The behaviour of Na implanted into Mo thin films during annealing

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Abstract

Na implants have been used to study diffusion of Na in rf diode sputtered Mo thin films used as back contacts for Cu(In,Ga)Se\textsubscript{2} solar cells. The samples were analysed with secondary ion mass spectrometry before and after vacuum anneals at 420°C and 550°C. In addition, X-ray photoelectron spectroscopy has been used for surface studies. The diffusion of Na within the Mo grains was found to be very slow as indicated by the unchanged shape and position of the implant peak after the anneal. An increased level of Na in the bulk of the Mo layer strongly suggests diffusion of Na out of the soda lime glass substrate into the Mo film. The oxygen content of the rf diode sputtered Mo films was 8 at% as found by Rutherford backscattering spectroscopy. It is suggested that Mo oxide phases are present in the grain boundaries and that these oxides, being intercalation hosts for Na, are responsible for the rapid diffusion and high solubility of Na in the sputter-deposited Mo films. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The fabrication of high-efficiency thin film solar cells based on Cu(In,Ga)Se\textsubscript{2} and related materials includes, as a crucial step, Cu(In,Ga)Se\textsubscript{2} deposition on Mo-coated...
soda lime glass substrates. The nucleation and growth of Cu(In,Ga)Se$_2$ grains are directly influenced by the thermal, morphological and chemical properties of the Mo back contact layer. It has been found that the use of soda lime glass as the substrate material for Cu(In,Ga)Se$_2$-based solar cells leads to high concentrations of Na both in the Mo and in Cu(In,Ga)Se$_2$ [1–6]. The substrate temperature during deposition of Cu(In,Ga)Se$_2$ reaches up to 550°C. During this high temperature step, Na diffuses out of the glass and through the Mo and affects the growth of Cu(In,Ga)Se$_2$ in a favourable way, resulting in large grains and high film density [3]. Secondary ion mass spectrometry (SIMS) analysis of Cu(In,Ga)Se$_2$ samples deposited on both Mo coated and uncoated soda lime glass shows no significant difference in the Na concentration of the Cu(In,Ga)Se$_2$ as seen in Fig. 1, which indicates that the Mo back contact layer can be a very efficient medium for Na diffusion. However, variations of the Mo properties, and hence the Na transport, may explain unintentional variations in Cu(In,Ga)Se$_2$ film properties. As the best solar cell results have been achieved for Cu(In,Ga)Se$_2$ grown in the presence of Na, the role of Mo as a medium for Na transport is an important issue. Of importance for the use of substrates other than soda lime glass and adding the Na by an Na precursor layer as e.g. Na$_2$S is the ability of Mo to absorb Na. Solubility of Na in Mo has been observed by Ruckh et al. [5], where an alkali-free sample with a Mo layer was coated with an Na precursor layer, then heated and analysed with X-ray photo electron spectroscopy (XPS) in situ and after a few days of air exposure. Na disappeared from the surface at 600°C (approximately the same temperature as the Cu(In,Ga)Se$_2$ deposition temperature) but reappeared after the air exposure.

In this study, we report on the diffusion of Na from ion implants in Mo films used as back contacts for Cu(In,Ga)Se$_2$ solar cells, and make comparisons with the sodium coming from the soda lime glass.
2. Experimental procedure

The Mo was rf diode sputtered on soda lime glass substrates from a high-purity Mo target in 2 Pa of ultrahigh purity Ar at 650 W. The background pressure of residual gases was \( \sim 5 \times 10^{-5} \) Pa and the deposition time 15–20 min depending on the thickness. The Mo films used for Na implants were 0.5 \( \mu \)m thick; Mo films used for back contacts to solar cells are typically 0.3–0.5 \( \mu \)m. The lateral grain size was \( \sim 0.1 \mu \)m and the vertical grain size was equal to the film thickness. The as-deposited films were in a state of tensile residual stress. This was determined from the bending of thin glass samples (cover glasses for optical microscopy) coated at the same time.

The layers were implanted with 100 keV Na\(^+\) to a dose of \( 1 \times 10^{15} \) cm\(^{-2}\). According to simulations using the Transport of Ions in Matter (TRIM96) computer code originally developed by Biersack et al. [7], this should have produced an approximately Gaussian implant with a peak concentration of Na in the Mo films of \( 8.6 \times 10^{19} \) cm\(^{-3}\), 81 nm below the surface and with a straggle of 40 nm.

In some of the samples, an approximately 2.5 \( \mu \)m thick film of Cu(In,Ga)Se\(_2\) was deposited on top of the Mo using a standard process for making device quality Cu(In,Ga)Se\(_2\) layers. This was done in order to compare the Mo layers used for the implant study with Mo layers after normal Cu(In,Ga)Se\(_2\) deposition, and to quantify the Na concentration in a typical device back contact layer. The deposition of Cu(In,Ga)Se\(_2\) was made by coevaporation in vacuum at a substrate temperature of 550°C. The deposition time was 1 h. A more detailed description of the Cu(In,Ga)Se\(_2\) deposition is given elsewhere [1]. Fig. 2 shows an SEM cross-sectional image of

![SEM cross-section as image of an rf diode sputtered Mo film with a Cu(In,Ga)Se\(_2\) layer on top. The lateral grain size of the Mo film is approximately 0.1 \( \mu \)m, while the vertical grain size is equal to the film thickness.](image)
a structure with Cu(In,Ga)Se$_2$ deposited on a Mo layer. The columnar grain structure
of the Mo film can clearly be seen.

The (SIMS) depth profiles were acquired in a Cameca IMS 5f instrument. The
primary ions were Cs$^+$ or O$_2^+$ depending upon the species being profiled. Secondary
ions with positive (for both Cs$^+$ and O$_2^+$ primary beams) or negative (for Cs$^+$ primary
beam) polarities were detected as appropriate for the species to be examined. Primary
ion energies were 12.5 keV for O$_2^+$ and 10 keV for Cs$^+$ with impact energies modified
by the 4.5 keV potential of the sample. Depth profiles were obtained with high
primary beam currents (35 and 250 nA for Cs$^+$ and O$_2^+$ beams, respectively) with the
beam rastered over a 250 $\mu$m $\times$ 250 $\mu$m area. We have used the molecular species,
O + Cs and Na + Cs, in order to minimise the matrix effects. In addition, all profiles
were normalised to the Mo + Cs signal.

XPS analyses were performed using monochromatised Al X-rays in a Perkin–Elmer
5500 instrument. The Mo layers were sputter cleaned in situ before being analysed by
XPS. The sputtering of the samples was done with 4 kV Ar ions and continued until the
C 1s peak decreased from 18 at% to about 3 at%, which typically took about 30 min.

Rutherford backscattering spectrometry (RBS) was used to quantify the oxygen and
sodium contents in the Mo. For this experiment we used Mo layers 50–70 nm thick
deposited on vitreous carbon. The He$^+$ primary beam energy was 2.4 MeV and the
backscatter angle was 168°.

In order to study the presence of secondary phases in the Mo films X-ray Diffraction
(XRD) was used. The radiation consisted of Cu K$_\alpha$ X-rays in a standard $\theta$/2$\theta$
diffractometer geometry.

3. Results

As-deposited Mo samples were analysed by XPS, SIMS, and RBS. The Mo films
were found by all the methods to contain significant amounts of oxygen. Mo was
found in the + 4 and + 6 valence states corresponding to MoO$_2$ and MoO$_3$ in
addition to metallic, + 0 valence, Mo. The Mo 3d XPS spectrum of an as-deposited
sample is shown in Fig. 3. There is a clear distortion of the 3d pair caused by the
presence of Mo oxides. The peak positions of the oxides and of the elemental Mo are
marked with arrows. The O concentration was estimated by XPS, based on atomic
sensitivity factors, to be 20–30 at%. RBS analysis indicated an average oxygen
concentration of 8 at%, and is expected to be more accurate as there may be artefacts
in the XPS measurements caused by the sputter cleaning. An RBS spectrum of an
as-deposited sample is shown in Fig. 4. It can be seen that the oxygen is distributed
throughout the film with some accumulation indicated at the surface and at the
interface between the Mo and the vitreous carbon substrate. In addition to O,
moderate amounts of C were detected by SIMS on our device-quality Mo deposited
on soda lime substrates. The C peak was not observed by XPS after sputter cleaning
the Mo surface.

In spite of the high oxygen content no evidence of crystalline Mo–O phases was
found with XRD in the as-deposited Mo films. The diffraction spectrum consisted of
Fig. 3. XPS Mo 3d spectra of the as-deposited Mo film on a soda lime glass substrate. The Mo is present in both +3 and +4 oxidized state together with the elemental (+0).

Mo in a cubic structure with a preferred (1 1 0) grain orientation according to JCPDS 4809. The absence of Mo oxides in the XRD spectrum indicates that the Mo-oxides are amorphous or microcrystalline. Amorphous Mo oxides are reported previously from similar sputtering geometries when no intentional substrate heating is used [8].

No Na was detected with XPS on Mo samples as-deposited on soda lime glass substrates. However, after heating the samples to 200°C in vacuum for 15 min a weak, but clear Na peak was found, as can be seen in Fig. 5. Heat treatment at 550°C for 15 min in vacuum yielded an Na surface concentration of the order of 10 at%.
Implanted Mo layers exhibited conventional implant-shape Na-profiles. The as deposited Na implanted Mo samples can be seen in Fig. 6, curve a. There is some Na in the bulk of the implanted samples before the anneal. This is explained by Na diffusion from the substrate already at room temperature or during the rf diode sputtering process which can result in substrate temperatures up to 150°C.

After SIMS analysis the implanted Mo samples were heated to 440°C or 550°C over 30 min. The high temperature was maintained for an additional 20 min after which the sample was cooled to room temperature. Following the annealing steps the sample was reanalysed by SIMS. The position of the implant peak and the general shape of
the implant were unchanged by the anneals, as can be seen from Fig. 6. The principal
difference between the three profiles is the Na signal intensity in the bulk of the Mo
layer. There was a minimum background level of Na already in the as-deposited
sample of approximately $1.3 \times 10^{19}$ cm$^{-3}$, at a depth of 0.4 μm. After annealing, the
positions of the minima remained at 0.4 μm, although the intensities increased to
$3.5 \times 10^{19}$ or $9 \times 10^{19}$ cm$^{-3}$, depending on the annealing temperature. There was
insufficient Na in the original implant to account for this Na especially given the
absence of a significant change in the implant shape following annealing. The peak
intensity was in all cases approximately $1.5 \times 10^{20}$ cm$^{-3}$. We conclude therefore that
this Na comes from the soda lime substrate on which the Mo was deposited,
consistent with the XPS measurements and with interpretations of solar cell fabrica-
tion results [3].

In order to investigate the Na solubility in an Mo film, it was exposed to evapor-
ation from an Na$_2$S source. This method of providing Na has been demonstrated to
influence the Cu(In,Ga)Se$_2$ growth in the same way as Na from the glass substrate
[4,5,9]. After Na exposure the sample was analysed by RBS. The spectrum is shown in
Fig. 7. The C signal comes from the vitreous carbon substrate. The Na profile shows
that the Na is distributed throughout the Mo layer at an Na concentration of 3 at%.
The average oxygen concentration in this Mo layer is 8 at%.

4. Discussion

4.1. Na diffusion

The diffusivity of the Na in the Mo layers cannot be calculated directly from the
above results because a well-defined change in the implant did not occur. We explain
the unchanged shape of the implant as follows. The majority of the implanted Na does not diffuse significantly. However, Na diffused completely through the layer sufficiently rapidly to bring the background concentration to a constant value. Since the implant will be distributed in both grains and grain boundaries we interpret these results as a slow intragrain diffusion combined with a fast diffusion in the grain boundaries.

The diffusion constant of Na in pure metallic Mo is very low. At 800°C it is only $2.3 \times 10^{-10} \text{ cm}^2/\text{s}$ [10] and should be significantly lower at 550°C. The low diffusion in pure Mo has also been observed in recent experiments [11]. Studies of reactively sputtered Mo–O alloys show that at an oxygen content of 10 at% the resulting films are made up from Mo grains and some amorphous phase [8]. This amorphous phase crystallises above 600°C to MoO$_3$. MoO$_3$ is a well-known intercalation host for alkali metals, and as such has a very high diffusion constant for Na [12]. This also holds for MoO$_2$ and other less defined amorphous Mo oxide phases [13]. As the sputtered Mo film has a relatively high oxygen concentration the results suggest that considerable amounts of MoO$_3$ or related compounds are present in the grain boundaries creating efficient channels for Na diffusion.

4.2. Na concentration

The bulk concentration of Na observed in the Mo layer after annealing corresponds to approximately 0.06 at% for the 440°C anneal and 0.14 at% for the 550°C anneal. Quantification of the Na concentration in the Mo on which Cu(In,Ga)Se$_2$ had been grown was carried out by comparison with the Na-implanted Mo samples. The result was an Na concentration in the same range. Since Na diffusion in the Mo films is rapid, as indicated by the flat concentration profiles, we therefore conclude that the main influence on the Na concentration is the supply from the soda lime glass, which is related to the thermal budget of the deposition process.

Assuming that the oxygen is present in MoO$_2$ or MoO$_3$ which intercalate up to two Na ions per formula unit, the Na saturation concentration would be in the order of 4 at%, far above what is observed in these Mo layers. Indeed, in a separate experiment where an Na-containing compound (Na$_2$S) was evaporated on an Mo film, an Na concentration of 3 at% was detected within the Mo by RBS (Fig. 7).

4.3. The effect of stress

The Mo layers studied were initially in a state of tensile stress. An Mo layer in a state of tensile stress typically is more porous than a similar stress-free Mo layer or an Mo layer in compressive stress. The porosity is mainly due to the increase in the inter columnar gaps [14]. Microcracks have also been observed by Probst et al. and they have also observed an increase of the Na in-diffusion from the glass substrate with the increased porosity of the Mo layer [15]. It must be noted here that during heating the thermally induced stress on the Mo layers by the soda lime glass will always be tensile when reaching the higher temperatures in the Cu(In,Ga)Se$_2$ fabrication process. Furthermore, this stress is believed to be relaxed during the high
temperature stage of the Cu(In,Ga)Se$_2$ deposition, typically 550°C in 30 min [16]. Thus, the intrinsic stress is not likely to govern the sodium transport, if it does very short process times or low temperatures are to be used for the Cu(In,Ga)Se$_2$ fabrication. In Mo films such as ours, which contain large amounts of Na transport channels in the form of Mo oxides, the intrinsic Mo stress will be even less important.

5. Conclusions

The findings in this work are important contributions to the understanding of how Na is supplied during growth of Cu(In,Ga)Se$_2$, a supply which is critical in order to achieve best device performance. Our normal deposition process for Cu(In,Ga)Se$_2$ on soda lime glass leads to Na concentrations of about 0.1% in the Mo layer, which is enough to give solar cells with high conversion efficiencies.

Na diffuses rapidly in sputtered Mo-containing oxide phases, i.e. in the grain boundaries of the Mo films. Cu(In,Ga)Se$_2$ grown on soda lime glass has been observed by SIMS to have the same Na concentration regardless of whether the soda lime glass was Mo coated or not.

Since the Na implant peak position was unchanged in depth by the anneals, we conclude that the Mo film consists of grains with pure Mo where Na does not diffuse, surrounded by oxygen-rich grain boundaries.

The Na concentration is not saturated in the Mo in typical layers used for solar cells. Higher concentrations could be obtained by using Na precursor layers, suggesting a possible limitation of the Na supply from the substrate. The flat Na SIMS profile of the Mo layer and the fact that the Na concentration in the bulk of the Mo increases with temperature also point to the same conclusion.

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