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The Luminescent Properties of $CuAlO_2$

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Supporting information

Sample Preparation

Preparation of $CuAlO_2$ films on Al_2O_3

Al_2O_3 plates were first cleaned. A few crystals of copper nitrate were placed on the surface of the substrate which was then heated to 150°C on a hotplate. When the nitrate salt melted, a small pin was used to paint the entire substrate with the molten salt. Over the course of 15 minutes the temperature was increased to 300°C to decompose the nitrate, leaving a CuO film on the substrate surface. The coated substrate was then inserted into a pre-heated furnace at 1100°C and heating continued for a further 5 hours. The substrates were quickly removed from the furnace under a stream of nitrogen and cooled to room temperature. Excess Cu_xO was removed by soaking the substrate in 36% HCl for 10 minutes, rinsing with fresh HCl, DI-H_2O and drying at 60°C for 1 hour. The substrates were then for a further 3 hours at 1100°C, after which the film appearance changed from black to a light grey colour.

2.3 Preparation of $CuAlO_2$ films on polycrystalline Cu_2O

Cu_2O substrates were prepared in a manner similar to that described elsewhere.[1] Cu sheets were oxidised in a pre-heated furnace at 1030°C for 1 hour and at 1100°C for a further 2 hours. Post annealing, the polycrystalline Cu_2O substrates were polished with successively finer grades of commercial silicon carbide paper to remove surface buckling that occurs during oxidation. The Cu_2O plates were then finally briefly etched in a H_2O_2: 25 / H_2SO_4: 75 mixtures and quickly rinsed with copious amounts of DI-H_2O.

A 0.6% w/w Boehmite (AlOOH) sol was prepared from aluminium isopropoxide (AIP) using methods developed by Nagai *et al*.[2] The Boehmite sol was drop-coated onto the Cu_2O substrates prepared as described in section 2.1 and allowed to gel and finally dried on a hot plate at 70°C, after which the samples were pre-annealed at 350°C for 15 minutes. The substrates were then annealed at 1100°C in a pre-heated furnace for 5 hours before being removed and quickly cooled using a nitrogen stream yielding a pale blue film on the Cu_2O substrate.

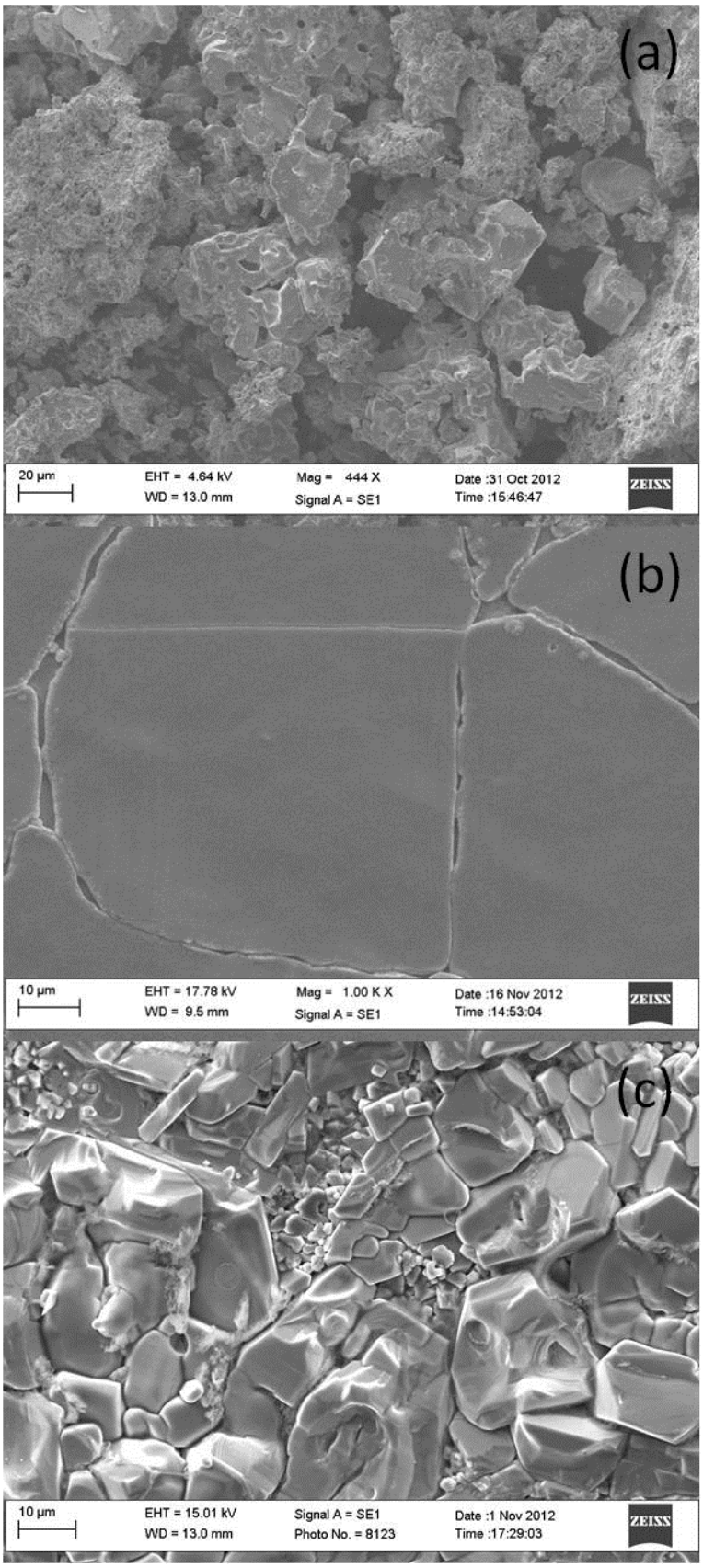

Figure S1: SEM images of (a) $CuAlO_2$ powder (b) $CuAlO_2$ film on a Cu_2O substrate (c) $CuAlO_2$ film on an Al_2O_3 substrate.

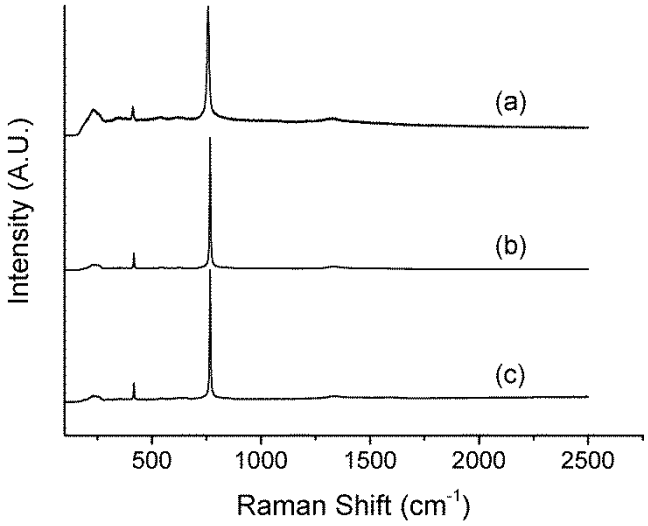

Figure S2: Raman spectrum from $CuAlO_2$ samples acquired using 363.8 nm laser excitation (a) powder (b) film on Cu_2O substrate (c) film on Al_2O_3 substrate.

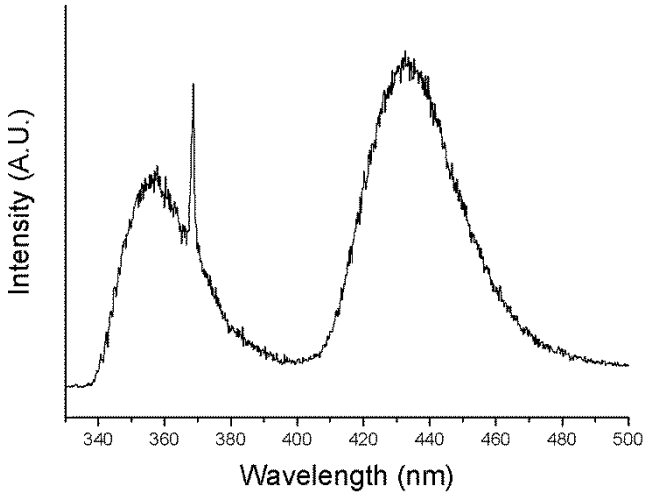

Figure S3: Photoluminescence spectra of a $CuAlO_2$ film on Cu_2O substrate measured at 14.5K

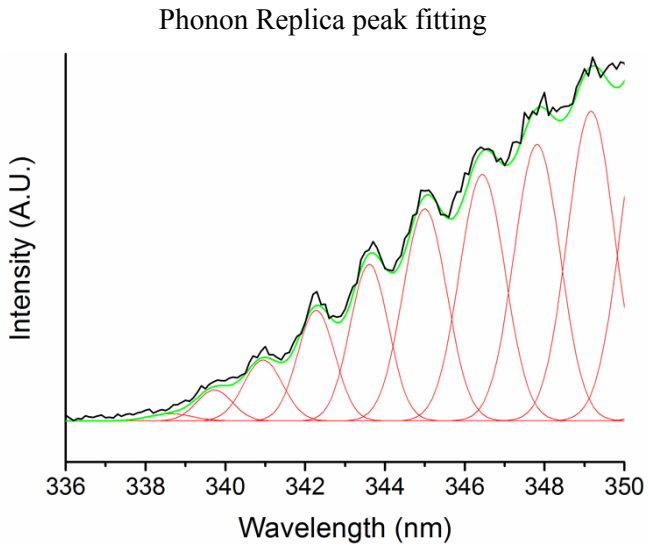

Figure S4: Gaussian peak fit of the successive phonon replicas of the UV emission band. Black line: Pl spectrum, Green line: sum of individual Gaussian peaks, Red lines: individual peaks.

Each resolvable peak on the high energy side of the UV band was fitted to a Gaussian peak shape until an adjusted R-Square value of greater than 0.99 was achieved. In the Harmonic oscillator model the intensities of successive phonon peak intensities are given by:

$$I_n = Ae^{-S}\frac{n^j}{n!}$$

Therefore the ratio of successive phonon intensities is given by:

$$I_n / I_{n+1} = \frac{(n+x)+1}{S}$$

Where x is an additional degree of freedom included given that the initial zero phonon line could not be observed. The ratio of success phonon replicates were plotted given an arbitrary phonon number assignment and fitted to the above equation as shown below, yielding a Huang Rhys factor of 8.7 ± 1.2 with a zero phonon line position of ~337.3 nm (3.68 eV)

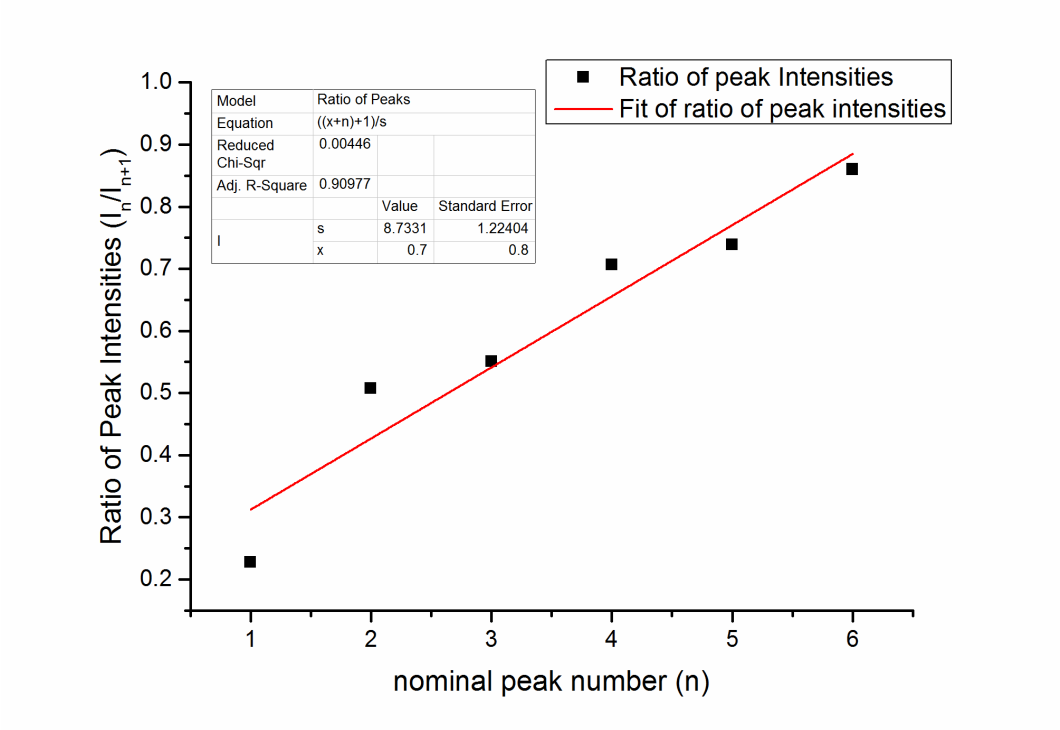

Figure S5: Fit of the ratio of the integrated intensity for successive phonon modes observed in the low temperature UV luminescence band from $CuAlO_2$.

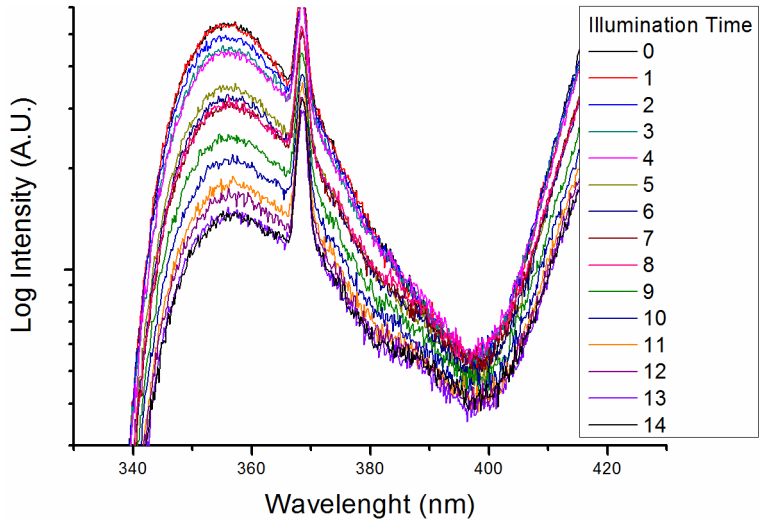

Figure S6: Overlaid PL spectra from a $CuAlO_2$ sample illuminated continuously for 14 hours, showing the decrease in the UV emission and the emergence of a shoulder on the low energy side.

References

(1) Toth, R. S.; Kilkson, R.; Trivich, D. *Journal of Applied Physics* **1960,** *31* (6) 1117-1121
(2) Nagai, N.; Mizukami, F. *Journal of Materials Chemistry* **2011,** *21* (38) 14884-14889