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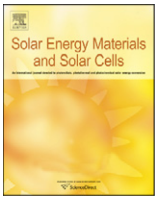

Co-evaporated $Cu_2ZnSnSe_4$ films and devices

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ABSTRACT

The use of vacuum co-evaporation to produce $Cu_2ZnSnSe_4$ photovoltaic devices with 9.15% total-area efficiency is described. These new results suggest that the early success of the atmospheric techniques for kesterite photovoltaics may be related to the ease with which one can control film composition and volatile phases, rather than a fundamental benefit of atmospheric conditions for film properties. The co-evaporation growth recipe is documented, as is the motivation for various features of the recipe. Characteristics of the resulting kesterite films and devices are shown in scanning electron micrographs, including photoluminescence, current-voltage, and quantum efficiency. Current-voltage curves demonstrate low series resistance without the light-dark cross-over seen in many devices in the literature. Band gap indicated by quantum efficiency and photoluminescence is roughly consistent with that expected from first principles calculation.

1. Introduction

The number of manufactured $CuIn_xGa_{1-x}Se_2$ (CIGS) photovoltaic modules is quickly growing. The combination of relatively high efficiency (compared to CdTe or α-Si) and potentially low processing costs (compared to crystalline Si) has attracted considerable investment. A survey of companies participating in the manufacture of CIGS modules suggests that there are at least 21 companies [1] worldwide who are today either at pilot or commercial scale, and many more in earlier stages of production. The level of activity in the CIGS community is matched by the remarkable module efficiency progress demonstrated by these companies in recent years, notably a 17.2%-efficient, 900-cm^2 prototype module from Solar Frontier [2], and a 15.7%-efficient, 0.97-m^2 production module from Miasole [3]. Efficiencies in this range may be sufficient to achieve the 50¢/watt (W) module cost estimated by the U.S. Department of Energy (DOE) to make photovoltaics broadly competitive with traditional energy sources [4] and enable terawatt (TW)-scale deployment. Minimum efficiency to meet module cost goals is based on analysis of fixed costs (e.g., glass, junction boxes, encapsulant, edge seal, etc.) [5,6].

The greatest risk in achieving TW-scale deployment for CIGS seems to lie in the availability of key elements, such as indium (In), which is also used in more expensive devices, such as flat panel displays. Several studies of In availability exist in the literature [7–10]. The resulting estimates of when In scarcity will become important to module prices range in CIGS manufacturing volumes from 4 GW/yr to over 100 GW/yr. However, all these figures are below the desired TW-scale deployment. In fact, DOE estimates that, for all trajectories considered, In demand will exceed supply by 2015 [7]. While the current cost of In adds only 1¢ to 10¢/W to the price of module manufacturing [11], a significant increase in In price would be problematic for the necessary 50¢/W_p module cost.

To mitigate possible future effects of In scarcity on TW-scale deployment, it has been proposed that CIGS can be replaced by $Cu_2ZnSn(S,Se)_4$ (i.e., "CZTS") in the kesterite structure, where every two In or Ga atoms in the chalcopyrite structure are replaced by a Zn and Sn atom. This substitution both provides a better cost position by reducing the materials cost due to In and Ga, and improves the product's earth-abundancy. To date, solar cells with up to 10.1% efficiency [12] have been made using these kesterite absorbers. Other than the absorber layer, the CZTS device structure is the same as that for the CIGS device. The range of possible band gaps (and therefore resulting device voltages and currents) is nearly identical for the two families of materials. Thus, CZTS may function as a drop-in replacement for CIGS, leveraging the existing industrial progress in CIGS.

Previously, the most efficient kesterite devices ($\geq$8%) have been formed by reacting various precursors at atmospheric pressure. Such results include a 10.1% device made by spin-coating particle-containing hydrazine solutions, followed by an

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atmospheric 540 °C anneal [12,13]; an 8.1% device made via a similar technique but using diluted hydrazine [14]; an 8.4% device made by 500 °C selenization of nanoparticle ink precursors at atmospheric pressure [15,16]; and an 8.4% device made by co-evaporation of precursors at low temperature (150 °C) and subsequent 540 °C hot-plate annealing [17]. These methods afford precise control of difficult quaternary (or penternary/senary, in cases where alloying is used to tune band gap) composition, and minimize the volatilization of high vapor pressure compounds, specifically tin selenides, copper tin selenides, zinc, and the chalcogens. However, these methods do not allow real-time control of the sample composition and reaction path. In the case of CIGS, vacuum co-evaporation is used to control the absorber reaction path to induce growth of large grains with few impurities and intentional band gap gradients. In fact, it has been the only method to produce record-efficiency small-area CIGS devices in the last 20 years. Attempts to reproduce the success of co-evaporation for the kesterite family of materials have to date fallen short of the precursor/anneal approach, producing devices in the 4% to 6.1% efficiency range [18–20].

In this paper, we demonstrate the use of vacuum co-evaporation to produce CZTSe devices with an improved 9.15% total-area efficiency. Composition control via commercially available rate monitors, emissivity-based endpoint detection, and judicious choice of processing temperature is described. The growth recipe is documented, as is the motivation for various features of the recipe. The resulting characteristics of the kesterite films and devices are shown.

2. Materials and methods

2.1. Film growth

The device structure used for the kesterite devices is identical to that used for CIGS devices, except for the substitution of CZTSe for CIGSe. The device stack was formed by using a soda-lime glass (SLG) substrate, a sputtered Mo back contact, a 150 Å e-beam evaporated NaF precursor, co-evaporated CZTSe, chemical-bath-deposited (CBD) CdS, a sputtered resistive/conductive ZnO bi-layer, e-beam-evaporated Ni/Al grids, a MgF_2 antireflective coating, and photolithographic device isolation. The non-absorber device layers have been thoroughly described, as related to the CIGS device, in previous publications [21–25]. The use of a NaF precursor layer for CIGS devices is typically reserved for CIGS deposited on Na-free substrates, not SLG [26,27]. Here, however, it was used in conjunction with the SLG to compensate for the expected low out-diffusion of Na at the lower deposition temperatures. In the development of this process, the NaF precursor has been observed to improve open-circuit voltage (V_{oc}), fill factor (ff), and short-circuit current (J_{sc}), with no discernable change in SEM cross-section.

The kesterite absorbers were made using four-source thermal co-evaporation. Equipment and procedures used to make the kesterite films are nearly identical to those previously described related to CIGS processing [21,22,28–30], except that In and Ga shot were replaced in the evaporator by Zn and Sn shot, and appropriate optical filters (202.55 nm for Zn and 284.0 nm for Sn) were substituted for the Ga and In filters in the electron impact emission spectrometer rate monitor.

Deposition flux and temperature profiles for CZTSe film growth are shown in Fig. 1. Deposition rates are shown in the top portion of the graph. The thick lines represent metal (Cu, Zn, Sn) rate setpoints, and the thin lines show actual metals rate monitor data. Metals rates are read from the left axis, and Se rate is read from the right axis. Zero-rate optical background signals were removed from the graph. The lower portion of Fig. 1 shows temperature data. The left axis of the graph presents a full-scale view of the lamp setpoint (thick line) and substrate (thin line) temperatures. The right axis shows an expanded view of the substrate temperature, with the slight temperature increase near the end of the deposition illustrating the sample emissivity change as the sample exits the Cu-rich growth period. All temperature and rate controls are terminated at 42 minutes, and the sample is allowed to cool. All films described in this paper are grown by this recipe and exhibit similar characteristics.

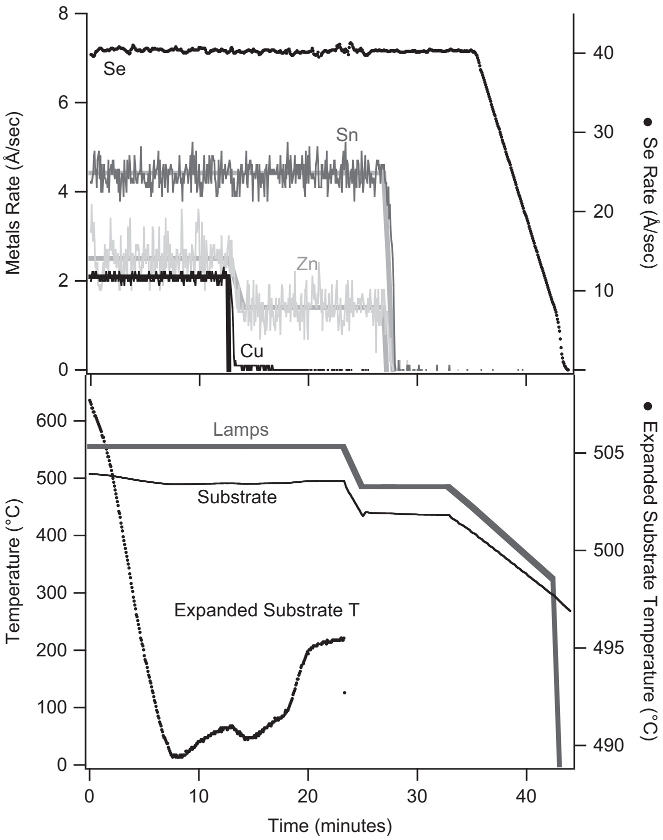

Fig. 1. Logged deposition data for CZTSe film M3464.

Choices of a number of the deposition conditions (Fig. 1) were made deliberately to achieve favorable film and device properties.

First, a Cu-rich growth period was incorporated for benefits in both grain growth and composition control. In the first 12.5 minutes of Fig. 1, Cu is supplied at a rate that slightly exceeds stoichiometry, i.e., the atomic ratio $Cu/(Zn+Sn) > 1$. Both CIGS [31–33] and kesterite [34] films have been observed to exhibit increased grain sizes when a period of Cu-rich growth is included in the deposition. This improved grain growth has been associated with a flux-recrystallization of chalcopyrite grains by a liquid Cu_xSe_y phase. Because many factors, such as temperature and composition, may affect morphology, defining the effect of the Cu-rich growth period for kesterites is an ongoing examination.

The Cu-rich growth period is also useful for composition control. It has been demonstrated for CIGS that subtle changes in the sample temperature indicate a lack or presence of Cu_xSe_y [35,36]. The same behavior is evident for the kesterites, as illustrated by the fine-scale temperature data of Fig. 1. In Fig. 1, the shutter opens at time 0, and the deposition begins onto the high-emissivity Mo substrate. As Mo becomes coated with Cu-rich CZTSe, the emissivity of the surface increases, and the temperature decreases until about 8 minutes. At 12.5 minutes,