Area-selective electrodeposition of micro islands for CuInSe2-based photovoltaics

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ABSTRACT

For mass fabrication of highly-efficient photovoltaic modules based on Cu(In,Ga)Se2 (CIGSe) absorber layers the availability and cost of the critical raw materials In and Ga present a potential bottleneck. The micro-concentrator solar cell concept provides a solution by using micro lenses to concentrate incoming sunlight on an array of micro-sized CIGSe solar cells. The challenge is to fabricate CIGSe micro islands in exactly the desired positions using only the required material. Here, we analyze the area-selective electrodeposition of CuInSe2 into holes in an insulating SiO2 template layer as a material-efficient fabrication approach. We observe that the deposition process shows a strong dependence on the hole size, with a faster deposition around the hole perimeter. Based on a model developed for electrochemical reactions at ultra-micro electrodes, we develop numerical simulations for the electrochemical deposition process. The simulations consider the changing micro-electrode geometry throughout the deposition process, and provide a reasonable fit to the experimental data. Finally, it is shown that CuInSe2 micro solar cells fabricated by electrodeposition reach efficiencies of 4.8% under 1 sun, providing a proof-of-concept demonstration meriting further development.

Introduction

Cu(In,Ga)Se2 (CIGSe) solar cells reach the highest power conversion efficiency of all thin-film photovoltaic technologies, with the present record at 22.9% [1,2]. The CIGSe absorber layer in highly efficient cells is deposited under vacuum, either by co-evaporation from elemental precursors [3] or by sputtering and subsequent reaction in selenium and/or sulfur atmosphere [2]. However, the availability and cost of In and Ga have been raised as a concern for large-scale fabrication and Ga have been raised as a concern for mass fabrication of highly-efficient photovoltaic modules based on Cu(In,Ga)Se2 (CIGSe) absorber layers the availability and cost of the critical raw materials In and Ga present a potential bottleneck. The micro-concentrator solar cell concept provides a solution by using micro lenses to concentrate incoming sunlight on an array of micro-sized CIGSe solar cells. The challenge is to fabricate CIGSe micro islands in exactly the desired positions using only the required material. Here, we analyze the area-selective electrodeposition of CuInSe2 into holes in an insulating SiO2 template layer as a material-efficient fabrication approach. We observe that the deposition process shows a strong dependence on the hole size, with a faster deposition around the hole perimeter. Based on a model developed for electrochemical reactions at ultra-micro electrodes, we develop numerical simulations for the electrochemical deposition process. The simulations consider the changing micro-electrode geometry throughout the deposition process, and provide a reasonable fit to the experimental data. Finally, it is shown that CuInSe2 micro solar cells fabricated by electrodeposition reach efficiencies of 4.8% under 1 sun, providing a proof-of-concept demonstration meriting further development.

For large area electrodes, the current (Ic) of an electrochemical process in solution depends essentially on the bulk concentration of the species j involved (Cj0), its diffusion coefficient (Dj), and the number of electrons (n) transferred in the process, as described by Cottrell [9]:

\[ I_c = \frac{n F A C_j^0 \sqrt{D_j}}{\sqrt{\pi t}} \]  

where \( t \) is the deposition time, \( F \) the Faraday constant, and \( A \) the area of deposition. The Cottrell equation applies for the deposition after a voltage change between the electrodes and for situations where the supply of the depositing species is limited by their diffusion in solution. When using a rotating disk electrode (RDE), the supply of species can be faster and the deposition follows the Levich equation [10]:

\[ I_c = 0.62 n F A D_j^{1/2} \omega^{1/2} v^{-1/6} C \]

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Experimental

To realize an area-selective electrodeposition process, we fabricated a patterned substrate allowing exposure to the deposition solution only in desired locations of the electrode surface. These pre-structured substrates consist of a soda lime glass sheet (1 mm thickness) with a Mo metallic contact (500 nm thickness deposited by sputtering). A 2 µm thick SiO2 layer is deposited by plasma-enhanced chemical vapor deposition. Photolithography using a direct write laser is used to pattern a resist, followed by a reactive ion etching to etch the SiO2 layer down to the Mo contact. The remaining resist is removed using plasma ashing, followed by rinsing with acetone. Details about the fabrication process can be found in Ref. [8]. For the present study, we fabricated a series of holes with diameters ranging from 4 µm to 500 µm.

The electrodeposition of CuInSe2 is realized potentiostatically using a three-electrode cell setup with a saturated calomel reference electrode (SCE). The counter electrode is a 3 × 3 cm2 Pt mesh and the working electrode is the pre-structured substrate with the series of holes. For all depositions a potential of −0.55 V vs. SCE was applied and the solution was stirred at 60 rpm. The sulfate-based solution contained 2 mM CuSO4, 3.89 mM In2(SO4)3, 4.0 mM SeO2, and 0.26 M Li2SO4 as supporting electrolyte [16]. The CuInSe2 micro islands were subsequently selenized for 15 min at 500 °C in a tube furnace; a Se atmosphere was ensured by providing elemental Se as a precursor powder.

For the preparation of micro solar cell devices, the sequential electrodeposition process was chosen to allow the additional incorporation of Ga in the future. To avoid any influence of differently-sized holes, substrates with arrays of identical holes were prepared according to the above described procedure. Initially, Cu was deposited into the holes using a rotating disk electrode (RDE) and a basic Cu solution containing 3.0 M NaOH, 0.2 mM sorbitol, and 0.1 M CuSO4. A deposition voltage of −1.15 V vs. a Ag/AgCl reference electrode was used. Subsequently, In and Ga were deposited simultaneously in an In-Ga electrolyte with 50 mM InCl3 and 25 mM GaCl3 in reline mixture of choline chloride and urea. The deposition was performed at 60 °C inside a N2-filled glovebox. Details about the electrodeposition can be found in Ref. [17]. To convert the Cu-In-Ga metallic precursor stack into CIGSe, the samples were pre-annealed for 30 min at 100 °C, followed by a seleniumization step of 20 min at 450 °C using an elemental Se source. To ensure good electrical performance, a KCN etch was performed to remove any residual Cu2-xSe phases. Complete solar cell devices were
then fabricated by a standard CdS chemical bath deposition (50–70 nm thickness) and sputtering of a 90 nm thick i-ZnO and a 350 nm thick ZnO:Al layer [18].

Results

Deposition of CuInSe₂ micro islands

The simultaneous deposition of Cu, In, and Se was realized on substrates containing a series of micro electrodes with diameters ranging from 4 µm to 500 µm. The micro electrodes consist of a Mo electrode at the bottom of a hole in a SiO₂ insulating layer of 2 µm thickness. Fig. 1(a)–(c) show exemplary results of the electrodeposition process for holes with diameter of 12 µm, 100 µm, and 500 µm, respectively. The optical microscopy images show clearly that the deposition only occurs at the position of the electrodes and not on the SiO₂ matrix, according to expectation. This was independently confirmed by scanning electron microscopy (SEM) imaging (Fig. 1(d)). The typical microstructure of the CuInSe₂ electrodeposited material can be observed in the close-up SEM image in Fig. 1(e). Energy dispersive x-ray spectroscopy experiments of the electrodeposited material in the holes confirm the CuInSe₂ composition and Raman measurements show clearly the A₁ vibrational mode at 172 cm⁻¹ of the tetragonal CuInSe₂ (Fig. 1(f)) [19]. However, irregular edges of the deposited material are observed, indicating some deposition around the circumference of the holes. The thickness of the deposited CuInSe₂ material was measured by profilometry and the respective curves are overlayed on the optical images in Fig. 1(a)–(c). For the smallest sizes, the holes are filled homogeneously and the material has grown out of the hole, see Fig. 1(a). For the larger holes, Fig. 1(b) and (c), we observe a thicker deposit at the perimeter of the holes, while at the center the CuInSe₂ material does not reach the thickness of the SiO₂ layer (i.e. 2 µm). The formation of this corona around the perimeter of the holes shows no dependence on the diameter of the hole and an average width of (15.3 ± 5.5) µm is found. The profilometer data is used to extract the thickness of the CuInSe₂ layer and the height of the corona; both values are plotted as a function of the hole diameter in Fig. 2(a). While the corona height is independent of the hole size, the thickness of the CuInSe₂ deposit at the center of the holes shows a clear decrease for holes with a diameter larger than 60 µm. These results clearly demonstrate the enhanced deposition in smaller holes.

To analyze the obtained results in more detail, we evaluate the Cottrell and Levich equations for the present deposition conditions. The thickness \( d \) of the deposited layer can be estimated according to:

\[
d = \frac{I_0}{F n F d A} \quad (5)
\]

where \( M \) is the molar mass of the deposited species (336.3 g/mol for CuInSe₂), \( t \) is the deposition time, \( \rho \) the density of the material (5.7 g/cm³ for CuInSe₂), and \( A \) the area of deposition. The compound electrodeposition was assumed to be self-limited by the diffusion of the slowest species (Cu, \( D = 6.5 \times 10^{-6} \text{ cm}^2/\text{s} \)). Using the currents \( I_c \) and \( I_L \) from Eqs. (1) and (2), it is clear that a dependence on the hole size cannot be described by these equations. The two deposition regimes give a constant thickness independent of the area, illustrated by the horizontal dashed lines in Fig. 2(a).

As described above, electrochemical processes at micro electrodes require the use of Eq. (3). The dependence of the deposition thickness for planar (dotted red line) and recessed (depth \( L = 2 \mu m \), dashed line) micro electrodes on the electrode diameter are also illustrated. While these dependencies apply for electrochemical processes, in the present case it has to be considered that the electrode shape and size change with time as more and more material is being deposited. We therefore performed numerical simulations of the thickness of the deposited material, the results of which are shown by the solid red lines in Fig. 2(a) and (b). Initially, it is considered that the depth \( L \) of the recessed electrode decreases with deposition time. The dependence of the correction factor (see Eq. (4)) for recessed electrodes as a function of electrode diameter and recess depth \( L \) is illustrated in Fig. 2(c). Once the hole is filled, the material grows on top of the surface, which we approximate by a hemispherical shape where the thickness and the radius of the electrode change. Fig. 2(b) shows the time dependence of the thickness for three different diameters where the numerical simulation for a fixed recess depth of 2 µm (dashed lines) is compared to our simulation for a deposition process with a variable electrode size and shape (solid lines). The thickness of the dot after a 20-minute deposition is extracted from these numerical simulations as a function of the initial electrode diameter, resulting in the solid line of Fig. 2(a).

Our numerical simulation of the deposition process for micro electrodes gives a better qualitative description of the size dependence, compared to the analytical solution for electrochemical processes according to Eqs. (3) and (4) and illustrated schematically in Fig. 3(a) and (c).
Unlike in the Cottrell regime, additional reaction species corresponding to what would be expected for a typical micro electrode. Initially recessed microelectrode. In fact, our experimental results for diameters up to 60 µm follow the schematic illustration in Fig. 3(c) and (d), corresponding to what would be expected for a typical micro electrode. For larger micro electrodes, the additional species that arrive from areas where no deposition occurs will lead to a corona effect increasing the thickness of deposited material (e) inside the recessed micro electrode and (f) leading to thicker deposit (hc) at the circumference of the initially recessed microelectrode. (b). However, a quantitative agreement is not reached. We attribute the discrepancies to two major reasons. (i) The deposited material in our study is CuInSe2, which is a semiconductor; thus, the growth of the film is accompanied by a voltage drop across the thickness of the electrode, which continuously shifts the effective electrochemical potential to more positive values during plating. (ii) The size range of the electrodes in our study goes beyond the range which is typically considered a micro electrode. In fact, our experimental results for diameters up to 60 µm follow the schematic illustration in Fig. 3(c) and (d), corresponding to what would be expected for a typical micro electrode. Unlike in the Cottrell regime, additional reaction species diffuse from regions outside the electrode, leading to higher currents and – in the case of electrodeposition – thicker deposited material. If the diameter of the electrode becomes larger, the diffusion of these species does not cover the full electrode anymore and enhanced deposition only occurs at the outer ring of the electrode. This enhanced deposition leads to the corona effect observed in our study, which is schematically illustrated in Fig. 3(e) and (f). The width of the corona should be related to the diffusion coefficient of the depositing species, independent of the electrode size, in agreement with our experimental observation.

**Cu(In,Ga)Se2 micro solar cells**

For the fabrication of micro solar cells, we used the sequential deposition of Cu and In, followed by a high-temperature anneal in Se atmosphere to convert the Cu-In precursor into CuInSe2. To test the suitability of the above described electrodeposition process, the deposition of the metallic precursor was performed into the same SiO2 matrices with holes. An array of 13 × 13 CuInSe2 micro absorbers with a diameter of 200 µm was then processed to full solar cell devices by deposition of CdS and the i-ZnO/ZnO:Al window layers. Subsequently, a single cell was isolated by scratching carefully the window layer stack on top of the SiO2 matrix around the selected device (Fig. 4(a)). For the measurement of the current density (J)-voltage (V) characteristics, four contacts were placed, two of them on the Mo back contact and the other two directly on the ZnO:Al layer on the SiO2 insulating layer close to the selected device. The JV characteristics presented in Fig. 4(b) show a well performing solar cell with an open-circuit voltage of $V_{oc} = 396$ mV, a short-circuit current of $J_{sc} = 25.2$ mA/cm², and a fill factor of $FF = 48\%$, leading to a power conversion efficiency of 4.8%.

These device results clearly show the suitability of the approach to electrodeposit CuInSe2 into holes in an insulating matrix to realize the materials-efficient fabrication of micro-concentrator solar cells. Optimization of the electrodeposition process is required to address the above-described geometry-dependent deposition results.

**Conclusion**

We have presented a detailed analysis of the electrodeposition process into recessed micro electrodes by extending the analytical equations for electrochemical reactions in microelectrodes using numerical simulations to account for the size and shape change of the electrodes throughout the deposition process. Our results provide a qualitative description of the electrodeposition of CuInSe2 into recessed micro electrodes, which are studied for their application in photovoltaic energy conversion implementing the micro-concentrator thin film solar cell concept. To demonstrate this novel PV concept, CuInSe2 micro solar cells of 200 µm diameter were fabricated and their efficiency was measured to be 4.8% under 1 sun. Our study provides valuable insights into microelectrode electroplating, which is also relevant for many
other applications from sensing to microfabrication. For the presented micro solar cells, we demonstrated proof-of-concept devices paving the way for further developments of this promising PV concept.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

References


