

Effects of post-deposition treatments on the photoactivity of CuInSe₂ thin films deposited by the induced co-deposition mechanism

Marianna Kemell, Mikko Ritala and Markku Leskelä

Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland.
E-mail: Marianna.Kemell@Helsinki.fi

Received 3rd May 2000, Accepted 2nd October 2000

First published as an Advance Article on the web 14th November 2000

CuInSe₂ thin films were electrodeposited potentiostatically from acidic aqueous solutions containing CuCl, InCl₃ and SeO₂. SCN⁻ ions were used as complexing agents for Cu⁺ ions in order to shift their reduction potentials in the negative direction. Different deposition solutions and post-deposition treatments were compared. The films were characterized by means of energy dispersive X-ray spectrometry, scanning electron microscopy, X-ray diffraction, time-of-flight elastic recoil detection analysis, electrochemical quartz crystal microbalance, cyclic photovoltammetry and photoelectrochemical measurements. The as-deposited films were found to be p-type. The photoactivity was lost after heat treatment, but etching in 0.5 M KCN regenerated it rapidly.

Introduction

Polycrystalline CuInSe₂ (CIS)-based chalcogenide materials such as Cu(In,Ga)Se₂ (CIGS) and Cu(In,Ga)(Se,S)₂ are gaining more and more importance as the absorber layers in thin film photovoltaic solar cells. Cell efficiencies of almost 19% have been achieved with these materials.¹ The absorber layers for these high efficiency cells have usually been prepared by gas phase techniques, such as evaporation. CIS and CIGS films prepared from electrodeposited precursors have generally yielded somewhat lower efficiencies of about 14% or less.²

On the other hand, the cost of the electricity produced by a photovoltaic solar cell is not only affected by the conversion efficiency, but also by the production cost of the cells. In this sense, electrodeposition is a potential alternative for the preparation of CIS and CIGS thin films, since it is a simple and inexpensive method with good large area processing capability.

We have previously developed a promising one-step electrodeposition process for the preparation of CuInSe₂ thin films. Constant film composition, corresponding to a Cu_{2-x}Se-rich stoichiometry of Cu_{1.30}In_{1.00}Se_{2.20} according to Rutherford backscattering spectrometry, was achieved over wide potential and concentration ranges.³ The deposition process was based on the induced co-deposition mechanism,⁴ of which CdTe is the most well-known example. Our study³ was the first where the induced co-deposition mechanism was utilized in a ternary system. In our process, the Cu⁺ ions were complexed by SCN⁻ ions in order to shift their reduction potential further apart from that of HSeO₃⁻ ions and, thus, make the induced co-deposition mechanism possible. Se deposited first and induced the reduction of Cu(SCN)₄³⁻ ions and the formation of Cu_{2-x}Se at more positive potentials than those at which the deposition of metallic Cu began. The formation of Cu_{2-x}Se in turn induced the formation of CIS at the same potential range, before the deposition of metallic Cu or In occurred.³ The deposition mechanisms were later confirmed by combined cyclic voltammetry and electrochemical quartz crystal microbalance experiments.^{5,6}

In this study, we examine the photoactivity of the CuInSe₂ thin films prepared by the induced co-deposition mechanism. The photoactivity is tested using an acidic sulfate solution.^{7,8}

The effect of different post-deposition treatments on the film composition, morphology, crystallinity and photoactivity are studied.

Additionally, since the SCN⁻ concentration of 4 M used in our earlier study³ is quite high for practical purposes and caused SCN⁻ residues in the films, we have modified our electrodeposition process by reducing the SCN⁻ concentration in the solution to 2 M. Although also the Cu⁺ concentration had to be lowered accordingly by a factor of five to avoid precipitation of CuSCN, the growth rate was not affected, since it is determined by the HSeO₃⁻ concentration. These two different deposition solutions are compared and the formation of CuInSe₂ is monitored using cyclic photovoltammetry.

Experimental

CuInSe₂ thin films were deposited using a set-up described previously.³ Two different deposition solutions were compared. The first deposition solution was one of those used in our earlier study³ and contained 0.05 M CuCl, 0.05 M InCl₃ and 0.001 M SeO₂. The induced co-deposition process yielded constant, near stoichiometric, film composition over a wide range of Cu/In concentration ratios,³ and here we have chosen an intermediate Cu/In ratio of 1. The KSCN concentration in this solution was 4 M. This high KSCN concentration was, however, quite impractical, since it caused SCN⁻ residues in the films³ and lowered the stability of the solution. Therefore, another deposition solution, containing only 2 M KSCN, was studied. Because of the decreased solubility of CuCl in the more dilute SCN⁻ solution, the CuCl concentration was lowered to 0.01 M. The concentration of InCl₃ was again chosen to be equal to that of CuCl, *i.e.* 0.01 M. The concentration of SeO₂ was the same as previously, 0.001 M. The natural pHs of the solutions were between 2.4 and 3.0. The deposition solutions will hereafter be referred to as 4 M (first solution) and 2 M (second solution), according to the concentration of the SCN⁻ ions.

The cyclic photovoltammetry (CPV) measurements and photoelectrochemical (PEC) characterizations were carried out using the Autolab PGSTAT20 potentiostat and chopped polychromatic illumination provided by a 50 W halogen

lamp. The light was modulated by a chopper made of a timer relay and the distance between the lamp and the working electrode was held constant, about 25 cm. A light chopping sequence of 0.5 s on, 0.5 s off was used since, according to the preliminary experiments, changing the on and off times seemed to have no effect on the magnitude of the photocurrent density. The photoelectrochemical characterization was carried out in 0.5 M K_2SO_4 (pH 4.0–4.5) in a single compartment cell. The cyclic photovoltammograms and the photoelectrochemical scans were measured at a scan rate of 10 mV s^{-1} . They were started from 0 V and were scanned first to the negative (cathodic) direction. All cyclic photovoltammetry and photoelectrochemical studies and film depositions were carried out at room temperature. The electrochemical quartz crystal microbalance (EQCM) measurements were performed as in our earlier studies.^{5,6}

The films in the PEC studies were about 400 nm thick (deposition time 4 h). Since both deposition solutions allowed wide potential ranges for the formation of near stoichiometric CIS films (see Fig. 1 below and ref. 3), an intermediate deposition potential of -0.5 V was selected in each case for preparation of the films for the PEC studies.

After the depositions, the films were subjected to different post-deposition treatments, such as annealing for 15 min at 400°C under a N_2 atmosphere and/or etching in 0.5 M KCN for different time periods (30 s–30 min). The SEM and EDX studies as well as the time-of-flight elastic recoil detection analysis (TOF-ERDA) experiments were performed as earlier.³

The crystallinity of the films was examined with Bruker AXS D8 and Philips MPD 1880 powder X-ray diffractometers using $Cu-K\alpha$ radiation. The films in the XRD studies were thicker (about $1 \mu\text{m}$; deposition time 17 h) than those in the PEC studies in order to better illustrate the effect of the post-deposition treatments on the crystal structure.

Results and discussion

Film depositions

Fig. 1 shows the composition of the films deposited from the 2 M solution containing 2 M KSCN, 0.01 M $CuCl$, 0.01 M $InCl_3$ and 0.001 M SeO_2 as a function of the deposition potential. The compositions were measured by EDX. As expected, constant composition was again achieved over a wide potential range and the film compositions were essentially the same as those obtained with the 4 M KSCN solution.³ Furthermore, the growth rates were very similar to those of the 4 M films,³ which indicates that the growth rate depends mainly on the concentration of SeO_2 in the solution. This is in agreement with the idea that the film growth proceeds *via* the induced co-deposition mechanism, where the selenium precursor reduces first and causes then the formation of $CuInSe_2$ at more positive potentials than those at which the reduction of metallic Cu or In takes place.

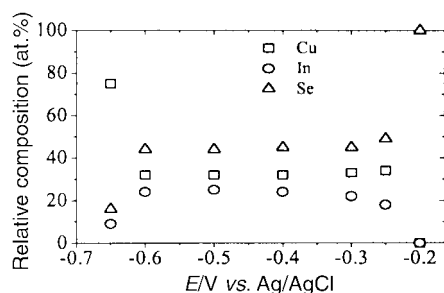


Fig. 1 The relative compositions of the CIS films deposited from a solution containing 2 M KSCN, 0.01 M $CuCl$, 0.01 M $InCl_3$ and 0.001 M SeO_2 as a function of the deposition potential. Compositions measured by EDX.

Composition, crystal structure and morphology

The as-deposited films were amorphous but the heat treatment made them crystalline, forming the chalcopyrite $CuInSe_2$ phase.⁹ As is the case with the 4 M films,³ the 2 M films also contain oxygen, hydrogen, sulfur, carbon and nitrogen as impurities. According to TOF-ERDA, the oxygen and hydrogen contents of the as-deposited films are now larger than in the 4 M films, about 18 at.% each, but the sulfur and nitrogen contents are lower, about 2–3 at.%, and the carbon content is about 6 at.%. The heat treatment decreases the oxygen, hydrogen and carbon contents and, thus, the annealed films contain 5–7 at.% oxygen and 2–3 at.% of the other impurities. Furthermore, most of the oxygen is located near the surface. This may be due to formation of a surface oxide after the annealing.

KCN etching is a well-known method for the removal of excess Cu and chalcogen from chalcopyrite thin films.¹⁰ As expected on the basis of literature reports,^{11,12} it reduced the Cu and Se contents of the films. The etching time did not seem to have any clear effect on the stoichiometry. According to EDX, the composition of the annealed film changed from $Cu_{1.33}In_{1.00}Se_{1.93}$ to $Cu_{0.95}In_{1.00}Se_{1.66}$ after 30 min etching in 0.5 M KCN. When an as-deposited film was etched in KCN, part of it detached. Just 1 min immersion caused a partial removal of the film. The Cu and Se contents decreased more rapidly than when the films were annealed prior to the etching, leading to a stoichiometry of $Cu_{0.48}In_{1.00}Se_{1.35}$ (EDX) after 1 min etching. This is in agreement with other studies.^{10–12} TOF-ERDA results revealed that when the annealed film was etched in 0.5 M KCN, the oxygen and hydrogen contents (especially near the film surface) increased (O to 14–18 at.%, H to 6–7 at.%). Additionally, the carbon content increased by a small amount. This is not surprising, since the water or hydroxyl groups and CN^- ions from the etching solution may become attached to the film. However, since the oxygen content increased more than the hydrogen content, it is possible that the etching treatment causes some oxide formation on the film surface. When an as-deposited film was etched in 0.5 M KCN, the impurity contents were almost unchanged.

Fig. 2 shows three X-ray diffractograms of CIS films after different post-deposition treatments: diffractogram a corresponds to a film annealed at 400°C and diffractogram b to an annealed film that has been etched for 30 min in 0.5 M KCN after the annealing treatment. The etching treatment does not seem to markedly alter the d -values nor the intensity ratios of the peaks. Both the annealed and the annealed then etched films produce patterns which exhibit the characteristic chalcopyrite peaks, although some of them are very weak. This is in an agreement with the results obtained for the 4 M films in our earlier study.³ Diffractogram c is of a film which was first etched for 1 min in 0.5 M KCN and then annealed at

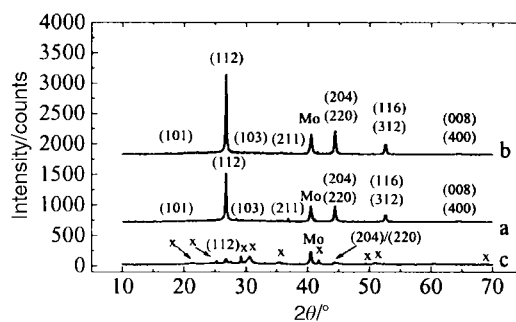


Fig. 2 X-Ray diffractograms of CIS films: (a) annealed for 15 min at 400°C under nitrogen; (b) annealed then etched for 30 min in 0.5 M KCN; (c) etched for 1 min in 0.5 M KCN then annealed for 15 min at 400°C under nitrogen. The indexing of the peaks refers to the chalcopyrite phase (40-1487). Peaks marked with an \times are due to different In_3Se or In_3Se -rich CIS phases.

400 °C. The diffractogram now exhibits several broad peaks. The only peaks that possibly correspond to the chalcopyrite phase are the (112) and (204/220) reflections. The remaining peaks (marked with an ×) most probably originate from different In_xSe or In_xSe -rich CIS phases which cannot be identified unambiguously. The indexing of the reflections in the figure refers to the chalcopyrite phase.⁹

Fig. 3 shows a SEM micrograph of a typical 2 M film. The morphology of the 2 M films is very similar to that of the 4 M films: the films consist of small grains, the size of which increases as the film thickness increases. The annealing and etching treatments do not affect the morphology to a great extent.

Cyclic photovoltammetry

The formation of a photoactive deposit can be detected by cyclic photovoltammetry. Fig. 4 shows the cyclic photovoltammograms measured in the two deposition solutions (thin line: 4 M solution, thick line: 2 M solution). As can be seen in the figure, the photocurrent starts to flow in both cases at about -0.33 V during the forward (cathodic) sweep. However, as is known from our earlier study,³ and from Fig. 1, the formation of CuInSe_2 begins earlier, at about -0.25 V. This difference is probably due to the fact that the photoactive deposit is not thick enough before the potential reaches -0.33 V. The photoactive behavior of the deposited CuInSe_2 film continues during the whole scan, although it becomes very weak during the oxidation (after -0.25 V during the reverse scan). The fact that the photocurrent is cathodic (negative) in both cases reveals that the deposits formed are p-type¹³ and, therefore, in this respect, suitable for use in photovoltaic cells. This is in agreement with the RBS and TOF-ERDA results obtained in our earlier study,³ which suggest that the as-deposited films are Cu_{2-x}Se -rich and should thus be p-type.¹⁴

The photocurrent density ($j_{\text{dark}} - j_{\text{ph}}$) was lower in the 2 M solution (about $10 \mu\text{A cm}^{-2}$) than in the 4 M solution (about $20 \mu\text{A cm}^{-2}$). When the cyclic photovoltammograms were measured on previously deposited CIS films, the photoactivities started earlier and were stronger than on a bare Mo electrode. This is in agreement with the fact that a thicker semiconductor film is capable of absorbing a larger part of the incident light than a thinner one. The scans measured in the 4 M solution again exhibited stronger photocurrent densities than those measured in the 2 M solution.

The electrochemical quartz crystal microbalance was also used in the cyclic photovoltammetry measurements. Fig. 5 presents the cyclic voltammogram and the simultaneous frequency (mass) change, measured in the 2 M solution on a Au surface. The fact that the photoactivity starts at the very beginning of the scan is due to the fact that the scan shown in the figure is a third successive scan. A weak photoeffect can

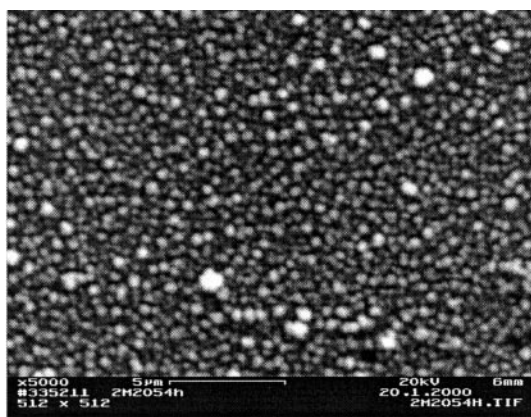


Fig. 3 A SEM micrograph of an annealed CIS film.

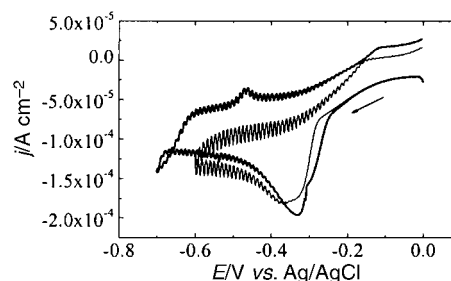


Fig. 4 Cyclic photovoltammograms measured in solutions containing 4 M KSCN, 0.05 M CuCl , 0.05 M InCl_3 and 0.001 M SeO_2 (thin line) and 2 M KSCN, 0.01 M CuCl , 0.01 M InCl_3 and 0.001 M SeO_2 (thick line).

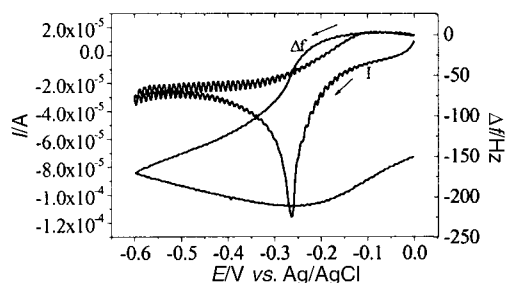
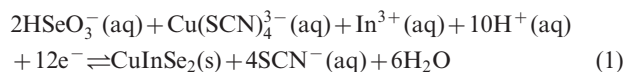


Fig. 5 Cyclic voltammogram and the simultaneous frequency change, measured in the 2 M solution on a Au surface, third scan.

also be seen in the frequency plot, although it is much weaker than that observed in the cyclic voltammogram. The maximum value of $I_{\text{dark}} - I_{\text{ph}}$ is about $7.4 \mu\text{A}$, which corresponds to a current density of about $30 \mu\text{A cm}^{-2}$, since the projected area of the Au electrode is 0.236 cm^2 . The current density was now (even during the first scan) much higher than when the cyclic voltammogram was measured on a Mo electrode. This is probably due to the different work functions of the two metals. As expected, the measurements yielded similar M/z values as in our earlier study with the 4 M solution.⁶ During the first scan, a M/z value of 31.68 g mol^{-1} was obtained between -0.14 V during the forward scan and -0.59 V during the reverse scan. This is very close to the theoretical value corresponding to the formation of CIS from Cu^+ , In^{3+} and Se^{4+} ions, according to the following reaction:



Theoretical $M/z = 28.02 \text{ g mol}^{-1}$.

The M/z (M = molar mass of the deposit, z = number of electrons involved in the reaction) values were calculated from eqn. 2, which was derived from the Sauerbrey equation¹⁵ and Faraday's law:

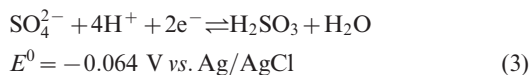
$$M/z = (\text{d}\Delta f / \text{d}\Delta Q)(F/K) \quad (2)$$

where Δf is the frequency change and ΔQ the charge change during the reaction (obtained by integrating the current), F is the Faraday constant ($96485.31 \text{ C mol}^{-1}$) and K is an experimentally determined constant ($225.95 \times 10^6 \text{ Hz g}^{-1}$).

Photoelectrochemical measurements

Suitable illumination of a semiconductor liquid junction generates electron-hole pairs. In a liquid junction with a p-type semiconductor, the electron goes to the surface of the semiconductor and reduces a species in the electrolyte. The hole moves to the back contact, causing an increase in the cathodic current.¹³ In the slightly acidic potassium sulfate solution used

in this study, the reducing species is the sulfate ion (SO_4^{2-}) since the standard potential of the sulfate/sulfite couple is $-0.064 \text{ V vs. Ag/AgCl}$.¹⁶



According to preliminary experiments, the photoactivities of the films deposited from 4 M or 2 M solutions are essentially equal. The data shown in the figures below correspond to the films deposited from the 2 M solution.

Fig. 6 shows a PEC curve of an as-deposited CIS film in 0.5 M K_2SO_4 . As can be seen, the film is only very slightly photoactive. The fact that the photoactivity is now much worse than during the cyclic photovoltammogram in the deposition solution is probably due to the different electrolyte solutions employed. Not only the redox systems are different, but also the band edge positions are known to be strongly dependent on the electrolyte.¹⁷ Thus, it appears that the redox systems present in the SCN^- solution correspond better to the band edge positions of our CIS films. On the other hand, part of the photocurrent observed during the CPV above may be because some CuSCN is formed during the scan. CuSCN is a p-type semiconductor that can also be prepared electrochemically.¹⁸ In the sulfate solution, there are no SCN^- ions present and, thus, no CuSCN can be formed. Also, the as-deposited films are known to contain S, C and N as impurities (see above and ref. 3) which may at least be partly due to CuSCN . The same reason may account for the fact that the photocurrent during the CPV scan was smaller in the solution that contained 2 M KSCN than in the 4 M solution: it is likely that less CuSCN is formed in the 2 M solution.

The photoactivity was lost completely after the annealing treatment, regardless of the annealing temperature, which was varied between 300 and 400 °C. It may be possible that, during the annealing, the excess Cu_{2-x}Se phase also crystallizes and may even segregate to the surface or grain boundaries, thus having a detrimental effect on the photoactivity. The loss of the photoactivity may also be attributed to the decrease in the impurity contents during annealing (see compositions above). If the films contain CuSCN , it probably decomposes during the annealing.

When the annealed films were etched in 0.5 M KCN, the photoactivity was recovered, and was now much better than before the post-deposition treatments. This is in agreement with the more stoichiometric composition after the etching treatment. Fig. 7 shows the photoelectrochemical response in 0.5 M K_2SO_4 for a CIS film which was first annealed and then etched in 0.5 M KCN for 1 min. The fact that the cathodic and anodic PEC scans are different can be attributed to changes in surface chemistry and related band edge shifts.^{7,17} The maximum photocurrent densities of the etched films vary between 35 and 50 $\mu\text{A cm}^{-2}$ and the maximum value was

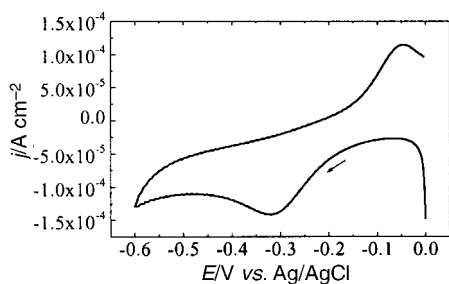


Fig. 6 Photoelectrochemical response of an as-deposited CIS film in 0.5 M K_2SO_4 . Deposition solution: 2 M KSCN , 0.01 M CuCl , 0.01 M InCl_3 and 0.001 M SeO_2 .

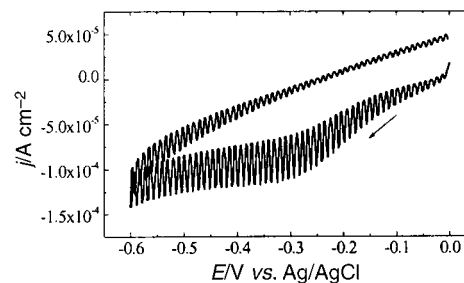


Fig. 7 Photoelectrochemical response of an annealed CIS film in 0.5 M K_2SO_4 after etching in 0.5 M KCN for 1 min.

achieved when the etching time was 1 min. This suggests that the presence of some excess Cu and Se leads to p-type activity.

Although the KCN treatment of the as-deposited film causes partial removal of the film, it also improves the photoactivity. When the etched film was annealed at 400 °C, the photoactivity got worse and was only slightly better than that of the as-deposited film. The conductivity remained p-type.

Hence, the best photoactivity was achieved when the annealing treatment was performed before the etching. This is in agreement with the results of other studies.^{7,8,12} The maximum photocurrent densities we obtained were about 50 $\mu\text{A cm}^{-2}$ which is nearly twice that obtained in ref. 8 under similar illumination circumstances. On the other hand, we did not observe any difference in the photoactivities depending on whether the annealed films were kept in air at room temperature before the etching treatment or not.

Conclusions

CuInSe_2 thin films were electrodeposited from two different solutions and the effect of different post-deposition treatments on their photoactivities studied. The as-deposited films were found to be slightly p-type. Annealing at 400 °C under N_2 improved the film crystallinity but decreased the photoactivity. Etching in 0.5 M KCN improved the photoactivity, whether performed before or after the annealing. In each case, the conductivity remained p-type. The best photoresponse of about 50 $\mu\text{A cm}^{-2}$ was achieved by first annealing the films at 400 °C under N_2 and then etching in 0.5 M KCN for 1 min. Thus, photoactive CuInSe_2 thin films can be prepared by a one-step electrodeposition process followed by thermal annealing under N_2 and chemical etching in KCN. No selenization step is needed.

Since the properties of the films deposited from the two different solutions seem to be essentially similar, the 2 M solution will be used hereafter because it is more stable and uses less metals (by a factor of five) and KSCN (by a factor of two) and still gives the same deposition rate and film quality.

Acknowledgements

This work was partly financed by the special funding of the University of Helsinki and the Academy of Finland. Mr Timo Sajavaara (the Accelerator Laboratory, University of Helsinki) is acknowledged for the TOF-ERDA measurements. Facilities provided by the Electron Microscopy Unit, Institute of Biotechnology, University of Helsinki were used for the SEM and EDX studies.

References

- 1 M. A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon and R. Noufi, *Prog. Photovoltaics: Res. Appl.*, 1999, 7, 311.
- 2 R. N. Bhattacharya, W. Batchelor, H. Wiesner, F. Hasoon, J. E. Granata, K. Ramanathan, J. Alleman, J. Keane, A. Mason,

- R. J. Matson and R. N. Noufi, *J. Electrochem. Soc.*, 1998, **145**, 3435.
- 3 M. Kemell, M. Ritala, H. Saloniemi, M. Leskelä, T. Sajavaara and E. Rauhala, *J. Electrochem. Soc.*, 2000, **147**, 1080.
- 4 F. A. Kröger, *J. Electrochem. Soc.*, 1978, **125**, 2028.
- 5 M. Kemell, H. Saloniemi, M. Ritala and M. Leskelä, *Electrochim. Acta*, 2000, **45**, 3737.
- 6 M. Kemell, H. Saloniemi, M. Ritala and M. Leskelä, *J. Electrochem. Soc.*, submitted.
- 7 C. Guillén, J. Herrero and D. Lincot, *J. Appl. Phys.*, 1994, **76**, 359.
- 8 R. Ugarte, R. Schrebler, R. Córdova, E. A. Dalchiele and H. Gómez, *Thin Solid Films*, 1999, **340**, 117.
- 9 Powder Diffraction Files, Card 40-1487, International Centre for Diffraction Data, Pennsylvania, PA.
- 10 R. N. Bhattacharya, D. Cahen and G. Hodes, *Sol. Energy Mater.*, 1984, **10**, 41.
- 11 F. J. Pern, R. Noufi, A. Mason and A. Franz, *Thin Solid Films*, 1991, **202**, 299.
- 12 C. Guillén and J. Herrero, *J. Electrochem. Soc.*, 1994, **141**, 225.
- 13 U. Stimming, *Electrochim. Acta*, 1986, **31**, 415.
- 14 G. Hodes, T. Engelhard, D. Cahen, L. L. Kazmerski and C. R. Herrington, *Thin Solid Films*, 1985, **128**, 93.
- 15 M. R. Deakin and D. A. Buttry, *Anal. Chem.*, 1989, **61**, 1147A.
- 16 S. I. Zhdanov, in *Standard Potentials in Aqueous Solutions*, ed. A. J. Bard, R. Parsons and J. Jordan, Marcel Dekker, Inc., New York, 1985, p. 102.
- 17 W. Siripala, J. Vedel, D. Lincot and D. Cahen, *Appl. Phys. Lett.*, 1993, **62**, 515.
- 18 C. Rost, I. Sieber, S. Siebentritt, M. C. Lux-Steiner and R. Könenkamp, *Appl. Phys. Lett.*, 1999, **75**, 692.