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Investigations of $CuInSe_2$ Thin Films and Contacts

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B. REPORT

1. Introduction

Solar cells made of CIS (CuInSe) polycrystalline thin films with close to 14% efficiency have been fabricated .

The objective of this work is to investigate the microstructure, the composition and the homogeneity of these CIS thin films and to study the contact stability between Mo and CIS in an effort to clarify limitation on these solar cells.

2. Approach

The whole study was carried out with two kind of samples provided by ARCO Solar Inc.:

- CIS #1 films deposited on a glass substrate
- CIS #2 films deposited on a Mo layer on a glass substrate

To investigate the stability of the metal/CIS interface by RBS, we have deposited thin Mo or W layers on the top of these samples using two techniques: rf magnetron sputtering and e-beam evaporation. Tungsten films were deposited in addition to Mo films because W has chemical, crystallographic, and electrical properties that are close to those of Mo. But W has a heavier mass than Mo and this bypasses the overlapping problem of the Mo and In signals in the RBS spectra of a sample.

We have carried out XTEM, SEM, EDX, and X-ray diffraction studies to obtain insights in the microstructure and defect chemistry of CIS. The interface stability after annealing at 600°C for 10 min to 1 hour in argon atmosphere was investigated by RBS and X-ray diffraction.

3. Results

3-1. CIS film analysis

3-1-1. XTEM

We have embedded the CIS film into epoxy and prepared cross-sectional TEM samples using a diamond knife. This technique is suspected to produce important mechanical damage that may alter the film in an unspecified way. The study of the CIS #2 samples is less comthan that of the CIS #1 samples. The TEM observations of these cross-sectional samples provided the following informations:

- For both types of films, electron diffraction patterns of as-deposited samples (fig. 1 and 2) are consistent with the tetragonal $CuInSe_2$ chalcopyrite structure (lattice parameters: a=0,5782 nm, c=1,1621 nm).

-The films are inhomogeneous. Figure 1 shows microvoids (see arrows) filled with epoxy during cross-section preparation for the CIS #1 film. Further TEM experiments are needed to confirm this observation for the CIS #2 film.

-EDX analyses performed on as-deposited CIS #1 film with a small electron beam on individual grains give an atomic ratio of Se/In=2 (+/-10%) which is consistent with the $CuInSe_2$ phase stoichiometry.

The two types of films present some differences:

-The average thickness of the films is near 1.5 μm. The thickness is regular for the CIS #2 film while irregular for the CIS #1 film, varying between 1 to 1.5 μm (figure 1 and 2).

-Bright and dark field images performed on CIS #1 films show that grains are sometimes elongated in the direction normal to the surface. The grain size varies from less than 0.1 μm in diameter to 0.3 μm in width and 1 μm in length for the biggest.
The CIS #2 grain size seems to be inferior to 0.5 μm in diameter. These grains show no obvious elongation.

3-1-2. X-RAY

We have used both a Read camera and a Θ-2Θ diffractometer for the X-ray analyses of the films. Both techniques confirm the chalcopyrite structure of the CIS films.

With the Read camera, we observe extra rings whose d spacings for both #1 and #2 do not fit with any of those listed in the ASTM files for any compound of a Cu-In-Se-O combination. All the diffraction rings sharpen and become punctuated for the films analyzed after annealing at 600°C. These observations suggest that the diffracting grains grow in size during annealing. The unexplained diffraction rings must therefore be part of the CIS film.

The diffractometer data allows the study of relative peak intensities of diffraction lines. The as-deposited films show a slight preferred grain orientation in (112) plane which appears during film growth. The preferred orientation factor of the (112) plane, f(112), determined by using the method described in refs. 1 and 2 are calculated from diffraction spectra (fig. 3) (The f factor varies between zero for a non-oriented polycrystal to 1 for a perfect orientation). The f value difference between the two type of films is not very pronounced (f=0.11 for CIS #1 and f=0.06 for CIS #2). The f factors do not change significantly after annealing the films at 600°C for 10 min to 1 hour.

3-1-3. SEM AND EDX

Figure 4 shows the surface morphology differences between the two types of CIS films, as-deposited. The CIS #1 film surface looks very irregular with cracks. The CIS #2 film surface is smoother than that of type 1 films, with some dispersed protusions. We do not observe any surface morphology evolution of the films after annealing. The EDX analysis performed with a small e-beam do not reveal real compositional differences between protrusions and sample bulk.

Fig. 1 Bright field XTEM view of a CIS #1 film, as-deposited, with a selected-area diffraction pattern. Arrows point to microvoids.

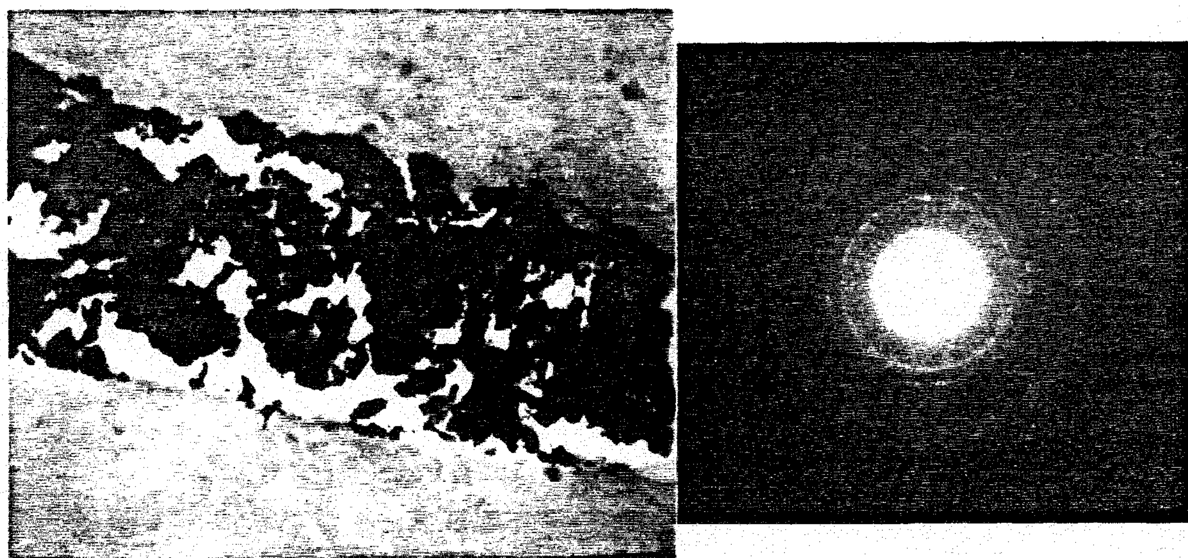
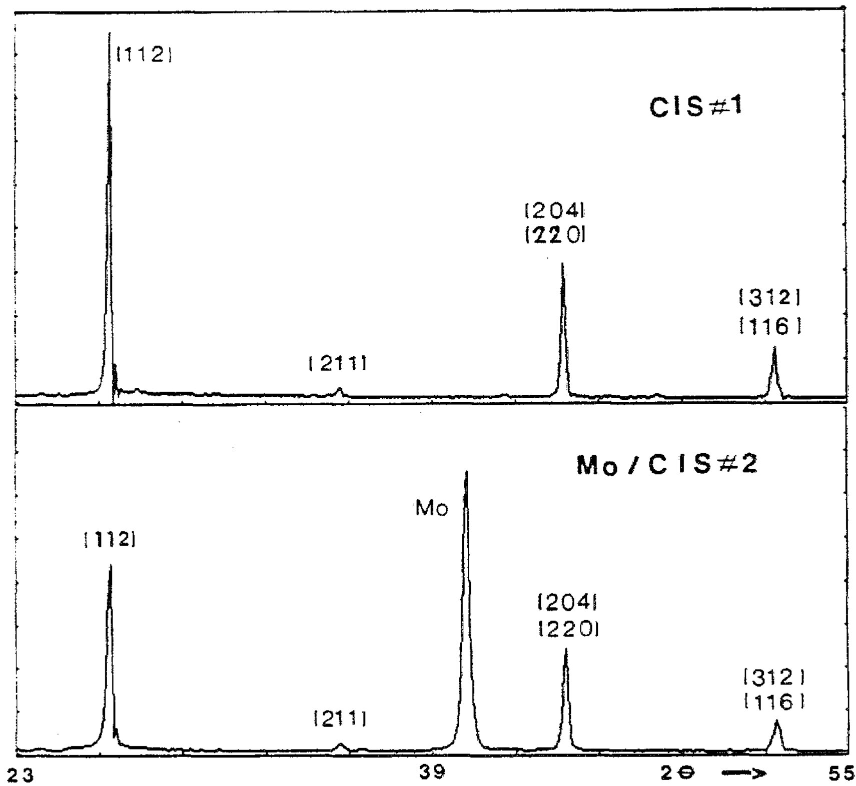


Fig. 2 Bright field XTEM view of a CIS #2 film, as-deposited, with a selected-area diffraction pattern.



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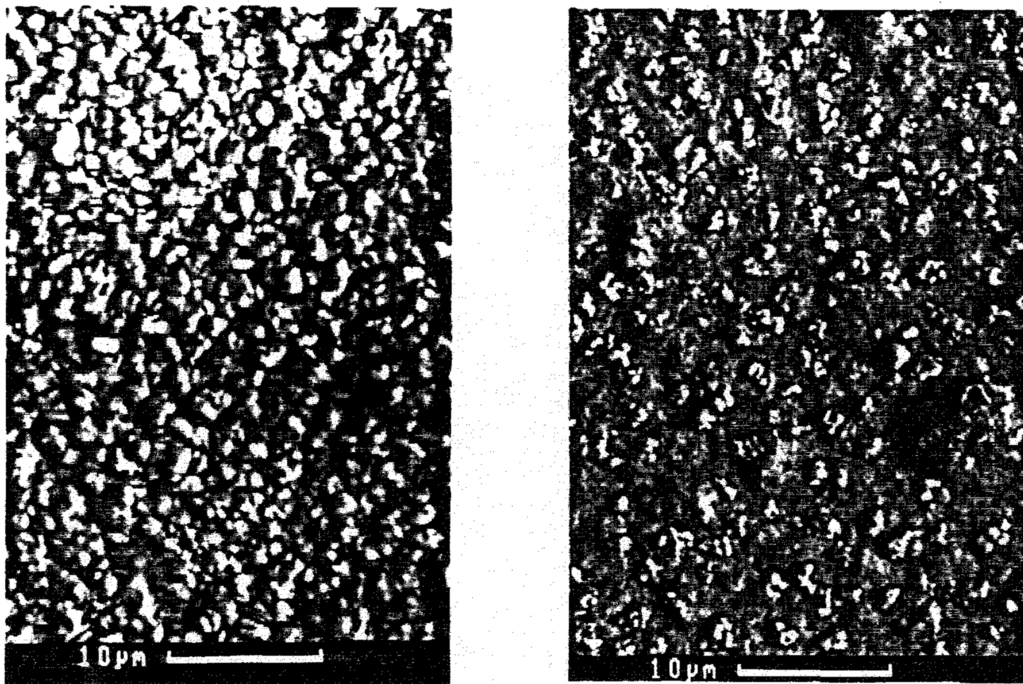

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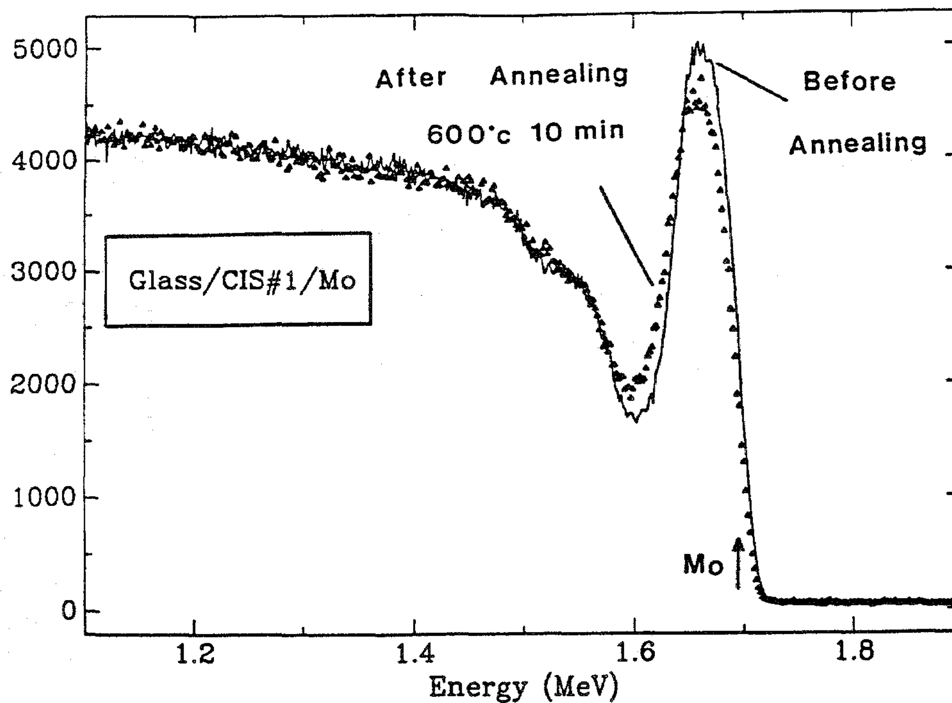


Fig. 7 2 MeV $^{4}He^{+}$ backscattering spectra of a CIS #1 film covered with a magnetron-sputtered 45 nm thick Mo layer before and after 10 min. annealing in vacuum at 600°C.

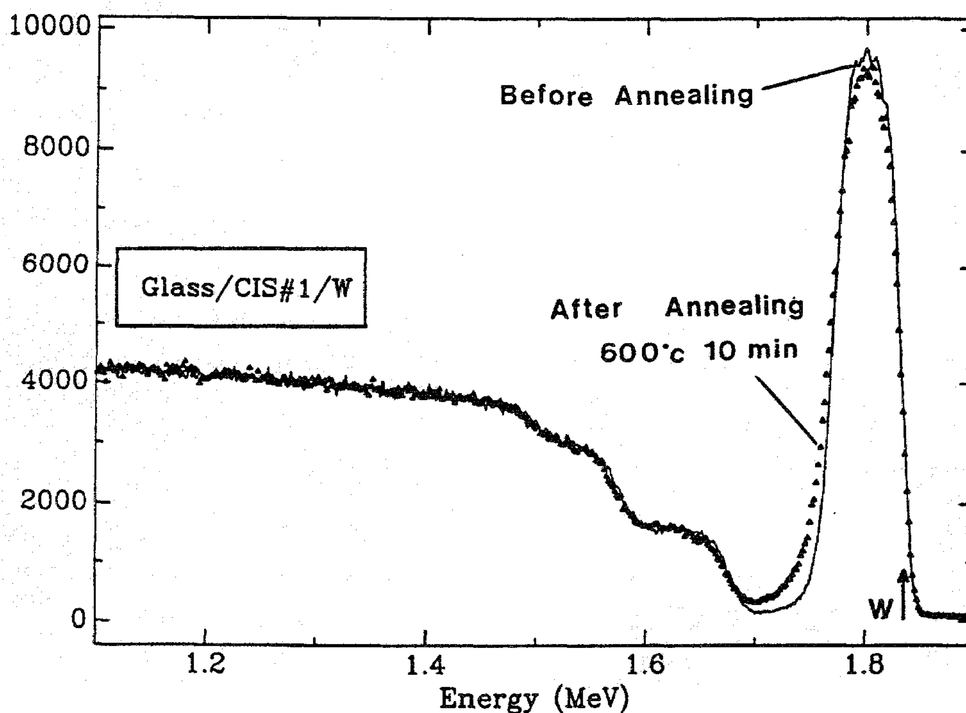


Fig. 8 2 MeV $^{4}He^{+}$ backscattering spectra of a CIS #1 film covered with a magnetron-sputtered 45 nm thick W layer before and after 10 min annealing in vacuum at 600°C.

The EDX technique which analyzes only the near-surface regions of samples (1 μm for 25 keV e-beam energy) reveals a decrease of about 17% in the Se initial concentration for species annealed at 600^{0}C for 1 hour.

3-1-4. RBS

Backscattering analyses were performed with ^{4}He ions with normal incidence of the beam on the sample and 170^{0} scattering angle.

Figure 5 shows an RBS spectrum that is characteristic of both types of CIS films. The composition calculated from the height of the surface signal of each element reveals that the films have the same composition. Within 5% of error the composition is determined as $Cu_{1.2}\ In_1\ Se_2$, i.e. the films are Cu-rich.

Figure 6 presents RBS spectra of a CIS #2 film before and after 10 min and 1 hour annealing at 600^{0}C in an argon atmosphere. After annealing, the spectra show a pronounced increase of the In signal at the surface associated with an atomique rearrangement in the near surface region of the sample. The thickness of this In rich transformed layer increases with annealing duration (about 100 nm after 1 hour).

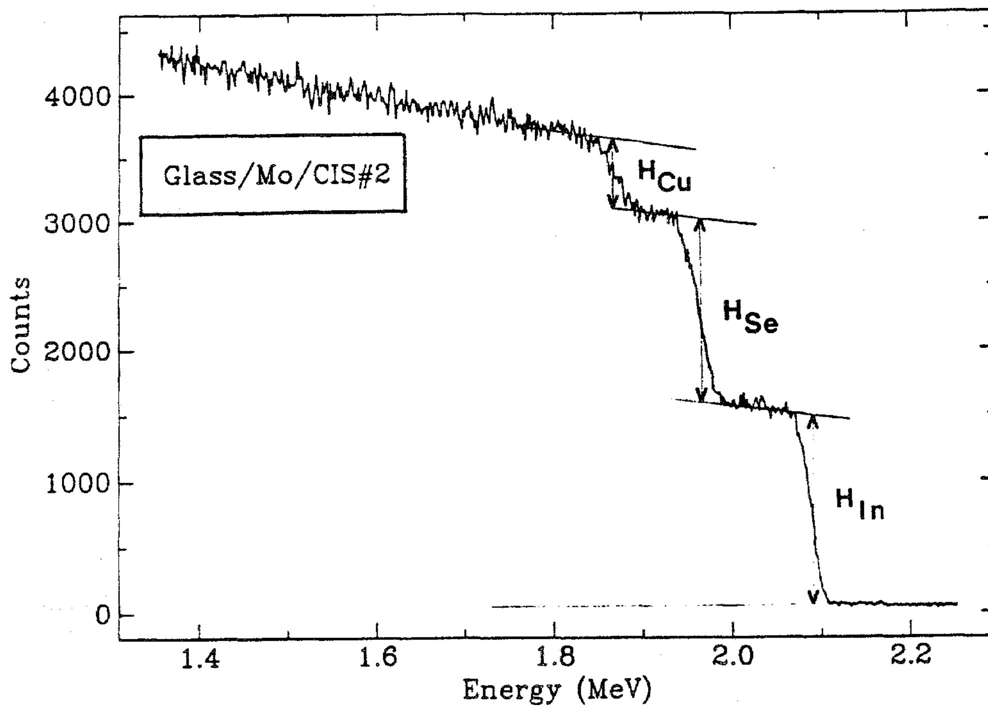
3-2. Contact study

For the purpose of these investigations, we have covered CIS films with a Mo or W top layer.

A CIS #1 film was covered by a rf magnetron-sputtered Mo film 45 nm thick (base chamber pressure: 7×10^{-7} Torr). An RBS analysis performed on a Mo film deposited on a carbon substrate reveals a 25% oxygen concentration in the deposited film. Planar TEM micrographs show that the Mo grain size of the as-deposited film is around 24 nm with a bcc structure. No Mo oxide compound could be detected in selected area diffraction patterns (SADP). Figure 7 presents RBS results for this specimen before and after 10 min annealing at 600^{0}C. It is evident that some interaction between Mo and CIS takes place but details are difficult to extract from these spectra. X-ray diffraction performed on these samples before and after annealing shows no difference in regards to new compound formation, or Mo grain size evolution.

A CIS #1 film was covered by an rf magnetron-sputtered film of W (rather than Mo) 45 nm thick (base chamber pressure: 7×10^{-7} Torr). The oxygen concentration in the W was not measured in this case. The RBS spectra are shown in figure 8 for a sample before and after 10 min annealing in vacuum at 600^{0}C. An interaction between the two layers is again evident. If the sample is laterally uniform, the spectra indicate a penetration of W into the CIS film (extended W signal towards lower energies near 1.75 MeV), and some possible diffusion of In, Se and/or Cu into W (reduced signal height of W).

A CIS #2 film was covered by an e-beam evaporated Mo film, 200 nm thick (base chamber pressure: 3.10^{-7} Torr). The RBS analyses of a film on carbon substrate reveals a 18% concentration of oxygen in the Mo film. The grain size measured from X-ray diffraction peak width is around 20 nm. The structure is bcc type without Mo oxide compound. Figure 9 presents RBS spectra for this CIS/Mo sample before and after 10 min and 1 hr. annealing at 600^{0}C. The main observation is a general interdiffusion between CIS and Mo



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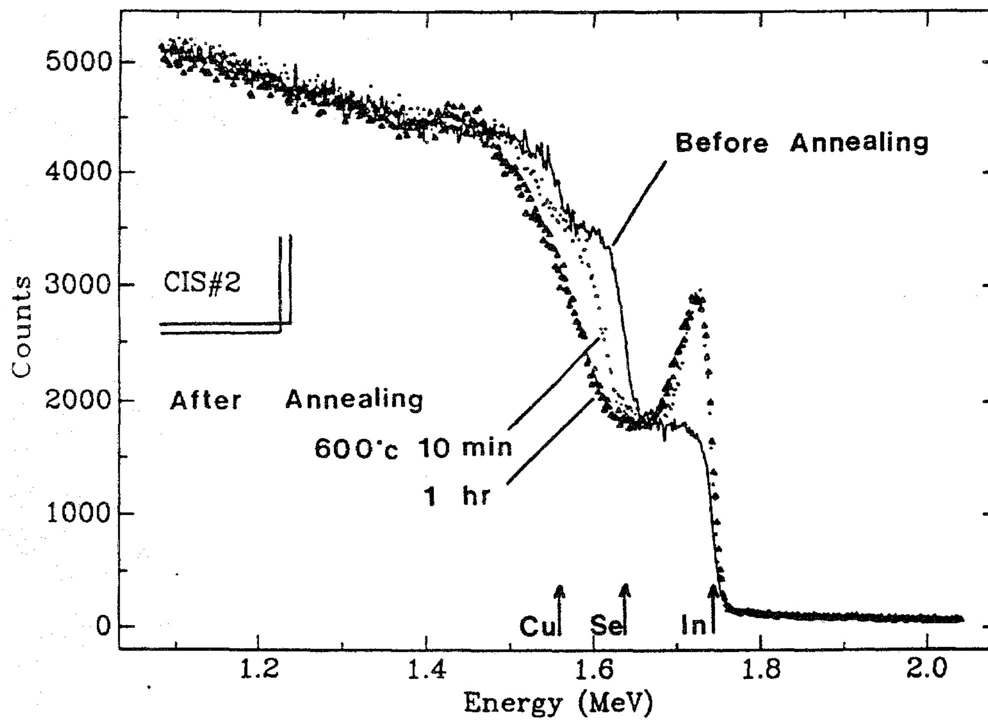

Fig. 6 2 MeV $^4He^+$ backscattering spectra of a CIS #2 film before and after 10 min, and 1 hour annealing at 600^oC.

which increases with annealing duration. The In peak which appears after annealing at the top surface reveals a diffusion of In through the whole Mo layer. X-ray diffraction again shows no difference between these samples before and after annealing, and no evolution of the Mo grain size.

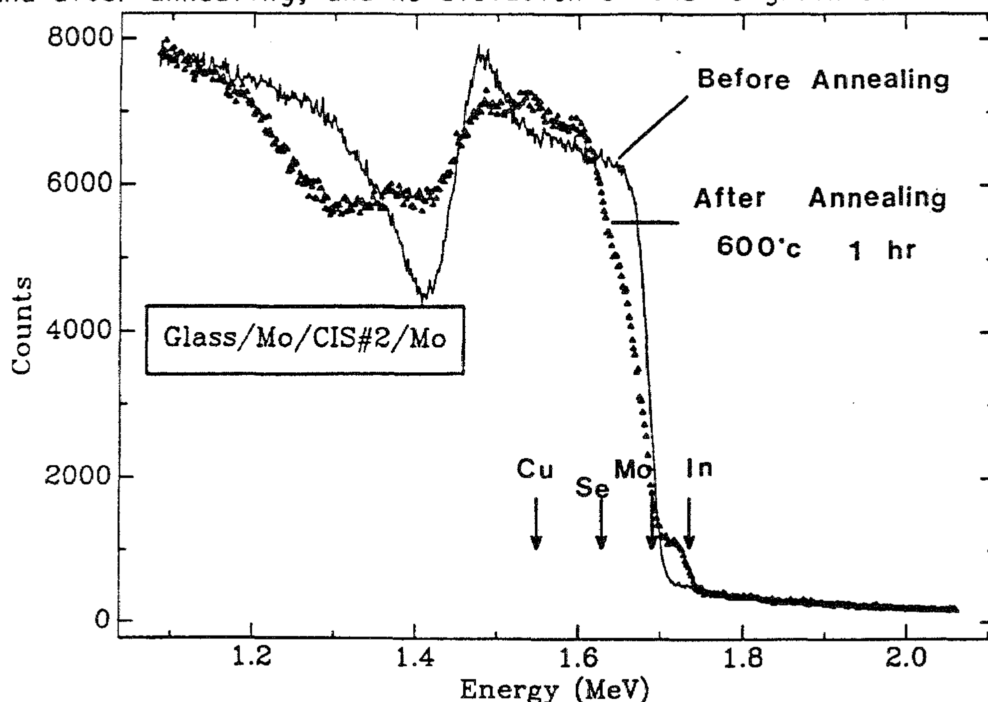

Fig. 9 2 MeV $^4He^+$ backscattering spectra of a CIS #2/film covered with an e-beam evaporated Mo film 200 nm thick before and after 1 hour annealing at 600°C.

4. Discussion

We have analyzed two kinds of CIS films, one deposited on glass, the other deposited on a Mo layer. Both films are Cu rich $[Cu_{1.2} In_1 Se_2]$, contain microvoids and have a chalcopyrite microstructure. The main differences, apparently due to the original surface of growth, are the surface morphology, an enhanced grain size and columnar structure which is observed for films growing on Mo (CIS #1). The [112] preferential grain orientation, perpendicular to the film surface seems to be slightly more important for films on Mo than on glass. X-ray diffraction reveals the existence of rings which are presently not interpretable. They could either originate from a second phase or from ordered vacancies in the CIS chalcopyrite structure. The RBS analyses of films on glass (CIS #2) before and after annealing reveals atomique rearrangements which are difficult to specify. The RBS spectra can be interpreted in correlation with EDX surface analyses, as being generated by an In rich (Cu, In) surface layer that is depleted of Se which evaporates from the samples during annealing.

We have investigated the metal/CIS interface stabililty using different samples. In all cases, the Mo seems to diffuse into the CIS films. We assume that the phenomenon is made easier by defects like microvoids that exist in CIS films. This is confirmed by the W/CIS interface study. The diffusion of Cu, In or Se into Mo are not clear and seems to depend partially

on the Mo layer quality and therefore on the elaboration process. Indeed, we observe an important In diffusion to the top surface of the e-beam evaporated Mo film. This diffusion process occurs probably at the grain boundaries. The process is not observed in the case of the rf magnetron-deposited Mo film of which the grain size is a little larger and the impurity content clearly bigger (25% of oxygen) than in evaporated Mo films. The resulting enhanced decoration of grain boundaries may be responsible. X-ray diffraction technique that we have used are not sensitive enough to detect the interaction between Mo/CIS.

5. Future plan

We will pursue CIS films characterization by RBS, TEM, and X-ray diffraction to clarify the issue of a possible second phase and to investigate the lateral, chemical and structural uniformity. Optical uniformity by IR transmission measurements will be performed and correlated with the previous study. A systematic investigation of thermally induced bilayer reactions of Mo with Cu, In and Se individually using RBS and XTEM analysis will be undertaken to seek a correlation with results obtained similary on Mo/CIS samples.

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16. Abstract (Limit: 200 words)

This report describes various studies of copper indium deselenide ($CuInSe_2$) thin-film materials and contacts. The $CuInSe_2$ films prepared on substrates of glass or Mo-coated glass show the same polycrystalline structure, a Cu-rich composition, and a preferential grain orientation; however, they exhibit different surface morphologies, grain sizes, and shapes. Rutherford back-scattering measurements were performed on different samples before and after 600°C annealing. This treatment induced Se evaporation from the $CuInSe_2$ films and interdiffusion between Mo and $CuInSe_2$.

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