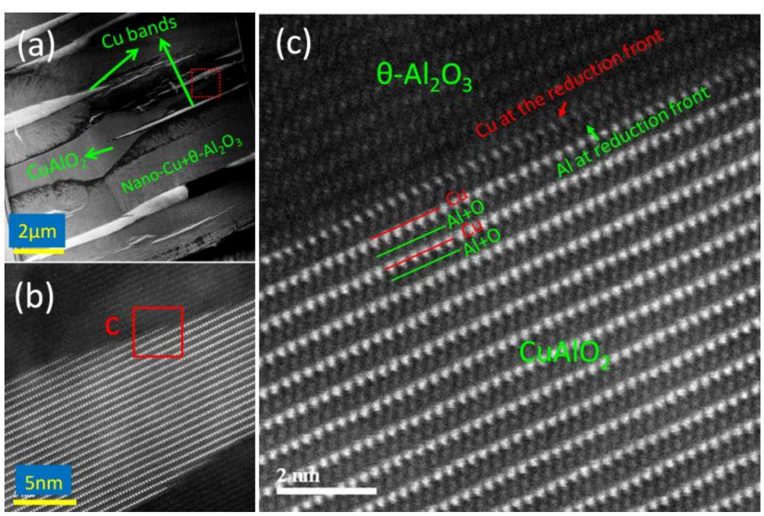

Figure 2. (a-b) The reduction front of delafossite $CuAlO_2$ at different magnifications. (c) High resolution HAADF images clearly showing the decrease in copper concentration in the vicinity of the plane ledges.

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