Epitaxial Strain-Induced Growth of CuO at Cu$_2$O/ZnO Interfaces

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ABSTRACT: Cu$_2$O/ZnO has been envisaged as a potential material system for the next-generation thin-film solar cells. Thus far, the experimental efforts to obtain conversion efficiencies close to the theoretically predicted value have failed. Combining aberration-corrected (scanning) transmission electron microscopy and density functional theory modeling, we studied the interfaces between single-crystal $c$-axis-oriented ZnO and high-quality magnetron-sputtered Cu$_2$O films. Strikingly, our study shows that the first ~5 nm of the Cu–oxide films has the structure of the monoclinic CuO phase. The CuO layer is textured with the (111), (111), (111), (111) (111), (111), (111) and (100) planes parallel to the (0001) and (0001) ZnO interfaces. The ionic arrangement on these planes resembles the hexagonal arrangement of the ZnO interface, and epitaxy exists across the interface. A continued epitaxial growth of [111]-oriented CuO follows resulting in epitaxial 180° rotation twins in the Cu$_2$O layer. For the case with the (100)$_{CuO}$ interfacial plane we have $\{111\}[1\bar{1}0]_{CuO}$$\parallel\{100\}[0\bar{1}1]_{ZnO}$ and $\{0001\}[\bar{1}1\bar{2}0]_{ZnO}$ - $\{0001\}[\bar{1}1\bar{2}0]_{ZnO}$. Because of a closer lattice matching of CuO with ZnO and Cu$_2$O, the total strain and energy is reduced compared to a pure $\{111\}[1\bar{1}0]_{CuO}$ and $\{0001\}[\bar{1}1\bar{2}0]_{ZnO}$ interface. The existence of CuO is anticipated to be a contributing factor for the low conversion efficiencies obtained experimentally.

INTRODUCTION

Cuprous oxide or cuprite (Cu$_2$O) is a low-cost and nontoxic “intrinsic” p-type semiconductor with a band gap of ~2.1 eV. Combined with n-type ZnO, which has a band gap of 3.4 eV, a Cu$_2$O/ZnO p–n heterojunction would be obtained. Cu$_2$O has a primitive cubic crystal structure ($Pn3m$; $a = 0.427$ nm) where the Cu$^{+}$ and O$^{2-}$ ions are located on fcc and bcc sublattices, respectively. ZnO has a unit cell with a hexagonal wurzite crystal structure ($P6_{3}mc$; $a = 0.325$ nm, $c = 0.521$ nm). A heterointerfacial relationship between ZnO and Cu$_2$O has been expected due to a relatively small lattice mismatch of 7.6% anticipated for the Cu$_2$O(111)/ZnO(0001) interface.

A most interesting prospect for the Cu$_2$O/ZnO materials system is related to its theoretically predicted conversion efficiency of 18%. With its low cost, nontoxic constituents, and potential high conversion efficiency it has been envisaged as a potential materials system for the next-generation thin-film-based solar cells. At the present, however, the highest reported conversion efficiencies are only 2% for Cu$_2$O/ZnO heterojunction thin films and 4.12% and 5.38% when an undoped Ga$_2$O$_3$ or ZnO thin interfacial layer is present in AZO/n-semiconductor/p-Cu$_2$O heterojunctions. Hence, there is an increasing effort to find solutions to improve the conversion efficiency.

The majority of the research efforts in this field are, however, focused on developing synthesis methods, and only few investigations are devoted to in-depth atomic-scale investigations. In order to obtain a fundamental understanding about the reasons behind the discrepancy between the theoretical and the experimentally obtained conversion efficiencies of Cu$_2$O/ZnO heterojunction solar cells, model systems of high-quality Cu$_2$O films on O- and Zn-polar single-crystal ZnO were used in the present study. A combination of atomically resolved scanning transmission electron microscopy (STEM), electron diffraction (ED), and density functional theory (DFT) based modeling was employed to investigate the material system and, in particular, the substrate–film interface, as the performance of thin film-based devices is well known to be largely affected by the quality of its interfaces.

EXPERIMENTAL SECTION

The Cu$_2$O films investigated in the present study were grown by direct current/radio frequency (dc/rf) reactive magnetron sputtering on $c$-axis-oriented single-crystal ZnO wafers purchased from Tokyo Denpa Co., Ltd. Detailed description of the deposition parameters is reported by Gan et al. In brief, the substrate wafers were double-side polished and pretreated to make sure they were free of any contamination before the sputtering deposition. One side of such a prepared wafer served as the Zn-polar substrate while the other side as the O-polar substrate. During the magnetron sputtering deposition, the substrate temperature was maintained at 400 °C and the base pressure of the chamber was below $4 \times 10^{-4}$ Pa.
Cross-section TEM specimens were prepared by the conventional tripod wedge mechanical polishing protocol. The final thinning of the specimens was done by ion milling for 1 h in a Fischione 1010 instrument with beam energy and current of 5 kV and 5 mA, respectively, and milling angle of ±6° on both sides of the specimen.

A JEOL 2100F microscope operated at 200 kV and an FEI Titan G2 60-300 microscope equipped with a DCOR probe Cs-aberration corrector, operated at 300 kV, were used in the present study. STEM high-angle annular dark field (HAADF) Z-contrast imaging was performed using the FEI microscope with a probe current of ∼100 pA and probe convergence and collection angles of 22 and 76–200 mrad range, respectively. The resulting spatial resolution was ∼0.08 nm. HAADF images show primarily atomic number (Z) contrast, and in the present case, high-resolution (HR) HAADF images offer advantage over HRTEM ones owing to the direct correlation between the image contrast and the cation positions in the sample. Fast Fourier transform (FFT) analysis was used on HR images, and lattice strain measurements were carried out using the geometric phase analysis (GPA) plugin for the DigitalMicrograph software. The DFT calculations were performed with the plane-wave-based VASP code using the Perdew–Burke–Ernzerhof gradient approximation and the projector augmented wave method. The plane-wave cutoff was 400 eV, and the k-point density was at least 4 points per Å\(^{-1}\) in each unit cell direction. The force relaxation criterion was 0.05 eV/Å, and the two outermost layers of one side of the slab structure were fixed. The interface structures were built using the ASE environment. The strain was divided equally between the two sides of the interface, and a 5 × 5 two-dimensional potential energy surface (PES) was generated by lateral translations of one of the sides relative to the other. Each PES point was obtained by relaxation of the whole interface structure, and the lowest energy was taken to represent the interface. A 1 nm thick layer of vacuum was inserted between the two phases on one side, so only one interface was formed. For reference energies, an additional layer of 1 nm vacuum was inserted between the two phases on the other side, creating two separate slabs divided by vacuum on both sides. The interface energy was defined as the energy difference between the interface model and the reference model.

RESULTS AND DISCUSSION

Figure 1 shows overview images of the cross sections of the (a) O-polar Cu\(_2\)O/ZnO and (b) Zn-polar Cu\(_2\)O/ZnO specimens. The Cu\(_2\)O films are in both cases dense and of high quality. Prior XRD analysis of the specimens showed strong (111)\(_{\text{Cu}_2\text{O}}\) and (002)\(_{\text{ZnO}}\) diffraction peaks consistent with previous reports where it has been interpreted as evidence for a heteroepitaxial relationship between Cu\(_2\)O and ZnO due to the 7.6% mismatch between the two lattices.

Representative selected area diffraction (SAD) patterns from the Cu\(_2\)O films and the ZnO substrates are shown in Figure 2. The SAD pattern from the Cu\(_2\)O films in Figure 2c can be indexed in agreement with a single-crystal zone pattern ([1 1 1]). However, the complex pattern seen in Figure 2f can be described as two single-crystal zone patterns ([1 1 0] and [1 1 0]) twin related with a 180° rotation around the common [111] axis. Such a twin relation has previously been reported for Cu\(_2\)O nanoparticles and in Cu\(_2\)O film upon oxidation of a single-crystal Cu. The additional reflexions located 1/3 and 2/3 between {111} rows are due to multiple scattering, i.e., the two twin regions are partly overlapping and the electrons will, due to their short scattering mean free path, scatter from both twin orientations resulting in additional reflexions. From the indexed patterns in Figure 2, it can be concluded that the substrate and the Cu\(_2\)O films have the two orientation variants: (1 1 1)\(_{\text{Cu}_2\text{O}}\)(0 0 0 1)\(_{\text{ZnO}}\) and (1 1 1)\(_{\text{Cu}_2\text{O}}\)(0 0 0 1)\(_{\text{ZnO}}\) and (1 1 1)\(_{\text{Cu}_2\text{O}}\)(0 0 0 1)\(_{\text{ZnO}}\).

The orientation relationship (111)\(_{\text{Cu}_2\text{O}}\)(0 0 0 1)\(_{\text{ZnO}}\) is in agreement with a heteroepitaxial relationship between the two phases reported by others and attributed to energetically favorable periodic lattice coincidence between these two crystal lattices. Wang et al. reported that the atomic arrangement of the first atomic layer of Cu\(_2\)O predicts the atomic arrangement throughout the film. This would imply that one get growth of textured Cu\(_2\)O films but not necessarily an epitaxial relationship between Cu\(_2\)O and ZnO. The observed twinned growth of Cu\(_2\)O is, however, regarded as evidence of epitaxial growth. As shown in Figure 3, the Cu ions across the grain boundary have a changed stacking order of their {111} plane, and the Cu planes (B, C, A, B, C... and C, B, A, B, C...) is consistent with two different starting growth sites on a substrate representing an “A” layer. Such twins can be described as epitaxial twins and have been observed for other oxide-based epitaxial heterostructures.
The XRD of the current specimens showed that the cell parameters of the Cu$_2$O films were 0.4318 and 0.4301 nm for the O- and Zn-polar substrates, respectively. This shows that the lattice is only 1.1% and 0.7% strained relative to unstrained Cu$_2$O ($a = 0.427$ nm). The twin growth could be assumed to have relaxed the strain induced by epitaxy. However, structural defects located close to the heterointerface could also cause the strain in the grown film to be reduced.

Figure 4 shows representative HAADF STEM images from Cu$_2$O/ZnO interfacial regions where bright spots correspond to Zn- and Cu-atom positions in the substrate and film region, respectively. Independent of substrate polarity, the first ~5 nm of the grown Cu–O films show distinct different atomic arrangement and grain sizes (5–10 nm in diameter) compared to the much larger twin domains of the Cu$_2$O film above (Figure 4a and 4b).

The XRD analysis and SAD from interfacial regions (Figure 2) did not show indications of secondary phases. In both cases this can be explained by the relative low volume fraction of the secondary phase and polycrystalline structure and in the case of XRD small grain sizes. However, X-ray energy-dispersive spectroscopy (EDS) and fast Fourier transform (FFT) image analysis of HR STEM images, as illustrated in Figure 4, performed at various positions along the interfacial regions showed that the interfacial layer was not consistent with Cu$_2$O. However, the monoclinic CuO phase with space group $C_{1}$ and lattice parameters $a = 0.469$ nm, $b = 0.343$ nm, $c = 0.51370$ nm, and $\beta = 99.546^\circ$ did give a good fit to the FFT data and is consistent with the EDS data. This is unexpected as the CuO layer was grown under oxygen-poor deposition conditions optimized for Cu$_2$O growth.

On the basis of the FFT analysis of the HR STEM data, it is clear that the CuO grains grow on the ZnO substrate with preferred orientation relationships. Figure 4 illustrates the (111)[110]$_{\text{CuO}}$∥(100)[011]$_{\text{CuO}}$∥(0001)[1120]$_{\text{ZnO}}$ orientation relationship which together with (0001)$_{\text{ZnO}}$∥(111), (111), (111) (111), (111)$_{\text{CuO}}$∥(111)$_{\text{CuO}}$ represents the common interfaces found. All CuO planes ((111), (111), (111), (111), and (100)) represent dense planes of Cu ions with Cu arrangements similar, but distorted, to the one present in {111}$_{\text{CuO}}$ planes. In the {111}$_{\text{CuO}}$ planes the Cu–Cu cation interionic bond length (CIBL) is 0.301 nm. The Cu–Cu CIBL values at the CuO interfaces are listed in Table 1,

Figure 3. (a) STEM image illustrating the stacking order of A,C,B,A... and A,B,C,A... in the twinned Cu$_2$O grains. (b) Illustration of the possible starting points with respect to orientation of the Cu$_2$O lattice giving rise to 180° rotation twins where the green spheres represent Cu positions.
and the similarity in atomic configuration with \{111\} planes of the face-centered cubic Cu sub lattice of Cu$_2$O (Figure 3) is illustrated for the (100)CuO plane in Figure 5. As such, either (100)CuO or any of the \{111\} type of planes of CuO ((111), (111$\bar{1}$), (11$\bar{1}$), (1$\bar{1}$1), (1$\bar{1}$1$\bar{1}$)) can act as suitable surfaces for epitaxial growth of \{111\}Cu$_2$O, and this behavior can justify the presence of Cu$_2$O twin-related grains instead of randomly oriented (111) textured Cu$_2$O grains one could expect with no epitaxial relations.

To further rationalize the formation of a CuO interfacial layer under oxygen-poor deposition conditions, DFT modeling was performed. A series of stoichiometric CuO/ZnO, Cu$_2$O/ZnO, and CuO/Cu$_2$O interface models were constructed after an automatic interface model search, based on the ASE environment, and relaxed to their low-energy configuration. Many hypothetical interface models with relatively small lattice mismatch were identified. However, in order to obtain a stable epitaxial interface, atomic columns have to match as much as possible at the interface plane and the local stoichiometry must be appropriate. This means that the most stable interface is not necessarily the one with the lowest lattice mismatch and that a hypothetical interface with low lattice mismatch may be impossible to realize in practice. This is demonstrated in Figure 6a and 6b, showing the Cu$_2$O(111)/ZnO(0001) interface with the lowest volumetric strain (3.1%) found with our automatic routine. The low structural compatibility due to nonmatching atomic columns indicates that this model is not likely to form. The model shown in Figure 6c and 6d represents the potential compatibility between the two phases; however, in this case the interface exhibits significantly higher strain (7.8%).

The interface models that are shown in Figure 6c and 6d (111) $[\overline{1}0\overline{0}]_{\text{Cu}_2\text{O}} // [0001]_{\text{ZnO}}$, Figure 6e and 6f (111) $[\overline{1}0\overline{0}]_{\text{Cu}_2\text{O}} // [100]_{\text{CuO}}$, and Figure 6g and 6h (100) $[011]_{\text{Cu}_2\text{O}} // [0001]_{\text{ZnO}}$ show excellent epitaxy in all directions and the lowest strain. Supporting the validity of the selection scheme, they also represent two of the experimentally observed interfaces (Figure 4).

A comparative evaluation of the stability of the competing interfaces has been performed based on the calculated interface energy $E_{\text{int}}$, defined as the energy required to pull apart the two constituting parts leaving two free surfaces, is largest for the

![Figure 5. Projection of (100) planes in CuO, where blue and red spheres represent Cu and O ions, respectively. Crossed and the uncrossed Cu ions are on alternating planes. Arrows represent interionic Cu–Cu distances: 0.308 nm (black), 0.310 nm (orange), and 0.343 nm (red) based on ref 24.](image-url)

![Figure 6. Energetically relaxed interface model structures from DFT calculations showing (a–d) (111)$_{\text{Cu}_2\text{O}} // (0001)_{\text{ZnO}}$, (e and f) (111)$_{\text{Cu}_2\text{O}} // (100)_{\text{CuO}}$, and (g and h) (100)$_{\text{CuO}} // (0001)_{\text{ZnO}}$ interfaces, seen in the (a, c, g) $[\overline{1}0\overline{0}]_{\text{ZnO}}$, (b, d, h) $[\overline{1}2\overline{0}]_{\text{ZnO}}$, (e) $[\overline{1}1\overline{2}]_{\text{ZnO}}$, and (f) $[\overline{1}0\overline{0}]_{\text{ZnO}}$ projections. (a and b) Interface with the lowest strain obtained by automatic routine, showing very low structural compatibility.](image-url)
most stable interface. The resulting DFT-calculated interface energy $E_{\text{int}}$ showed that both the (100)$_{\text{CuO}}$/(0001)$_{\text{ZnO}}$ and the (111)$_{\text{Cu}_2\text{O}}$//(100)$_{\text{CuO}}$ display relatively high interface energies (2.5 and 3.1 eV), whereas the (111)$_{\text{Cu}_2\text{O}}$//(0001)$_{\text{ZnO}}$ interface energy is lower (1.5 eV). In other words, the hypothetical (111)$_{\text{Cu}_2\text{O}}$//(0001)$_{\text{ZnO}}$ interface is thermodynamically relatively unstable, favoring the presence of a CuO interfacial layer.

As seen from Table 2, the main difference between the interface models is related to the strain between the constituting phases. The strain is very high in the case of (111)$_{\text{Cu}_2\text{O}}$//(0001)$_{\text{ZnO}}$; the linear strain is 7.8%, and the volume strain is 16.2%. This is associated with a large energy penalty, and it also means that if such an interface is formed, it would most likely abound with defects (such as dislocations) which may tend to relieve the build up of the stresses.

With a calculated volumetric strain of 5.8%, the (100)$_{\text{CuO}}$//(0001)$_{\text{ZnO}}$ interface is found to be much more favorable and hence gives a strong impetus to form epitaxial CuO instead of Cu$_2$O on top of ZnO. Nevertheless, the low oxygen content during synthesis means that there is a thermodynamic drive toward the formation of Cu$_2$O. Thus, even if the epitaxial growth of CuO is preferred over Cu$_2$O at the ZnO surface, it is reasonable to assume that Cu$_2$O will start forming when strain is reduced to a given level during CuO growth. CuO is in this way acting as a buffer layer accommodating the strain between ZnO and Cu$_2$O.

The picture that emerges is the following: instead of a direct interface between ZnO and Cu$_2$O as depicted in Figure 6a and 6b, CuO forms an intermediate layer to accommodate the strain between ZnO and Cu$_2$O. The latter situation can be illustrated by combining Figure 6c and 6e or alternatively Figure 6d and 6f. This corresponds very closely to the experimental micrograph in Figure 4b.

Table 2. Strain and Calculated Interface Energy from the DFT Study where Vectors 1 and 2 Represent in-Plane Atomic Bond Directions at the Interfaces

<table>
<thead>
<tr>
<th>interface</th>
<th>strain (%)</th>
<th>vector 1</th>
<th>vector 2</th>
<th>volume</th>
<th>$E_{\text{int}}$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>(100)$<em>{\text{CuO}}$//(0001)$</em>{\text{ZnO}}$</td>
<td>0.47</td>
<td>5.34</td>
<td>5.84</td>
<td>2.50</td>
<td></td>
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<tr>
<td>(111)$_{\text{Cu}<em>2\text{O}}$//(0001)$</em>{\text{ZnO}}$</td>
<td>7.80</td>
<td>7.80</td>
<td>16.22</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>(111)$_{\text{Cu}<em>2\text{O}}$//(100)$</em>{\text{CuO}}$</td>
<td>5.01</td>
<td>1.64</td>
<td>6.74</td>
<td>3.14</td>
<td></td>
</tr>
</tbody>
</table>

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Figure 7. (a and d) HRSTEM image showing burgers circuits around misfit dislocations at the CuO/ZnO interface, (b and e) corresponding GPA $\varepsilon_{xx}$ map, (c) FFT of a indicating the spots used for GPA, and (f and g) inverse FFT moire images enhancing the (110)$\bar{1}$ and (101)$\bar{1}$ ZnO planes indicated by white and red arrows in d.
lattice has, correspondingly, a CIBL of 0.325 nm in the (001) plane. Hence, in an unstrained state, along a (100)\text{CuO}/(001)\text{ZnO} interface, one has that \text{~19° Zn–Zn CIBL = 18°} averaged Cu–Cu CIBL. This is in good agreement with the observation of the dislocation spacing in Figure 7 pointing to total low strain in the CuO lattice.

The presence of the misfit dislocations along the CuO/ZnO interface reduces the strain relative to the DFT-calculated value, where no dislocations were taken into account and increasing the driving force to grow CuO even more. It is thus clear that attempts to form an epitaxial layer of Cu$_2$O directly on top of CuO is energetically unfavorable to grow CuO relative to Cu$_2$O.

By atomically resolved STEM and FFT analysis it was revealed that single-crystalline (0001) and (0001)\text{ZnO} substrates have an unintentional ~5 nm thin intermediate layer of CuO at the CuO/ZnO interfaces irrespective of ZnO surface polarity. The growth of CuO is textured on the ZnO substrates, showing evidence of a continuation of densely packed CuO planes of cations such as (111), (111), (111), (111), (111), (111), and (100) parallel with the (0001)\text{CuO}, (0001)\text{ZnO} and (111)\text{CuO} interfaces. The densely packed CuO planes are found to act as a template, facilitating growth of epitaxial twinned Cu$_2$O films.

The DFT study of the theoretical (111)[1\overline{1}0]\text{ZnO}[(0001)-][1\overline{1}0]\text{ZnO} and the experimentally observed (100)[1\overline{1}0]\text{CuO}[(0001)-][1\overline{1}0]\text{ZnO} and (111)[1\overline{1}0]\text{CuO}[(0001)-][1\overline{1}0]\text{ZnO} interfaces showed that both the strain and the interface energy were in favor of epitaxial growth of CuO on the ZnO (0001) surface.

GPA showed evidence of localized strain associated with 90° edge misfit dislocations with the Burgers vector 1/2 [1\overline{1}0]\text{ZnO} along the (100)\text{CuO}/(0001)\text{ZnO} interface. The misfit dislocations reduce the strain in the CuO layer, making it even more energetically favorable to grow CuO relative to Cu$_2$O.

The CuO interlayer, not resolved by XRD, is anticipated to be inherent to the interface between crystalline CuO and ZnO films in heterojunction structures. The CuO layer is highly detrimental for the current rectification and open-circuit voltage of the CuO/ZnO heterojunction due to the differences in the band alignment and the band gap (2.1 vs 1.2 eV) and can be one of the causes for the poor conversion efficiency obtained experimentally for CuO/ZnO solar cells relative to that predicted theoretically.

**CONCLUSIONS**

By atomically resolved STEM and FFT analysis it was revealed that single-crystalline (0001) and (0001)\text{ZnO} substrates have an unintentional ~5 nm thin intermediate layer of CuO at the CuO/ZnO interfaces irrespective of ZnO surface polarity. The growth of CuO is textured on the ZnO substrates, showing evidence of a continuation of densely packed CuO planes of cations such as (111), (111), (111), (111), (111), (111), and (100) parallel with the (0001)\text{CuO}, (0001)\text{ZnO} and (111)\text{CuO} interfaces. The densely packed CuO planes are found to act as a template, facilitating growth of epitaxial twinned Cu$_2$O films.

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**Notes**

The authors declare no competing financial interest.

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