

# Electronic Structure of Amorphous CuI, a p-type Transparent Semiconductor

J Robertson<sup>1\*</sup>, Z Zhang<sup>1</sup>, Y Guo<sup>2</sup>

<sup>1</sup> Engineering Dept, Cambridge University, Cambridge CB2 1PZ, UK

<sup>2</sup> School of Engineering, Swansea University, Swansea, UK

\* Phone: +44-1223-748331 E-mail: jr@eng.cam.ac.uk

## 1. Abstract

**The electronic and atomic structure of amorphous (a-)CuI is calculated by ab-initio molecular dynamics. Its valence band maximum has an effective hole mass of  $0.3m_e$  and mixed I(p)-Cu(d) character, but nevertheless it is relatively insensitive to disorder. The Fermi level can enter the valence band without reconstruction, explaining why there is high mobility and few hole traps.**

## 2. Introduction

Amorphous oxide semiconductors (AOS) like In-Ga-Zn-O are replacing a-Si:H due to their high electron mobility [1]. So far, the analogous p-type AOS have disappointing mobilities or are expensive (ZnRh<sub>2</sub>O<sub>4</sub>)[2]. Perhaps the best is the hole branch of the halide perovskites, but these have a small band gap and are not fully visible transparent. A suggestion is a-CuI, as crystalline (c-)CuI has a hole mobility of 8 cm<sup>2</sup>/V.s [3]. Recently, Jun et al [4] prepared a-CuI. Here we use density functional molecular dynamics (MD) on supercells to calculate its properties.

## 3. Methods.

We use plane wave pseudo-potential method with the GGA+U method for exchange-correlation functional during the MD, with U=4.8 eV applied to Cu 3d states to open the band gap, and avoid Cu-Cu clustering. We anneal at 2000K for 4ps then quench at 10K/ps to 300K at 5.40 g/cm<sup>3</sup>. Later we use the HSE functional with  $\alpha=33\%$  for more accurate calculation of band gap and density of states (DOS).

## 3. Results and discussion.

CuI has various crystal phases with different coordination, as well as the zincblende phase. The bonding after MD depends strongly on the potentials and density functional used.

The random network of a-CuI is shown in Fig 1. A-CuI is largely tetrahedrally bonded. A partial radial distribution function (RDF) is shown in Fig. 2, with first neighbor distance of 2.70Å. While the I-I distribution corresponds to second neighbors, many Cu-Cu neighbors have much closer contacts, with a peak at 2.8Å. Smaller U values during MD allow Cu atoms to cluster with Cu-Cu distances of down to 2.6 Å. The network shows some tendency towards

layered bonding with some 3-fold coordinated sites, reminiscent of its crystalline rhombohedral phase.

Fig 3 shows the HSE band structure of c-CuI. Its band gap is 3.05 eV similar to the experimental value [3]. Fig 4 compares the partial DOS found by GGA+U and HSE for a-CuI, and for c-CuI by HSE [5]. Overall the GGA+U DOS is reasonable, but with a narrower band gap. The DOS for a-CuI has similar band features to that of c-CuI. The VB is 6 eV wide as in experiment [6]. The band gap of a-CuI in HSE is 3.0 eV. There is a strong Cu 3d peak due to  $\Gamma_{12}$  states at -2.8 eV. The valence band maximum (VBM) is mixed I(p)-Cu(d t<sub>2g</sub>) states. The relatively high hole mobility implies that the VBM energy is insensitive to disorder. This is achieved by the bonding unit being delocalized over 3 sites as shown in Fig 5. It is not because the state is pure I(p)-like with pseudo-s-like character as suggested [4].

A critical factor for the p-type mobility of a-CuI is that the Fermi level can enter the valence band, for example by adding an excess of  $\Gamma$  ions, without creating a compensating bond reconstruction as would occur in a-Si:H [7]. This is seen for the calculated DOS of the network of a-Cu<sub>44</sub>I<sub>46</sub> in Fig 6(a). Thus, it avoids the pinning of E<sub>F</sub> above the VB mobility edge, which would strongly reduce the field effect mobility. The VBM then becomes a state on the iodine dangling bond as seen in Fig 6(b).

The weak point about a-CuI compared to an oxide is its low heat of formation of only -0.73 eV. CuI has a relatively weak lattice and is not strongly endothermic [8].

The Cu clustering which can occur for a poorly controlled MD arises because of the superionic character of CuI with mobile Cu ions.

## References

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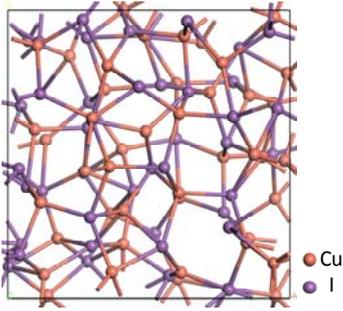


Fig. 1. Random network of a-CuI by ab-initio molecular dynamics.

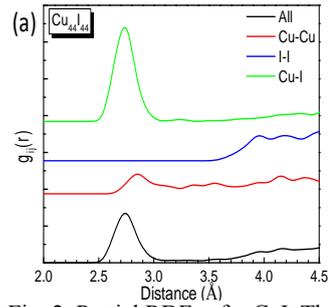


Fig. 2. Partial RDFs of a-CuI. The Cu-I first neighbor peak occurs at 2.70Å. The Cu-Cu distribution spreads to shorter distances.

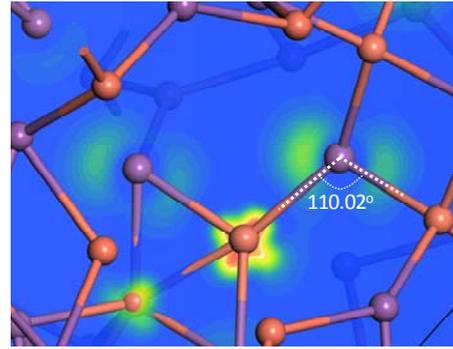


Fig.5. Valence band maximum state of a-CuI with I(p)-Cu(d)-I(p) character..

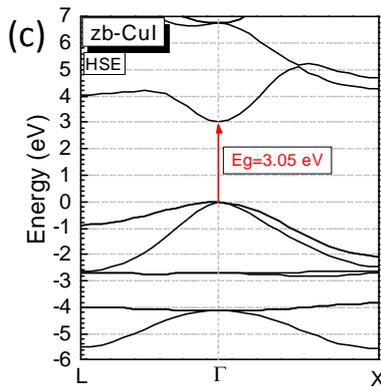


Fig. 3. HSE band structure of c-CuI

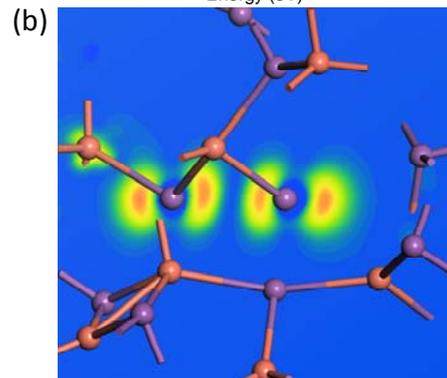
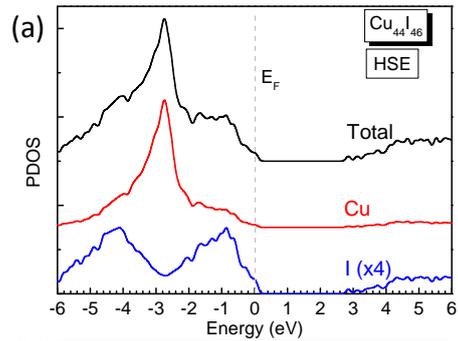


Fig. 6(a). PDOS of I-excess a-CuI, with  $E_f$  entering the valence band due to hole doping. Notice there is no reconstruction to pin  $E_f$  above the VB. (b) Iodine dangling bond site of excess I causing hole doping.

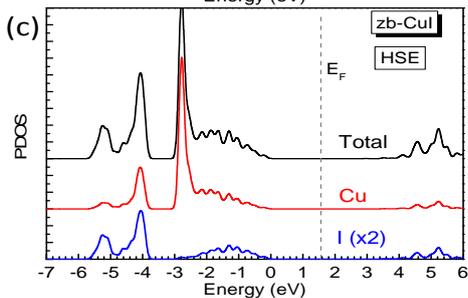
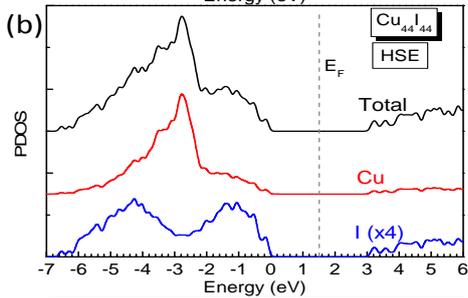
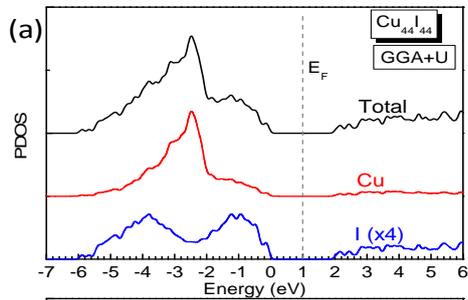


Fig. 4. Calculated PDOS for a-CuI and c-CuI.