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Investigations on $CuInSe_2$ Thin Films and Contacts

Annual Subcontract Report 1 January 1990 - 28 February 1991

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Pasadena, California

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B. REPORT

1. Introduction

$CuInSe_2$ (CIS) polycrystalline thin films with molybdenum as metal contacts has been one of the most promising configurations for thin-film heterojunction solar cells.[1]

The first part of this work is to study the contact stability by a systematic investigation of thermally induced bilayer reactions of Mo with Cu, In and Se individually[2]. Influence of oxygen in Mo layer on interdiffusion of metal couples is simulated by a Cu/Mo/Au trilayers system[3]. As to the $CuInSe_2$, since selenization has become a successful process used to fabricate CIS thin films for photovoltaic cells,[4,5] the second part of this work is to investigate how the morphologies, phases and reactions of pre-selenization Cu-In structure are affected by the deposition process and subsequent heat treatments[6].

2. Approach

To investigate the interaction between Mo and $CuInSe_2$, the binary thin-film couples Mo/Cu, Mo/In and Mo/Se were deposited on oxidized Si wafers by e-beam evaporation or rf magnetron sputtering. All couples were annealed in the vacuum furnace (Mo/Cu) or in an Ar-flowing furnace (for Mo/In, Mo/Se) at temperatures ranging from 100°C to 600°C for 10 min to 1 h. All samples were analyzed by RBS and x-ray diffraction before and after annealing.

Influence of oxygen on diffusion is studied using the polycrystalline Cu/Mo/Au trilayers deposited on oxidized Si wafers by rf magnetron sputtering in two systems with different base pressures (System #1: 9×10^{-8} torr; System #2: 5×10^{-6} torr) such that the oxygen content in Mo films are different. Annealings were performed in a vacuum furnace at 600°C for 30 min. Analyses of the films have been carried out using RBS and X-ray diffraction.

For the study of pre-selenization Cu-In structures, bilayers of slightly Cu-rich overall composition of Cu and In prepared on oxidized Si wafers at room temperature by vacuum evaporation, electroplating and rf sputtering have been analyzed by RBS, SEM and x-ray diffraction before and after annealing at 400°C in vacuum for 1 h.

3. Results

3.1 Interactions of Mo Contact with Cu, In and Se

3.1.1 Mo/Cu

Figure 1(a) shows 3 MeV $^4He^{++}$ normal incidence RBS spectra obtained before and after annealing at 600°C for 1 hour of a trilayer of Cu/Mo/Cu. It is clear that no reaction occurs. No reaction either is observed with samples formed by e-beam evaporation.

3.1.2 Mo/In

The 4.7 $^4He^+$ normal incidence RBS spectra of Fig. 1(b) are for a Mo layer deposited by e-beam evaporation and covered by an In layer.

Up to 200°C annealing, the RBS spectra of annealed samples are practically identical to the as-deposited spectrum. After 600°C and 10 min, the signal peaks decrease slightly and we observe a non-zero count between peaks. At the small thicknesses of our samples (thickness of In about 20 nm, thickness of Mo about 30 nm), the RBS system resolution is inadequate to display the full height of the signals. A small difference in thickness would thus be reflected in a difference in signal heights. The non-zero count between the peaks is not due to an interdiffusion between the layers, but to a non-uniform thickness of the top layer due to a balling up effect of the In which has melted at this annealing temperature. Optical microscope observation of the surface reveals the presence of innumerable tiny In balls on the surface.

3.1.3 Se/Mo

The Se/Mo bilayer was prepared by e-beam evaporation of a Se film on an oxidized Si wafer, followed by a Mo layer deposition. Figure 1(c) shows 4.7 MeV $^4He^+$ normal incidence RBS spectrum of the bilayers before and after annealing at 600°C. A detailed analysis of the as-deposited spectrum indicates that the Se has probably already penetrated into the Mo layer during deposition though the system resolution combined with the small thickness of the films preclude any definitive conclusion. No change was detected after annealing at 150°C and 30 min. After annealing at 200°C for 30 min, we observe a slight decrease in the Se signal, and a slight shift to higher energy. This evolution becomes pronounced after annealing at 600°C for 10 min and is attributed to a complete intermixing of the Se and the Mo layers. The x-ray analysis of

this sample performed with a Read camera reveals the existence of small amounts of $MoSe_2$. The total number of counts of the Se signal decreases, suggesting a loss of Se by evaporation at the surface.

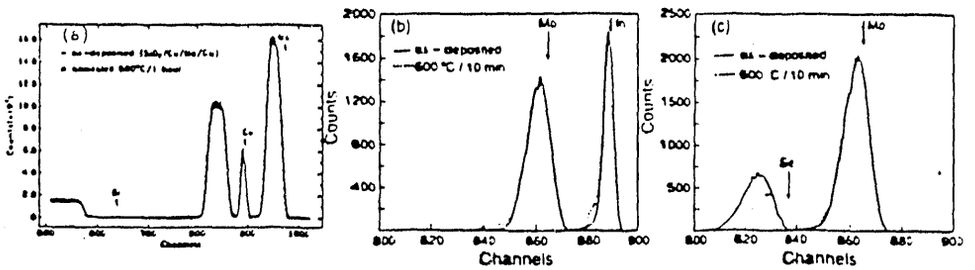

Fig. 1
(a) 3 MeV $^4He^+$ normal incidence RBS spectrum of Cu/Mo/Cu as-deposited and after annealing in vacuum at 600°C for 1 hour, (b) 4.7 MeV $^4He^+$ normal incidence RBS spectrum of Mo/In as-deposited and after annealing in flowing argon at 600°C for 10 min, (c) 4.7 MeV $^4He^+$ normal incidence RBS spectrum of Se/Mo as-deposited and after annealing in flowing argon at 600°C for 10 min.

3.2 Influence of Oxygen on Diffusion in the Cu/Mo/Au System

The Cu/Mo/Au trilayers were deposited on a thermally oxidized Si wafer sequentially together with a carbon substrate for each deposition of metal layer. We evaluated the oxygen concentration in the films deposited on carbon substrates using backscattering spectrometry. No impurities were detected in any of the Cu or Au films, or in the Mo layer deposited in system #1 (Fig. 2(a)). According to the sensitivity limit of our backscattering system, we estimate that the impurity concentration is below 2% for elements heavier than carbon. A uniform concentration of 5.5 at% of oxygen is measured in the Mo film from system #2 as shown in Fig. 2(b).

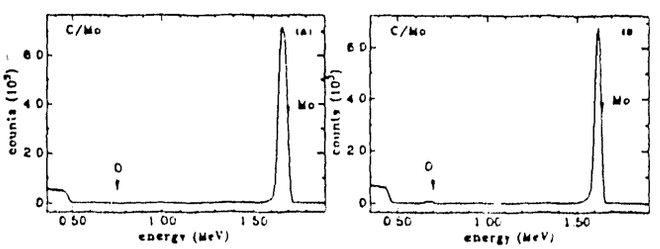

Fig. 2.
2.0 MeV He^+ normal incidence backscattering spectra of a Mo layer (a) deposited in system #1, (b) deposited in system #2, on a carbon substrate.

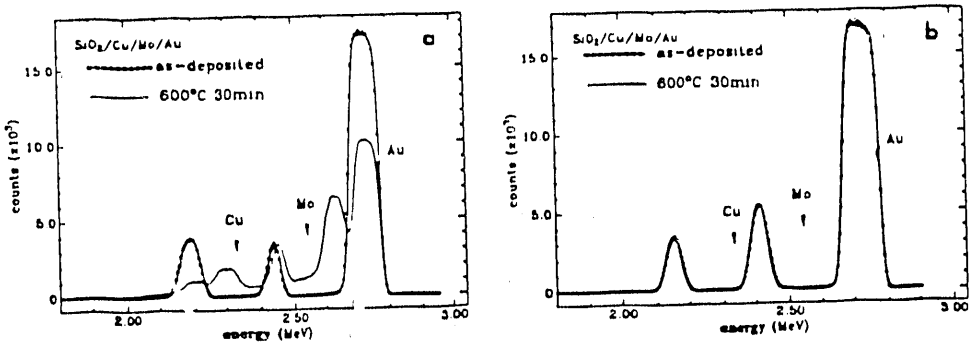

Fig. 3
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Fig. 3 shows backscattering spectra of two sets of Cu/Mo/Au samples before and after annealing at 600°C for 30 min. It is clear that a rapid diffusion of Cu and Au across Mo film after annealing when no impurities are detected in the as-deposited polycrystalline Mo layer (Fig. 3(a)). When oxygen is introduced in the as-deposited Mo layer, the two spectra overlap perfectly (Fig. 3(b)) which indicates that no detectable intermixing occurs during heat treatment.

X-ray diffraction using the theta 2-theta technique reveals the formation of AuCu compound after annealing for the sample without impurities in the Mo film (Fig. 4). The spectra taken from the samples with oxygen contamination before and after annealing are both similar to the spectrum of the as-deposited sample without oxygen contamination. No molybdenum oxide compound was detected in all of the samples.

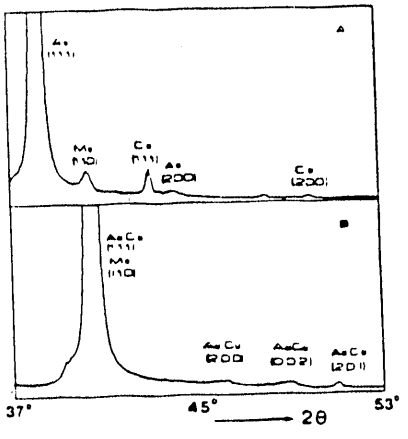


Fig. 4
X-ray diffraction spectra of a Cu/Mo/Au trilayer without detectable amounts of oxygen in Mo layers (a) as-deposited and (b) after annealing in vacuum at 600°C for 30 min.

3.3 Morphology, Phases and Reactions in the Pre-Selenized Cu-In Samples

3.3.1 As-Deposited Samples

The Cu-In bilayers were prepared by different deposition techniques. That the deposition process affects the surface morphology is apparent. Fig. 5 shows representative scanning electron micrographs of the three types of samples, as well as their $^4He^{2+}$ backscattering spectra. The sample deposited by e-beam evaporation of both Cu and In (Fig. 5(a)) consists of many distinct grains about 1 um in size. Energy dispersive X-ray analysis reveals that the grains are In-rich. The picture suggests a melting and island forming process of the In. The surface layer of the samples deposited by e-beam evaporation of Cu and electrodeposition of In is bumpy, but remains singly connected (Fig 5(b)). The surface roughness of the samples deposited by low-power rf sputtering is several orders of magnitude finer in scale than for the previous two cases, and essentially flat, except for a few bubble-like shallow protrusions (as shown in Fig. 5(c)) of an approximate areal density of $10^4/cm^2$.

The drooping low-energy edge of the In and Cu signals in the backscattering spectra of the first two samples are characteristic of laterally nonuniform layers, consistent with the scanning electron micrographs. The spectra further shows that Cu is present on the sample surface and that the shape of the In and Cu signals are similar, all of which is highly suggestive of a fully intermixed Cu-In layer with a laterally varying thickness. In the spectrum of the low-power sputtered sample, the Cu signal position is clearly shifted below the energy of a surface Cu signal (arrow labeled Cu). This fact proves that the Cu and In layers are distinct; but the non-symmetric shape of both the Cu and In signals reveals that some slight interfacial mixing may exist.

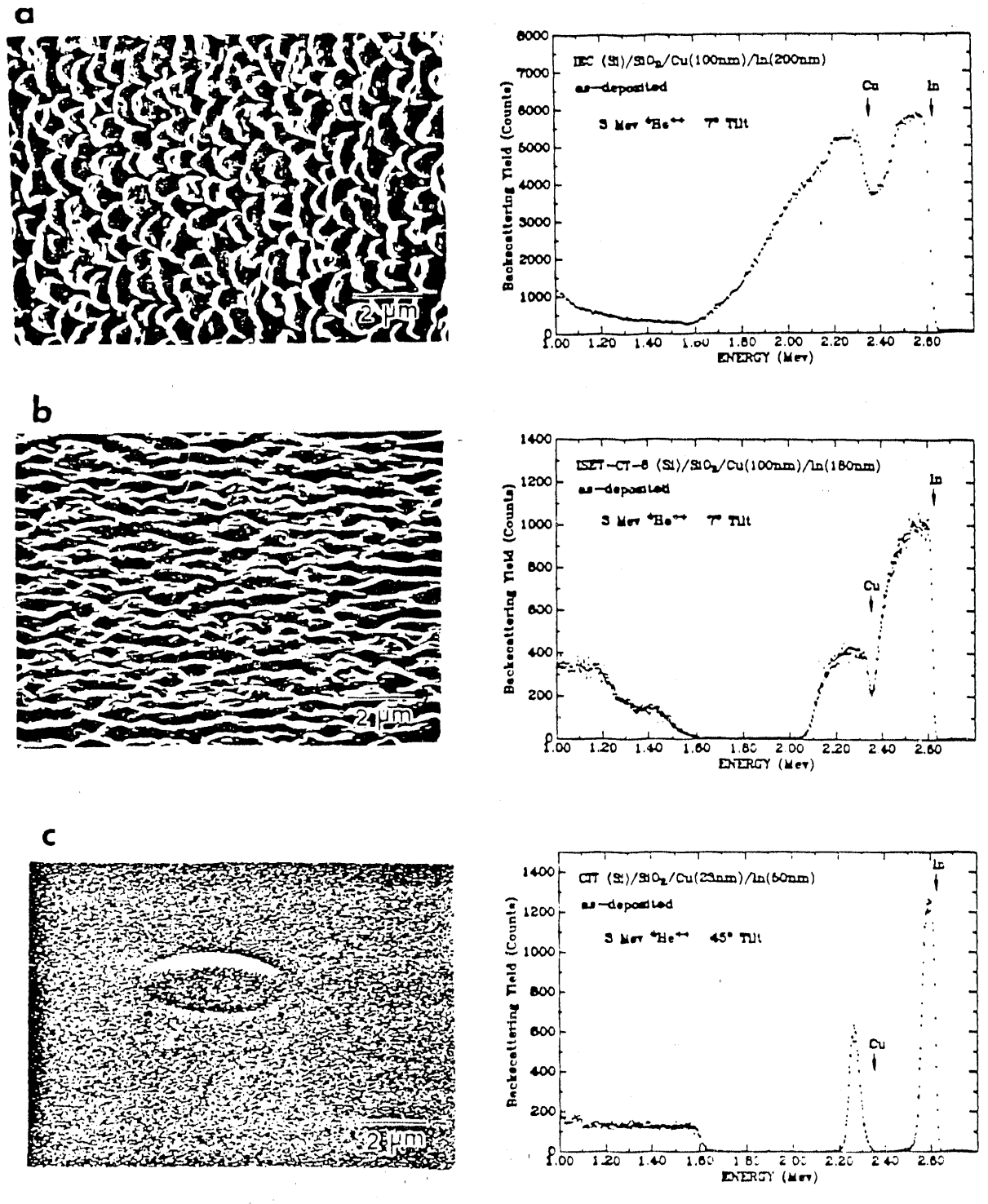
X-ray diffraction shows that all the as-deposited samples contain the Cu fcc phase and CuIn compound. The In diffraction lines of the low power sputtered sample are consistent with ASTM file; but for the samples with electroplated In, the most intensive In diffraction line is shifted by + 2% comparing to the ASTM file.

3.3.2 Annealed Samples

After vacuum annealing (400°C, 1h) scanning electron micrographs and backscattering spectra indicate that the initially rough samples have smoothened much (shrinking low energy tails of Cu and In signals in backscattering spectra, Fig. 6(a) and (b)).

The surface morphology of low-power sputtered samples hardly changes, except for a collapse of the small bubble-like features, as shown in Fig. 6(c). The widening of the backscattering signals of Cu and In in that figure and the shift of the Cu signal to its surface energy position reveal that Cu and In are now intermixed.

By X-ray diffraction analysis, the Cu and CuIn phases have disappeared from the samples and some Cu-rich compounds (Cu_9In_4 and Cu_7In_4) appear; the In phase remains.



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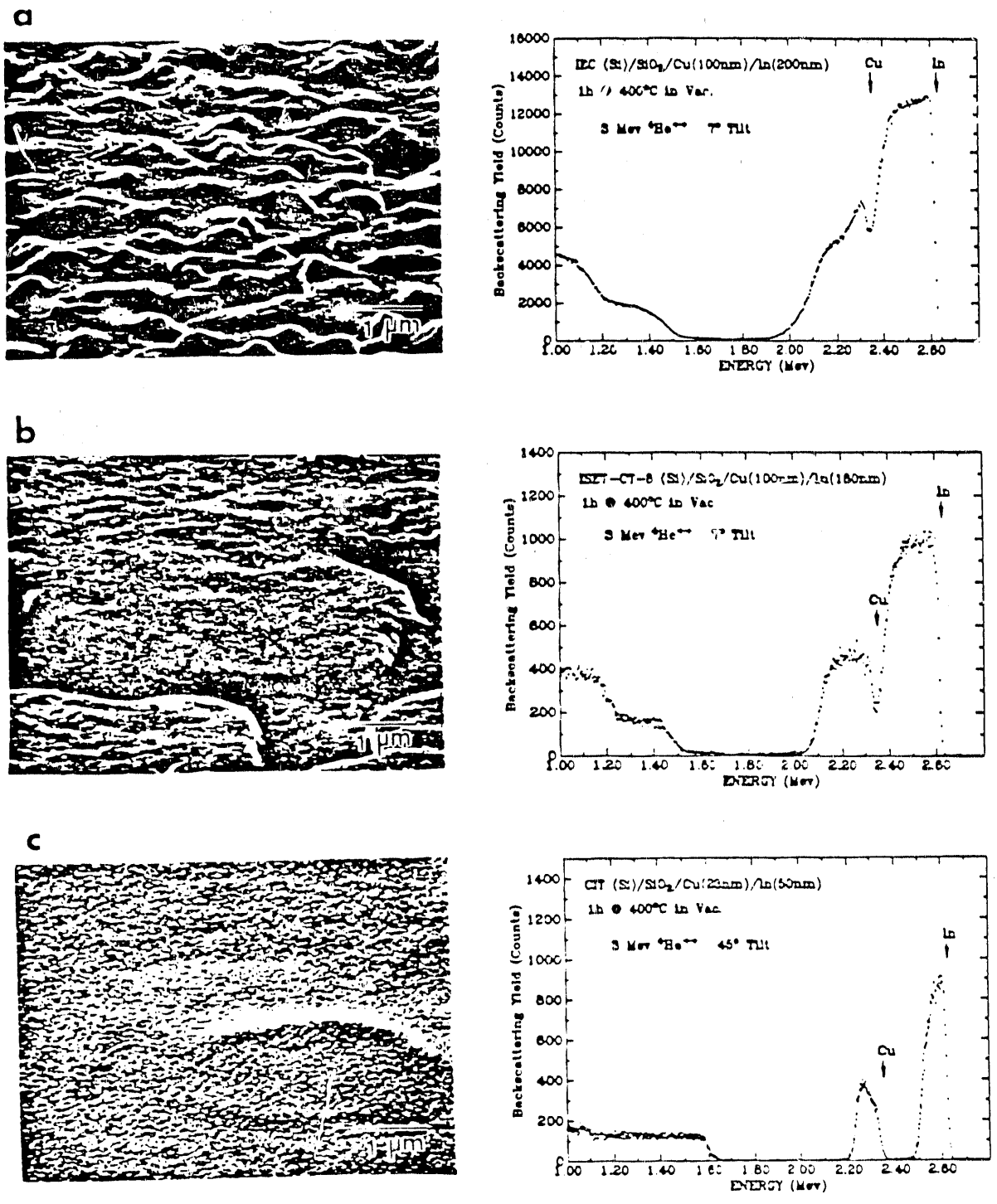

Fig. 6
Scanning electron micrographs and 3 MeV $^4He^{++}$ backscattering spectra of Cu/In bilayers after annealing for 1 h at 400°C, in vacuum, deposited by (a) e-beam evaporation of both layers (b) e-beam evaporation of Cu and electrodeposition of In (c) rf sputtering of both layers.

4. Discussion

According to the phase diagrams, no compounds exist in the Mo-Cu and Mo-In systems and the mutual solid solubilities are quite small[7]. Our experiments show insignificant interaction between bilayers of Mo/Cu and Mo/In, up to 600°C annealing. This absence of interdiffusion and compound formation is advantageous from the point of view of contacting CIS layers. However, impurities such as oxygen may be decisively involved in limiting interdiffusion. Indeed, the oxygen concentration in all Mo films is at least 5 at%, as measured by RBS.

Cu, In and Au are all mutually immiscible with Mo. According to the results of interdiffusion studies in Cu/Mo/Au trilayers, a rapid diffusion of Cu and Au across the Mo film and the formation of AuCu after annealing at 600°C for 30 min in vacuum occurs only when no impurity is present in the Mo layer. The Au-Cu interaction is impeded when 5.5 at% of oxygen is introduced to the Mo layer during deposition. The results of this investigation are relevant in the application of Mo thin films used as the contacts to $CuInSe_2$.

The phase diagram of the Mo-Se[7] system indicates the existence of $MoSe_2$ and Mo_3Se_4 below 1150°C. The atomic ratio of molybdeium to selenium, estimated from the RBS spectra of the as-deposited bilayer sample, suggests that the equilibrium in this bilayer system can be reached by the formation of a Mo_3Se_4 compound accompanied by an excess of Mo. However the Mo_3Se_4 was not observed. Instead, the $MoSe_2$ phase was detected in the Se/Mo sample annealed at 600°C by X-ray diffraction. In fact, some intermixing between the layers takes place already in the as-deposited sample. During subsequent annealing the reaction proceeds further and after 600°C annealing the two layers are completely intermixed, with the Se present on the sample surface.

For the pre-selenized Cu-In structures, every Cu/In bilayer sample we analyzed contained the CuIn phase in the as-deposited state, regardless of the deposition process employed. This phase is metastable at room temperature and must form by virtue of a fast interdiffusion mechanism. Probably related to that mechanism, and possibly associated with an actual melting of the In, is the observation that a planar Cu/In bilayer is an unstable configuration which breaks up easily into heavily intermixed lumps of about 1 um in size. The details of the sample morphology depend sensitively on the deposition technique. Annealing tends to smoothen out this initial roughness and to induce the formation of Cu-rich compounds.

5. Future Plan

We will further clarify the influence of the microstructure, surface morphology and different phases in the pre-selenized Cu-In samples on the performance of the $CuInSe_2$ after selenization. An investigation of diffusion in Cu/Mo/In trilayers will be undertaken to seek the correlation of diffusion with the contact stability on $CuInSe_2$. Substitution of Mo contacts by some other low diffusivity, stable metal compounds is studied with the collaboration of the Institute of Energy Conversion, University of Delaware.

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16. Abstract (Limit: 200 words)

This report describes research into electrical contacts for copper indium diselenide ($CuInSe_2$) polycrystalline thin films used for solar cell applications. Molybdenum contacts have historically been the most promising for heterojunction solar cells. This program studied contact stability by investigating thermally induced bilayer reactions between molybdenum and copper, indium, and selenium. Because selenization is widely used to fabricate $CuInSe_2$ thin films for photovoltaic cells, a second part of the program investigated how the morphologies, phases, and reactions of pre-selenization Cu-In structures are affected by the deposition process and heat treatments.

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