Perspective: Maintaining surface-phase purity is key to efficient open air fabricated cuprous oxide solar cells

Robert L. Z. Hoye, Riley E. Brandt, Yulia Ievskaya, Shane Heffernan, Kevin P. Musselman, Tonio Buonassisi, and Judith L. MacManus-Driscoll

Citation: APL Materials 3, 020901 (2015); doi: 10.1063/1.4913442
View online: https://doi.org/10.1063/1.4913442
View Table of Contents: http://aip.scitation.org/toc/apm/3/2
Published by the American Institute of Physics

Articles you may be interested in
Band offsets of n-type electron-selective contacts on cuprous oxide (Cu2O) for photovoltaics

Research Update: Atmospheric pressure spatial atomic layer deposition of ZnO thin films: Reactors, doping, and devices
APL Materials 3, 040701 (2015); 10.1063/1.4916525

Selective growth of single phase VO2(A, B, and M) polymorph thin films
APL Materials 3, 026101 (2015); 10.1063/1.4906880

All-perovskite transparent high mobility field effect using epitaxial BaSnO3 and LaInO3
APL Materials 3, 036101 (2015); 10.1063/1.4913587

Characterization of Lorenz number with Seebeck coefficient measurement
APL Materials 3, 041506 (2015); 10.1063/1.4908244

Determining interface properties limiting open-circuit voltage in heterojunction solar cells
Journal of Applied Physics 121, 185301 (2017); 10.1063/1.4982752
Perspective: Maintaining surface-phase purity is key to efficient open air fabricated cuprous oxide solar cells

Robert L. Z. Hoye,1,a Riley E. Brandt,2 Yulia Ievskaya,1 Shane Heffernan,3 Kevin P. Musselman,4,1 Tonio Buonassisi,2 and Judith L. MacManus-Driscoll1,a

1Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom
2Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
3Electrical Engineering Division, Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA, United Kingdom
4Department of Physics, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom

(Received 24 December 2014; accepted 6 February 2015; published online 20 February 2015)

Electrochemically deposited Cu$_2$O solar cells are receiving growing attention owing to a recent doubling in efficiency. This was enabled by the controlled chemical environment used in depositing doped ZnO layers by atomic layer deposition, which is not well suited to large-scale industrial production. While open air fabrication with atmospheric pressure spatial atomic layer deposition overcomes this limitation, we find that this approach is limited by an inability to remove the detrimental CuO layer that forms on the Cu$_2$O surface. Herein, we propose strategies for achieving efficiencies in atmospherically processed cells that are equivalent to the high values achieved in vacuum processed cells. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4913442]

Earth-abundant thin film solar cells, such as Cu$_2$O and Cu$_2$ZnSnS$_4$, are highly promising absorber materials because they are non-toxic and capable of delivering renewable energy on a terawatt level.1 An important step to enable scalable manufacturing is the fabrication of all components in the cells by low-cost methods.2 In line with this demand, atmospheric pressure spatial atomic layer deposition (AP-SALD) has evolved from conventional atomic layer deposition (ALD). ALD is a vacuum-based, batch-processed and slow technique, whereas AP-SALD enables the metal oxide deposition to occur rapidly, in open air, at low temperature, and in a roll-to-roll compatible manner, while retaining the high quality of the metal oxides produced by conventional ALD.3 AP-SALD has proven to be a versatile technique, with the capability of producing ZnO, TiO$_2$, and Cu$_2$O for high-performing solar cells, in addition to having the ability to introduce dopants into the metal oxides to tune their electronic properties.3

While to date only single-digit efficiencies have been demonstrated in all-inorganic Cu$_2$O-based solar cells, Cu$_2$O has the strong advantages of compositional simplicity and the use of non-toxic precursor chemicals, which means it has excellent potential for photovoltaic applications, such as use as the top cell in a multijunction device or for water splitting. Recently, the efficiency of electrochemically deposited Cu$_2$O solar cells has increased from below 2% to reach a certified value of 3.97%.1,4 These efficiency improvements were mainly due to two factors: reducing the native CuO layer on the surface of the Cu$_2$O during the deposition of the metal oxide onto the Cu$_2$O by conventional ALD and reducing the conduction band offset between the $p$-type Cu$_2$O.

---

1 Authors to whom correspondence should be addressed. Electronic addresses: rlzh2@cam.ac.uk and jld35@cam.ac.uk. Tel.: (44) (0) 1223-334468.
and n-type metal oxide. The presence of surface CuO is detrimental to device performance because its conduction band energy is further from the vacuum level than that of Cu$_2$O, and so it produces interfacial defect states that can enhance recombination and reduce photovoltaic device performance.

A similar approach of minimizing both CuO formation, and the conduction band offset was adopted using AP-SALD Zn$_{1-x}$Mg$_x$O (where Mg incorporation was used to reduce the conduction band offset), but the efficiencies obtained could not reach those achieved using ALD ZnO-based materials. Even when Cu$_2$O was produced by thermal oxidation, in order to increase the mobility in the absorber, the efficiencies only reached ∼2.2%. These were nevertheless the highest obtained for Cu$_2$O solar cells with the p-n junction fabricated in open air. In this perspective, we investigate the limiting factors for open air fabrication of Cu$_2$O-based solar cells and propose strategies for overcoming them. These are important for enabling solar cells with high efficiency absorbers that also face similar surface oxidation limitations, e.g., Cu$_2$ZnSnS$_4$, to achieve >10% efficiency when fabricated in open air.

We performed X-ray photoelectron spectroscopy (XPS) measurements on electrochemically deposited Cu$_2$O films (measurement process detailed in Ref. 6), as shown in Figure 1(a). A Cu$^{2+}$ peak (binding energy of 934.2 eV) and satellite peaks at 940–945 eV (Ref. 5) attributed to Cu$^{2+}$ were present in the Cu$_2$O film left in ambient air for over a week. It was only when the Cu$_2$O was stored in a nitrogen-filled glovebox immediately after deposition that peaks associated only with Cu$^{1+}$ states were found (Figure 1(a)). It can also be seen from Figures 1(b) and 1(c) that almost all Cu$_2$O samples that had been stored in air for a week had higher intensity Cu$^{2+}$ peaks than Cu$_2$O stored in a nitrogen-filled glovebox for a week. Additional Cu$^{2+}$ was introduced because these samples were processed by AP-SALD (details below) at 80 °C (for electrochemically deposited Cu$_2$O) or 100 °C (for thermally oxidized Cu$_2$O) after storage. These XPS results strongly indicate that CuO readily forms on the Cu$_2$O surface when it is exposed to air at room temperature, as indicated by the negative Gibbs free energy in Reaction 1 of Table I. The first technique for minimizing CuO formation is therefore to store the Cu$_2$O in an inert environment immediately after deposition.

We investigated whether scanning the Cu$_2$O under the flowing vapors of the organometallic precursors for ZnO (diethylzinc) and Mg$_{0.2}$Zn$_{0.8}$O (diethylzinc and bis(ethylcyclopentadienyl) magnesium) from the AP-SALD gas manifold reduced the surface CuO. It has previously been shown that diethylzinc reduces CuO to Cu$_2$O in a conventional ALD chamber. However, it could be seen from Figures 1(b) and 1(c) that after organometallic precursor treatment, Cu$^{2+}$ peaks remained. This may result from the exposure time of the sample under the organometallic precursors not being long enough to remove the entire CuO layer. Oxygen could also diffuse through the thin (<1 mm) AP-SALD inert gas channels to oxidize Cu$_2$O. The difficulty in removing surface CuO may explain the inability of Cu$_2$O solar cells formed in open air from reaching the efficiencies achieved by the vacuum production of Cu$_2$O solar cells.
The third technique we consider is introducing reducing $H_2$ to the inert $N_2$ gas channels. From Reaction 2 of Table I, it can be seen that the reduction of $CuO$ to $Cu_2O$ by $H_2$ gas is thermodynamically favored. But $H_2$ can also reduce $CuO$ or $Cu_2O$ to metallic $Cu$ (Reactions 3 and 4 of Table I). The partial pressure of $H_2$ ($p_{H_2}$) in the gas mixture and exposure time to the $Cu_2O$ therefore need to be controlled. We found that thermodynamic considerations are not applicable in the temperature range considered (deposition temperatures of 70–150 °C). By considering the kinetics of the system, $CuO$ formation is minimized when the rate of $CuO$ reduction to $Cu_2O$ (Reaction 2) is greater than the rate of $Cu_2O$ oxidation (Reaction 1), as well as being larger than the rates of metallic $Cu$ formation (Reactions 3 and 4). Achieving this balance through $H_2$ partial pressure control is also dependent on the partial pressure of $O_2$ that diffuses into the gases under the AP-SALD gas manifold. Previous time-resolved in-situ XRD patterns showed that it is possible to maintain $CuO$ under a flowing mixture of 5% $H_2$/95% $N_2$ without forming metallic $Cu$ at temperatures below 300 °C. These studies also showed that the heating rate is another important parameter to control for the reduction of $CuO$ to $Cu_2O$. Thus, the forming gas composition and exposure time to the sample, deposition temperature and heating rate are all parameters that need to be experimentally optimized when minimizing $CuO$ formation by open air AP-SALD processing.

Adopting these three strategies could allow open air fabricated $p$-$n$ junction $Cu_2O$ solar cells to achieve a similar efficiency as vacuum-processed $Cu_2O$ solar cells, which can reach 5%. Our strategies are:

- Storing the $Cu_2O$ in an inert environment immediately after deposition
- Balancing $CuO$ formation with its reduction using forming gas. The forming gas in the AP-SALD gas manifold will prevent $CuO$ oxidation to $CuO$. At the same time, limiting $H_2$ partial pressure and reaction kinetics will prevent the reduction of $Cu_2O$ to $Cu$
- Using the organometallic precursors to reduce any remnant surface $CuO$

In summary, the above strategies should ensure no higher oxidation state species are on the surface of absorber materials prone to surface oxidation, such as $Cu_2O$, $Cu_2ZnSnS_4$, $CuIn_xGa_{1-x}Se_2$ and GaAs. This would make AP-SALD a powerful technique for scalably producing efficient (>10%) solar cells.

The authors acknowledge funding from the Cambridge Commonwealth, European and International Trusts (R.L.Z.H. and Y.I.), Rutherford Foundation of New Zealand (R.L.Z.H.), an NSF Graduate Research Fellowship (R.E.B.), EPSRC of the UK (S.H.), University of Cambridge EP-SRC Centre for Doctoral Training in Nanoscience (S.H.), Girton College Cambridge (K.P.M.), an NSF CAREER Award ECCS-1150878 (T.B.), the National Research Foundation Singapore through the Singapore Massachusetts Institute of Technology Alliance for Research and Technology’s Low Energy Electronics Systems Research Program (T.B.), and an ERC Advanced Investigator Grant, Novox, ERC-2009-adG247276 (J.L.D.).


---

**TABLE I.** Essential reactions that need to be considered when using forming gas to minimize the oxidation of $Cu_2O$ to $CuO$, while avoiding the reduction of $Cu_2O$ or $CuO$ to metallic $Cu$. All Gibbs free energies are calculated from standard Gibbs formation energies at 298.15 K.\(^{11}\)

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
<th>$\Delta G^o_2$ (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$Cu_2O(s)_2 + 4(O_2(g)) \rightarrow 2CuO(s)_2$</td>
<td>-113.4</td>
</tr>
<tr>
<td>2</td>
<td>$2CuO(s)_2 + H_2(g) \rightarrow Cu_2O(s)_2 + H_2O(g)$</td>
<td>-115.0</td>
</tr>
<tr>
<td>3</td>
<td>$Cu_2O(s)_2 + H_2(g) \rightarrow 2Cu(s)_2 + H_2O(g)$</td>
<td>-82.6</td>
</tr>
<tr>
<td>4</td>
<td>$CuO(s)_2 + H_2(g) \rightarrow Cu(s)_2 + H_2O(g)$</td>
<td>-98.9</td>
</tr>
</tbody>
</table>

---

---
11 See supplementary materials at http://dx.doi.org/10.1063/1.4913442 for Gibbs free energy calculations and an analysis of the thermodynamics and kinetics of the oxidation and reduction of copper oxide species.