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The Effect of Mo Back Contact on Na Out-Diffusion and Device Performance of Mo/Cu(In,Ga)Se₂/CdS/ZnO Solar Cells

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ABSTRACT

Molybdenum thin films were deposited on soda lime glass (SLG) substrates using direct-current planar magnetron sputtering, with a sputtering power density of 1.2 W/cm². The working gas (Ar) pressure was varied from 0.6 to 16 mtorr to induce changes in the Mo films' morphology and microstructure. Thin films of Cu(In,Ga)Se₂ (CIGS) were deposited on the Mo-coated glass using the 3-stage co-evaporation process. The morphology of both the Mo-coated SLG and the CIGS thin films grown on it was examined using high-resolution scanning electron microscopy. Na was depth profiled in the Mo and CIGS films by secondary ion mass spectrometry. The device performance was evaluated under standard conditions of 1000 W/m² and 25°C. Optimum device performance is found for an intermediate Mo sputtering pressure.

INTRODUCTION

Cu(In,Ga)Se₂ (CIGS) is one of the most promising materials for thin-film photovoltaic devices. This is due largely to the capability of preparing it in either n- or p-type form, its high absorption of the solar spectrum, and excellent stability under operating conditions [1]. It also has a desirable variable direct band gap from 1.02 to 1.68 eV, depending on the $x = \text{Ga}/(\text{Ga}+\text{In})$ ratio [2]. Unacceptable device performance had been reported for photovoltaic structures with high Ga content ($x > 0.3-0.4$) [3], however, a thin-film conversion efficiency of 18.8% has been achieved with CIGS solar cells [4].

The highest efficiencies for CIGS based solar cells have been obtained by using soda lime glass (SLG) as substrate material [4]. SLG contains significant amounts (15.6 wt.%) of sodium in the form of Na₂O [5]. The SLG is coated with molybdenum, which serves as the back contact for the solar cell. The interest in using Mo thin films arises from its high thermal stability (high melting point), mechanical strength, and its electronic properties (low resistivity) [6-8]. During the growth of CIGS films at substrate temperatures (T_{sub}) close to the softening point of the glass substrate, Na ions diffuse from the SLG through the Mo back contact into the semiconductor material. The Mo thin film back contact plays an important role in the fabrication of CIGS based solar cells. It can be considered as the main transport gate for the Na out-diffused from SLG to the CIGS absorber material. Na diffusion is advantageous during CIGS growth because it increases the grain size and provides a high degree of surface flatness for the CIGS solar cells. Fur-

thermore, a moderate level of Na improves the efficiency of the cells by enhancing the p-type conductivity [9].

The properties of the Mo thin films and the type of the glass substrate [9] control the Na diffusion process. Significant changes in the properties of Mo films may be induced because of the residual stress that the film experiences during the growth. Strong correlations exist among the energy of the sputtered Mo particles, the working gas sputtering pressure, and the discharge voltage. The films experience compressive stress with dense microstructure at relatively low pressure, which is due to the high kinetic energy of the arriving atoms. When less energy is provided to the film at relatively high sputtering pressures, the films exhibit tensile stress with open porous microstructure [10-12]. The purpose of this paper is to study the effect of various Mo microstructural properties, induced by different sputtering pressures, on the Na out-diffusion during the CIGS deposition process, and the subsequent effect of the variations in the Na supply on the CIGS device performance.

EXPERIMENTAL

Mo films of thickness 0.6–0.7 μm were deposited on 10.2 cm × 10.2 cm SLG substrates by (DC) planar magnetron sputtering. The cathode electrode (Mo target) was 12.7 cm × 20.3 cm × 0.3 cm, at a distance of 75 mm from the SLG substrates. The substrates were rotated into the path of the cathode and held stationary for a predetermined time to deposit the desired film thickness. Prior to deposition, the vacuum base pressure was less than 4×10^{-7} torr. To induce changes in the morphology and microstructure properties of the Mo films, the sputtering process was operated in the Ar gas pressure range of 0.6–16 mtorr. An average sputtering power density of 1.2 W/cm² was used with a discharge current of 1 A and a discharge voltage in the 290–320 V range. The deposition rate averaged 11 Å/s. The substrate temperature was difficult to maintain at constant level during the deposition; it increased gradually from room temperature to about 400 K. CIGS thin films were deposited on the Mo-coated SLG by the "3-stage" process, described elsewhere [13]. Device fabrication was completed by chemical-bath deposition of about 500 Å CdS followed by 500 Å intrinsic ZnO and 3500 Å Al-doped ZnO using RF sputtering. Grids of Ni/Al were applied as a front contact.

The morphology of both the Mo-coated SLG and the as-grown CIGS films was examined using high-resolution field-emission scanning electron microscopy (FESEM). Also, secondary ion mass spectrometry (SIMS) was employed to characterize the Na out-diffusion through the as-sputtered Mo thin films and through the as-deposited CIGS thin films (including the Mo back contact layer). The performance of these devices was evaluated under standard conditions of 1000 W/m^2 and 25°C .

RESULTS AND DISCUSSION

The effect of sputtering pressure on microstructure of the Mo films is illustrated by the plan-view SEM images. At 0.8 mtorr, Fig. 1 reveals that this film had a densely packed, small-grain microstructure with closed grain boundaries. No evidence of the presence of voids was obtained. The cross-sectional SEM image of this sample (not shown here) exhibits a tightly packed columnar structure. This microstructure was expected at low sputtering pressures based on the peening effect caused by the energetic Mo particles [14-19] that cause the atoms to be forced into the small spaces within the growing film. Film deposited at 5 mtorr had porous and fibrous grains with fine valleys (see Fig. 2). The morphology consisted of elongated grains with open grain boundary structure of tapered crystallites with domed tops. The cross-sectional view reveals that this film had closed intercolumnar gaps. However, films deposited at higher sputtering pressures such as 8 mtorr had an open columnar structure, consisting of free-standing columns with an increasing amount of column boundary voids. Also, they had fibrous, large, aligned, elongated grains with the presence of micro-cracks.

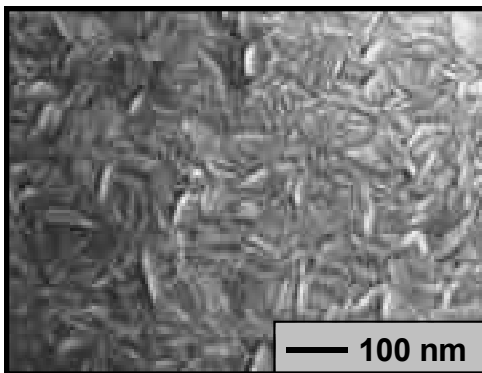


Fig. 1. SEM plan-view of a Mo film sputtered at 0.8 mtorr.

SEM investigations show that the morphology of the CIGS films varies from one sample to another on the Mo prepared at different pressures in spite of the fixed deposition conditions for the CIGS films, such as the deposition rate and the substrate temperature. The surface of the CIGS film deposited on the Mo film grown at 0.8 mtorr exhibits two micro structural features. One is the formation of the lamellar-type structure, in which the

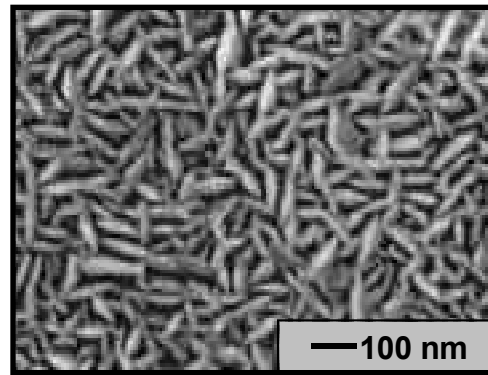


Fig. 2. SEM plan-view of a Mo film sputtered at 5 mtorr.

layers are positioned at various angles to the substrate [20], and the other is the presence of tightly packed and faceted grains. It has been reported [20] that the lamellar-type layered structure is actually a mixed lamellar intergrowth resulting from the presence of In_2Se_3 and CIGS- phases, represented on the $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3$ pseudo-binary phase diagram. On the other hand, the morphology of CIGS films deposited on Mo grown at 5 mtorr has less faceted, very dense, and smooth grains. Fig. 3 shows the cross-sectional view for this film. The CIGS grains were large in size, and the columnar structure of the corresponding Mo film was clearly observed. However, the morphology of the CIGS film deposited on a Mo film grown at 8 mtorr had again rough surfaces with more faceted grains.

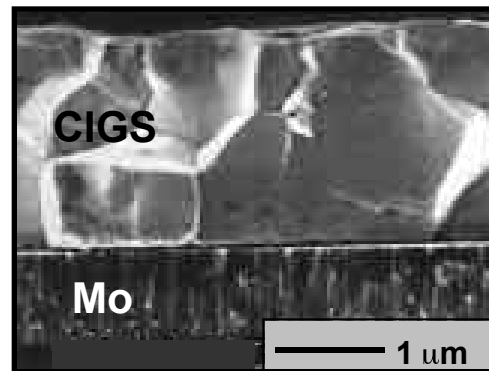


Fig. 3. SEM cross-sectional view of a CIGS film deposited on a Mo film sputtered at 5 mtorr.

A Cs source as the primary ions was used to obtain SIMS depth profiles for both positive (Na, Cu, Ga, In, Se, and Mo) and negative (C, O, S, Cl, Cu, Se, Mo, and In) secondary ions, although data presented below are for positive secondary ions. Na depth profiles for Mo films sputtered at 0.6, 2, 5, and 8 mtorr are shown in Fig. 4. The Na level correlates well with the increasing growth pressure and increasing O levels in the films (the O profiles are not shown). Almost no Na is detected in

the Mo film grown at the lowest pressure of 0.6 mtorr. This will correspond to about 10^{16} at-cm⁻³. Also, there is still very little Na apparent in the Mo grown at 2 mtorr. However, a dramatic increase was observed in the Mo film grown at higher pressure of 5 mtorr, and a further large increase was noted in the Mo film grown at the highest pressure of 8 mtorr. The increase in Na is a factor of 100 between the lowest growth pressure (0.6 mtorr) and those 8 mtorr.

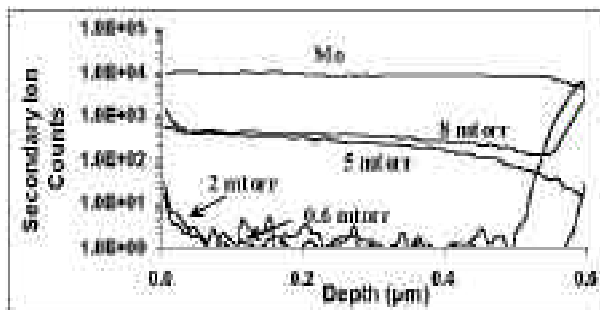


Fig. 4. SIMS depth profiles for Na in as-sputtered Mo films under different sputtering pressures.

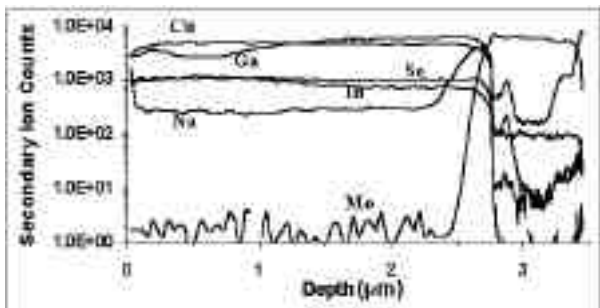


Fig. 5. SIMS depth profiles for a CIGS film deposited on Mo film sputtered at 5 mtorr.

SIMS depth profiles for the Mo films following deposition of a CIGS absorber layer show differences in Na levels between the CIGS thin films that is much smaller than the differences in the Mo thin films themselves. There is a slight increase from the lowest to the highest Mo sputter pressure in the overall Na. In all cases, there is an increase of Na level at the CIGS/Mo interface and at the CIGS surface (see Fig. 5). For the lowest Mo sputtering pressure (0.6 mtorr), this increase is modest. At the higher Mo pressures (8 mtorr), however, the increase is substantial and essentially flat across the Mo and CIGS layers. The increase of Na at the interface correlates well with the increased Se seen in the negative ion profiles of these same samples (not shown here).

Table 1 presents average performance of CIGS solar cells fabricated with total areas of 0.43 cm² and without antireflective coatings. For each substrate prepared with

a given Mo sputtering pressure, 24 cells were made to yield the average values and standard deviations shown. Both the open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) of the CIGS solar cells start increasing with increasing the Mo sputtering pressures up to 5 mtorr. For the CIGS device with a Mo sputter pressure of 8 mtorr, the J_{sc} starts decreasing and the V_{oc} increases slightly. However, as the sputtering pressure further increase beyond 8 mtorr, both V_{oc} and J_{sc} decrease. The cell corresponding to the CIGS film deposited on Mo film sputtered at 5 mtorr has the highest average efficiency of 15.99%, with an average V_{oc} of 0.671 V and average J_{sc} of 32.57 mA/cm². There is a trend of better device performance at the intermediate Mo sputtering pressures.

Table 1. Average Device Performance Results for CIGS Devices. Standard Deviations are Shown in Parentheses (last significant figures).

| P_{Ar} (mtorr) | V_{oc} (SD) (V) | J_{sc} (SD) (mA/cm ²) | FF (SD) (%) | (SD) (%) |
|---------------------|----------------------|--|----------------|-------------|
| 0.6 | 0.614(10) | 31.1(6) | 73.3(1.9) | 13.98(53) |
| 0.8 | 0.624(14) | 30.9(9) | 74.6(2.4) | 14.36(72) |
| 2 | 0.658(17) | 31.7(6) | 73.1(3.0) | 15.25(79) |
| 5 | 0.671(7) | 32.6(6) | 73.2(1.3) | 15.99(45) |
| 8 | 0.676(9) | 32.1(8) | 73.0(2.6) | 15.86(73) |
| 12 | 0.643(18) | 31.2(1) | 73.6(1.9) | 14.79(77) |
| 16 | 0.574(14) | 30.6(1) | 69.6(0.9) | 12.35(53) |

It is well known that Na incorporation leads to increases in the V_{oc} , J_{sc} , and fill factor of CIGS-based solar cells [9,21,22]. It incorporates into the lattice of the CIGS by reacting with Se and forming Na-Se compounds [23,24]. These compounds slow the growth of CIGS and facilitate the Se incorporation in the film [25]. Furthermore, the Na-Se compounds react with air at the CIGS/air interface to form a Na-Se-O compound. The remainder of Na replaces In or Ga and creates extrinsic defects, Na_{In} or Na_{Ga} , which act as acceptors and increase the p-type conductivity [24]. However, excessive Na diffusion may limit the efficiency of the cells because of the introduction of additional deep states, but the addition of sulfur has been reported to passivate these deep states [26]. Accordingly, we explain the CIGS device performance results as a function of the Mo sputtering pressures as follows:

At low pressures, the amount of Na out-diffused from the SLG is low, caused by the highly dense close grain-boundary structure of the Mo film. This is confirmed by the low Na and Se signals in the SIMS data and the rough CIGS surface. Therefore, the formation of the Na-Se bonds, which is a signature of creating any kind of acceptors Na_{In} or Na_{Ga} , is expected to be less compared to the set of Mo films sputtered at higher pressures. Consequently, the CIGS device performance is low.

At an intermediate Mo sputtering pressure of about 5 mtorr, the open grain boundary structure assists in Na out-diffusion. This was indicated by the CIGS film that had a smooth surface and less faceted grains. Also, as mentioned earlier, the SIMS data show a correlation between the Na and Se levels, which increase with increasing the sputtering pressures. This amount of Na out-diffused seems to be sufficient to cause the observed enhancement in the CIGS device performance. This enhancement might be due to the amount of the acceptor states that lead to the increase in the p-type conductivity in the CIGS absorber.

At the highest Mo sputtering pressures (8 mtorr), resulting from to the formation of intercolumnar microvoids and micro-cracks, the amount of Na out-diffused exceeded the limit that is desired to improve the device performance. Also, this excess amount of Na might introduce additional deep states causing lower device performance.

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