CuInSe$_2$ thin films produced by rf sputtering in Ar/H$_2$ atmospheres

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Structural, compositional, optical, and electrical properties of CuInSe$_2$ thin films grown by rf reactive sputtering from a Se excess target in Ar/H$_2$ atmospheres are presented. The addition of H$_2$ to the sputtering atmospheres allows the control of stoichiometry of films giving rise to remarkable changes in the film properties. Variation of substrate temperature causes changes in film composition because of the variation of hydrogen reactivity at the substrate. Measurements of resistivity at variable temperatures indicate a hopping conduction mechanism through gap states for films grown at low temperature (100–250 °C), the existence of three acceptor levels at about 0.046, 0.098, and 0.144 eV above valence band for films grown at intermediate temperature (250–350 °C), and a pseudometallic behavior for film grown at high temperatures (350–450 °C). Chalcopyrite polycrystalline thin films of CuInSe$_2$ with an average grain size of 1 μm, an optical gap of 1.01 eV, and resistivities from $10^{-1}$ to $10^3$ Ω cm can be obtained by adding 1.5% of H$_2$ to the sputtering atmosphere and by varying the substrate temperature from 300 to 400 °C.

I. INTRODUCTION

CuInSe$_2$ is one of the most promising materials for the growth of thin-film heterojunction solar cells. Efficiencies as high as 12%–13% have been reported for all thin-film solar cells.$^1$ Among the more frequently used deposition techniques are spray,$^2$ thermal coevaporation of the constituents,$^3$ and sputtering in its different modes (ion beam,$^4$ reactive from Cu/In alloys in Ar/H$_2$ Se atmospheres,$^5$ dc diode,$^6$ rf diode,$^7$ etc.

The main problem that arises in the growth of thin films of ternary compound semiconductors is the tight control of stoichiometry needed to obtain the required structural and electro-optical properties. This problem is easily solved by using the three-source evaporation technique in which a control of the temperature of the different sources is enough to control the film stoichiometry. However, this technique has the disadvantage that the scaling to practical production volumes is not straightforward. In this sense sputtering is a very attractive approach, although control of the film stoichiometry is not so easily achieved.

In sputtering, Se content of films can be modified in many ways, for example, sputtering Cu-In alloy targets in H$_2$ Se/Ar atmospheres, sputtering Se-excess compound targets in pure Ar and varying deposition parameters, or as we do,$^8$ sputtering Se-excess compound targets in Ar/H$_2$ atmospheres. In the latter case, H$_2$ reacts with Se in target and substrate surfaces forming H$_2$Se and HSe volatile species that do not incorporate to the film. The change of Se content also provides a way to vary the Cu/In ratio because of the dependence of the sticking coefficient of metals at the substrate, on the Se/Cu + In ratio at the surface of the growing film.$^9$ The efficiencies (4%–5%) achieved in hybrid$^5$ (sputtered CuInSe$_2$/evaporated CdS) and all sputtered$^{10}$ CdS/CuInSe$_2$ solar cells reveal the great potential offered by this technique. In order to obtain higher efficiencies, it has been suggested$^{11}$ that CuInSe$_2$ should be grown in two stages: a low-resistivity ($10^{-1}$ Ω cm) Cu-rich layer to ensure a low contact resistance with Mo back electrode and low series resistance values, and a high-resistivity ($10^3$ Ω cm) one to form the junction with the window material (CdS or CdZnS).

In this paper we present a study of the structural, compositional, optical, and electrical properties of the films produced by sputtering a Se-excess compound target in Ar/H$_2$ atmospheres. Deposition conditions to obtain the high- and low-resistivity layers are also analyzed in order to grow photovoltaic devices.

II. EXPERIMENT

Films were grown in a GCA Vacuum Industries rf diode sputtering apparatus described elsewhere.$^{12}$ The target (3 in. in diameter) was CuInSe$_2$ with a 5 wt. % Se excess (99.999% pure) and was supplied by Cerac. The chamber was pumped down to a base pressure of $10^{-7}$ Torr before the gases Ar and H$_2$ (99.999% pure) were admitted in various ratios. The Ar and H$_2$ partial pressures were fixed by a MKS flux and pressure controller.

The production conditions were 1000-V target voltage, floating substrate mode, growth temperature ranging between 100 and 450 °C, 10 mTorr total pressure, and H$_2$ partial pressure ranging between 0% and 2% of the total pressure. The substrates were glass plates ($20 \times 20 \times 1$ mm$^3$) ultrasonically cleaned and sometimes coated by an rf sputtered Mo film 1000–2000 Å thick. Film thickness was measured with a Sloan–Dektak profile analyzer and ranged between 1 and 2 μm.

The film characterization consisted in (a) surface morphology observations and compositional analysis with a SEM (Jeol JSM-35C) provided with an EDS system (KE-VEK), (b) structural characterization by x-ray diffraction technique in a Siemens diffractometer, (c) optical characterization by transmittance measurements in the range 500–2500 nm with a Cary-17 spectrophotometer (optical constants were obtained with the method described elsewhere$^{13}$), (d) resistivity measurements at variable temperature (from 77 to 450 K in dry N$_2$) by the Van der Pauw
method with the use of 610-C and 602 Keithley electrometers (contacts were sputtered Mo spots on the edges of $1 \times 1$-cm$^2$ films); the type of carrier was determined by using the hot-point probe.

III. RESULTS AND DISCUSSION
A. Structure and composition

Before discussing the effects of hydrogen, we show results of the films produced in pure Ar atmospheres. In Fig. 1 we represent the variations of the Se/Cu + In and Cu/In ratios versus growth temperature for films produced in pure Ar atmospheres. Atomic percentages of Se, Cu, and In for films grown at three different temperatures are shown in Table I. No remarkable changes in the Se/Cu + In ratio can be seen over the whole temperature range, the films always being Se rich. The Cu/In ratio remains constant until the 300°C limit is reached. For higher temperatures the Cu/In ratio increases sharply, probably because of a selective reevaporation of not too tightly bonded In atoms, becoming Cu rich for temperatures higher than 400°C. X-ray diffraction patterns of films grown in pure Ar showed only sphalerite phase reflections (112), (220,204), and (116,312), even at the highest growth temperature reached (450°C), as can be seen in Fig. 2(a). X-ray diffraction patterns of films grown at lower substrate temperatures showed the same sphalerite reflections with no evidence of characteristic reflections of

<table>
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<th>TABLE I: Se, Cu, and In atomic percentages for three films grown in pure Ar atmospheres at different growth temperatures.</th>
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<td><strong>Temperature (°C)</strong></td>
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FIG. 2. X-ray diffraction patterns of films grown at (a) pure Ar atmosphere and 450°C, (b) 1.5% H$_2$ and 360°C, and (c) 1.5% H$_2$ and 214°C.
binary In$_2$Se$_3$ or Cu$_{2-x}$Se phases. We think that the high Se content inhibits the formation of the ordered chalcopyrite phase necessary to produce efficient photovoltaic devices.

In order to reduce the Se content, small amounts of H$_2$ were introduced in the sputtering atmosphere to form H$_2$Se and HSe volatile species, which do not incorporate to the film. In Fig. 3 variations of the Se/Cu + In and Cu/In ratios with hydrogen percentage at 350 °C substrate temperature are shown. A decrease in the Se content can be seen when hydrogen content increases, as well as a variation in the Cu/In ratio. Hydrogen reacts with Se at the substrate forming H$_2$Se and HSe volatile species, which do not incorporate to the film; Se removal probably causes variations in the sticking coefficients of metals, hence modifying the Cu/In ratio. A percentage of 1.5 yielded near stoichiometric chalcopyrite films for a growth temperature about 350 °C. We will now present results of films grown at this hydrogen percentage.

Figure 4 shows the dependence of the Se/Cu + In and Cu/In ratios on the growth temperature for films produced at 1.5% of H$_2$. Atomic percentages of Se, Cu, and In for films grown at several substrate temperatures are presented in Table II. The Se/Cu + In ratio falls for temperatures higher than 250 °C. The Cu/In ratio shows a more pronounced increase than that observed for pure argon atmospheres for temperatures higher than 250 °C. The decrease in the Se content can be explained in terms of a thermally activated reaction between Se and H$_2$ at the target and substrate surfaces. The increase in the Cu/In ratio should be justified not only in terms of a preferential In reevaporation, as we did with films produced in pure Ar atmospheres, but also in terms of a change in the sticking coefficients of metals when the Se/Cu + In ratio is reduced, as has been suggested by other authors. In fact, the raise in the Cu/In ratio takes place at lower temperatures than in pure Ar atmospheres, and it is coincident with the falling in the Se/Cu + In ratio.

In Fig. 2(b) an x-ray diffraction pattern of a film produced at 350 °C is presented. The characteristic chalcopyrite reflections, (101), (103), (211), and (105,213), can be readily observed. In Fig. 2(c) we present an x-ray diffraction pattern of a film produced at 214 °C. Only sphalerite reflections can be observed; the poor film crystallinity did not allow us to ascertain whether the films had sphalerite structure or the weak chalcopyrite reflections were not observed. In any case, no evidence of binary phases can be seen. At higher substrate temperatures (400 °C), x-ray diffraction patterns were very similar to those presented in Fig. 2(b) with no evidence of binary phases (Cu$_{2-x}$Se, In$_{2-x}$Se$_3$) reflections. SEM observations of the surface topography allowed us to measure the average grain size, which reached values around 1 μm for the films produced at 350 °C. For temperatures lower than 300 °C the grain size showed a rapid decrease, and for films produced at 100 °C an average grain size of about 200 Å was deduced from the x-ray diffraction patterns.

### B. Optical properties

Figure 5 shows the absorption coefficient versus photon energy for films grown at 1.5% H$_2$ and various temperatures. An improvement in definition and abruptness of absorption edge can be observed when the temperature is increased. This behavior is consistent with the improvement in crystallinity and stoichiometry quoted above. A plot of \((a\cdot h\nu)^2\) as a function of \(h\nu\) yielded a linear behavior in the

<table>
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<tr>
<th>Temperature (°C)</th>
<th>100</th>
<th>214</th>
<th>260</th>
<th>305</th>
<th>350</th>
<th>390</th>
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<tbody>
<tr>
<td>Se</td>
<td>53.90</td>
<td>53.33</td>
<td>52.23</td>
<td>52.17</td>
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<td>Cu</td>
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<td>20.68</td>
<td>22.34</td>
<td>22.73</td>
<td>24.79</td>
<td>27.98</td>
</tr>
<tr>
<td>In</td>
<td>25.78</td>
<td>25.98</td>
<td>24.91</td>
<td>25.13</td>
<td>24.81</td>
<td>26.38</td>
</tr>
</tbody>
</table>

Table II. Se, Cu, and In atomic percentages for several representative films grown in 1.5% H$_2$/Ar atmosphere at different growth temperatures.
FIG. 5. Log of absorption coefficient vs photon energy for films grown at 1.5% H₂, 10 mTorr, and 1000-V target voltage, and (●) 110 °C, (●) 230 °C, (■) 290 °C, and (▲) 375 °C.

region of strong absorption near the absorption edge, indicating that absorption takes place through allowed direct interband transitions. In this case the absorption coefficient can be written as

$$\alpha = \frac{A}{h} (h \nu - E_g)^{1/2}.$$  

This is shown in Fig. 6 for films grown at 130 and 360 °C. The extrapolation to \((a h \nu)^2 = 0\) leads to gap values of 0.95 and 1.01 eV, respectively. Figure 7 shows the dependence of the gap values on the growth temperature. Our 350 °C films yield gap values of 1.01 eV, identical to those reported by Neuman et al. for their rf sputtered films and very close to the value reported for single crystal (1.04 eV). The reduced energy gap values for lower temperatures can be explained according to the discussion in Sec. III A by the poor crystallinity that probably results in a large quantity of gap states near band edges caused by structural defects in grains and grain boundaries. These gap states are responsible for transitions that measure lower optical bandgap values. A similar effect has been reported by other authors for this and other polycrystalline compound semiconductors.

The absorption coefficient could not be measured on films produced at temperatures higher than 380 °C. The surface roughness exhibited by these films partially destroyed the interference effects in the weak absorption zone of the spectrum needed for the application of our calculation method.

In Fig. 6 an additional absorption is observed for \(h \nu > 1.2 \text{ eV}\). This has been observed in CuInSe₂ (Ref. 15) and is due to a forbidden direct transition. The refractive index did not show pronounced changes with the deposition conditions, yielding values between 2.6 and 2.7, similar to those reported by other authors.

C. Electrical properties

All the films analyzed were \(p\) type. Only in a few cases could mobility be measured because of the very small values of Hall voltages, and it was always lower than 2 cm² V⁻¹ s⁻¹. Similar results have been observed in rf sputtered films by other authors.

Figure 8 shows the dependence of the resistivity on the growth temperature for films produced at 1.5% H₂. Three zones can be observed: zone I, between 100 and 250 °C, where resistivity values increase from \(10^{-1}\) to \(10^1 \text{ Ω cm}\); zone II, between 250 and 350 °C, where resistivity remains roughly constant at \(10^1 \text{ Ω cm}\); and zone III, for temperatures higher than 350 °C, where resistivity falls abruptly to \(10^{-1} \text{ Ω cm}\) again. Resistivity of CuInSe₂ films shows a strong dependence on stoichiometry, because both vacancies and interstitial of the constituents act as acceptor or donor levels. Thus it is reasonable to relate resistivity with composition. Behavior in zones II and III can be explained in these terms.
In fact, in zone II films are Se and In rich; this implies high resistivity.\textsuperscript{21} In zone III films become pronouncedly Se poor and Cu rich, and resistivity drops. However, in zone I stoichiometry remains roughly constant, the films being Se and In rich; this means that, provided they are $p$-type, they ought to have high resistivity.\textsuperscript{21} Since no binary phases have been found, this behavior should be explained in terms of crystallinity. In order to clarify this point, measurements at variable temperatures will be presented. In the following paragraphs we show the results of resistivity measurements at variable temperature for representative films of the three zones.

1. Zone I (100–250 °C)

Resistivity showed a weak temperature dependence for these films. The analysis carried out (see Fig. 9) showed that for temperatures lower than 150 K the conductivity fitted a "variable range hopping" law in the form

$$\rho T^{-1/2} = \rho_0 \exp\left[-\frac{T_0}{T}\right].$$ (1)

This conduction mechanism, well known in amorphous semiconductors,\textsuperscript{22} has been reported to take place also in polycrystalline semiconductors such as CdTe, Si, InSb,\textsuperscript{23} and even in ternary compounds similar to CuInSe$_2$ such as CuInTe$_2$.\textsuperscript{24} Hopping conduction can take place in the grain through gap states in the vicinity of the Fermi level or through states in the grain boundaries.\textsuperscript{23} The value of the parameter $T_0$ is related with the degree of disorder of the semiconductor. Obviously, this conduction mechanism only takes place in materials with a very high degree of disorder. The evidence of such disorder in our films has been established in the preceding paragraphs: average grain size in the order of 200 Å, poorly defined absorption edge, and low band-gap values, suggesting the presence of a large density of gap states. The fitting of experimental data to Eq. (1) leads to a $T_0$ value of $2.3 \times 10^3$ K, which is consistent with results given for other polycrystalline materials.\textsuperscript{23}

For temperatures higher than 150 K, the conductivity shows a temperature dependence (see Fig. 10) that can be written as

$$\rho T^{-1/2} = \rho_0 \exp(-E_p/KT),$$

indicating a thermal activation over grain boundaries.\textsuperscript{25} An estimation of the thermal activation yielded a value of 0.015 eV for those barriers.

In conclusion, the anomalously low values of resistivity for films grown at low temperature ($T < 250$ °C) are due to a hopping conduction mechanism through gap states caused by the disorder in the film.

2. Zone II (250 °C–350 °C)

In Fig. 11 a plot of log ($\rho T^{1/2}$) vs $1000/T$ is shown for a representative film grown at 300 °C. Three activation energies (typical in polycrystalline films), with values 0.061,
0.113, and 0.169 eV, can be seen. Carriers are thermally activated from acceptor centers in the forbidden gap to the valence band. To obtain information about the energetic position \( E_A \) of these acceptor states, mobility should have been measured at variable temperatures to deduce the height of the intercrystalline barrier \( \Phi \). In this way the activation energy measured in the conductivity \( \rho(T) \) can be written as

\[
E_A = \Phi + E_A.
\]

Unfortunately, mobility could not be measured in these films, but if we use the activation energy deduced in the zone-I measurements for the barrier height as an estimation for that magnitude in the zone-II films, we can deduce an approximate position for the referred acceptor states. The \( E_A \) values deduced under this assumption (0.046, 0.098, and 0.114 eV) are in very good agreement with the acceptor levels reported by other authors.25

3. Zone III (temperature higher than 350 °C)

Films grown at a temperature of 400 °C showed low values of resistivity (see Fig. 8). Measurements of resistivity at variable temperature yielded a pseudometallic behavior, as can be seen in Fig. 12. This result is consistent with the composition of these films, which are Se deficient and Cu rich (see Fig. 4). The great quantity of acceptor levels due to stoichiometric defects degrades the semiconductor. The same behavior has been observed by the SERI group for their low-resistivity films.27

Summarizing, the resistivity of CuInSe\(_2\) thin films grown by reactive sputtering in Ar/H\(_2\) atmospheres is governed by stoichiometry in zones II and III and by crystallinity in zone I; in this latter case the disorder in the film is responsible for the presence of a large amount of gap states through which a hopping conduction takes place.

IV. CONCLUSIONS

\( p \)-CuInSe\(_2\) thin films have been grown by sputtering a Se-excess compound target in Ar/H\(_2\) atmospheres. Film compositions were controlled by introducing small amounts of H\(_2\) in the discharge and varying its reactivity with growth temperature. Hydrogen modifies Se content and, as a consequence, the Cu/In ratio, because of variations in sticking coefficients of metals. Films produced in pure Ar atmospheres only showed sphalerite structure, even at high substrate temperature. The introduction of a hydrogen percentage of 1.5% resulted in optimum conditions for obtaining near-stoichiometric chalcopyrite films at substrate temperatures higher than 300 °C. High values of the average grain size (up to 1 \( \mu m \)), high values of absorption coefficient, a well-defined absorption edge, and resistivity values controlled by growth temperature make reactive rf sputtered CuInSe\(_2\) films in Ar/H\(_2\) atmospheres very suitable for solar cell applications. Preliminary results of devices grown with CuInSe\(_2\) of zone II (substrate temperature at 350 °C) and rf sputtered CdS window layer are the following: \( V_{oc} = 0.25 \) V, \( I_{sc} = 18 \) mA cm\(^{-2}\), FF = 0.32, under AM1 illumination conditions.

Measurements of resistivity at variable temperature allowed us to identify a hopping conduction mechanism taking place in films grown at low substrate temperatures and to obtain information about acceptor levels in films grown at high and intermediate temperatures.

20 Although no evidence for the presence of binary phases have been found in x-ray diffraction patterns of films produced at low substrate temperatures, this might be because of the poor crystallinity exhibited by those samples. In fact, according to a referee’s comments, the growth of low-temperature films containing only single-phase CuInSe₂ seems to be very unlikely to us.