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ABSTRACT

We present a summary of our work on the preparation of $CuInGaSe_2$ (CIGS) absorbers that has led to fabricating record-efficiency solar cells. The use of the three-stage process in conjunction with composition monitoring facilitates the fabrication of solar cells with efficiencies between 18% and 19.5% for absorber bandgap in the range of 1.1–1.2 eV. We describe our recent results in reducing absorber thickness and low-temperature deposition. Our preliminary results on absorbers grown from low-purity source materials show promise of reducing the cost of fabricating the absorber.

1. Introduction

There is now a growing appreciation for the importance of photovoltaic (PV) technologies in the world's energy production. Silicon-based technologies have a commanding lead in the market. However, it is generally believed that thin film photovoltaics are needed to meet the low-cost goals. CIGS thin-film solar cells have demonstrated high efficiency in the laboratory and on the industrial scale, and their long-term performance in the field shows good stability. The investment in R&D by the DOE PV Program has paid dividends as the two prominent thin-film technologies continue to make headway into the commercial market. However, much work remains to be done to ensure continued growth and advancement: developing faster, simpler processes for depositing the absorbers at high rates; lowering process temperatures; simplifying junction-forming process steps; reducing absorber thickness; and, maintaining high efficiency.

Over the past five years, our group has devoted its efforts to two major areas: reproducible fabrication of high-efficiency CIGS cells by the three-stage process, and the basic science of junction formation. Cell efficiencies above 19% were reported [1-3]. We have begun to address the issue of cost reduction in a multi-megawatt manufacturing scenario. We report our results on CIGS solar cells fabricated on absorbers that are ≤1 μm in thickness. Another approach to lowering the cost is to prepare the absorbers from starting materials of lower purity than typically used (99.9% vs. 99.999%). These results are presented below.

2. Salient Results

2.1 High-Efficiency Solar Cells

CIGS absorbers were fabricated by varying the Ga content of the $(In,Ga)_2Se_3$ precursor layer. The energy gap ranged from 1.1 to 1.22 eV, and the corresponding Ga/(In+Ga) ratios ranged from 0.26 to 0.31. Table I shows a summary of the properties of solar cells characterized under standard reporting conditions. Clearly, solar cells with high open circuit voltages and high fill factors can be fabricated in a reproducible manner.

2.2 Thinner Absorbers

The price of In has risen sharply in recent times and the concern about using it in large quantities resurfaces from time to time. Reducing the thickness of the absorbers from 2.5 μm to ≤1 μm reduces the quantity of In used in the cell. This must be done without adversely affecting the efficiency. This aspect has been studied previously [4], and the efficiency has been shown to decrease when the absorber thickness is reduced below 1 μm. We have revisited the growth of thin absorbers by using a modified three-stage process and a co-evaporation process similar to the one used by Boeing [5]. To apply the three-stage process for thinner films, the deposition rates of all the elements were reduced in the first two stages, and the heating rates were also adjusted. Compositional monitoring was still possible in spite of the reduced film thickness. In the co-evaporation process, film growth was initiated in a Cu-rich $CuGaSe_2$ layer and the overall composition was converted to device quality, Cu-poor $Cu(InGa)Se_2$. This type of growth often resulted in some voids and poor adhesion at the Mo interface. These observations are consistent with an earlier study by Kessler et al [6]. However, compositional uniformity was easily achieved, and the deposition time was considerably shorter (5–10 min) than the three-stage process. With the latter, it was possible to produce dense and smooth thin films. The distribution of Ga through the depth of the film was governed by the ramp rates and the kinetics of the reaction between the binary selenides. Hence, we observed a difference in the solar cell properties fabricated from absorbers made by the two methods. Table II shows the properties of the best solar cells fabricated as a function of absorber thickness.

Table I. Parameters of high-efficiency CIGS solar cells.

Band gap (eV)	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (%)	Eff (%)
1.12	0.701	34.60	79.65	19.3
1.15	0.717	33.58	79.41	19.1
1.18	0.731	31.84	80.33	18.7
1.22	0.740	31.72	78.47	18.4
1.12 (Record))	0.692	35.22	79.87	19.5

Table II. Properties of thin CIGS solar cells.

Thickness (μm)	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (%)	Eff (%)
1.0 (3-stg)	0.654	31.6	78.3	16.2
1.0 (codep)	0.699	30.6	75.4	16.1
0.75 (codep)	0.652	26.0	74.0	12.5
0.5 (codep)	0.607	23.9	60.0	8.7
0.4 (3-stg)	0.565	21.3	75.7	9.1

The last sample in the above table was fabricated on a substrate specially prepared to allow optical measurements to be made. On a 7.5x7.5 cm substrate coated with Mo, we made 1x1 cm size openings. The CIGS film deposited on these windows was used for optical measurements. Transmittance and reflectance were measured as a function of wavelength, and the absorption was calculated. This was further corrected for the reflectance of the solar cell made from the Mo-coated areas. The external quantum efficiency (QE) of the solar cell and the absorption in

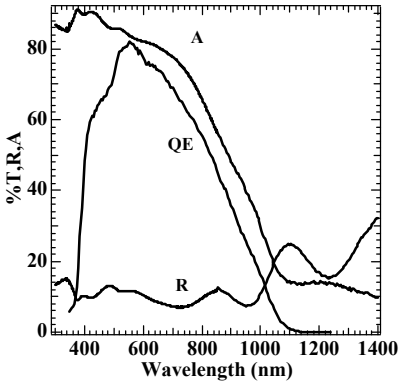

Fig. 1: Absorption (A) of a 0.4 μm thick CIGS film on glass. Quantum efficiency (QE) and reflectance (R) of the solar cell made from the absorber are also shown.

the CIGS film are shown in Fig. 1. The shape of the absorption and long wavelength edge of the QE are similar. The current collection in the device is efficient because the QE curve nearly matches the absorption curve. The difference between the two is the collection loss in the long wavelength region, but it is surprisingly low. To the extent that the thin-film absorbs light, current is efficiently generated and collected, but the consequence of not having adequate thickness to absorb all the light (some light is transmitted) is apparent. The short wavelength response is reduced by the window layer absorption and loss of collection. The measured current density of the cell is close to what is expected, and the fill factor is high. The efficiency of the cell is reduced by a lower V_{oc}, and it is likely that the recombination in the back contact region is playing a role. This is the major loss in thin cells.

2.3 Growth from Low-Purity Elements

Impurities are generally detrimental to performance of electronic devices. The standard practice in thin film deposition is to use source materials of the highest purity available and affordable, typically 99.999% or better. Electronic-grade materials are expensive. One approach to reducing cost would be to use lower-purity materials if we know that the trace elements do not adversely affect the cell performance. Impurities in the source materials may not evaporate at the same rate as the elements. They may be less soluble, not at all soluble, or segregate out of the solid film. If they do incorporate in the film, the impurities may not be electrically active. A case in point is the variety of impurities found in soda lime glass. In addition to Si, the primary component, significant amounts of Na, K, Ca, Mg, Al and Fe are present in the glass forming network as oxides, and the elements diffuse through the semiconductor films. The electrical properties of II-VI and I-III-VI_2 semiconductors are dictated by native defects and complexes, and only a few extrinsic impurities exhibit a strong effect in changing the carrier concentration or type of conduction. Hence, one cannot assume *a priori* that an increase in impurity content of the source materials will lead to poor device performance. To test this hypothesis, we purchased 99.9% pure Cu, In, and Ga and prepared CIGS absorbers from them. Solar cells were fabricated and compared with cells made from high-purity elements. At this time, we do not have a statistically significant set of samples to draw firm conclusions from, and we have not performed any analysis of the impurity content of the samples. Nevertheless, a one-to-one comparison of the parameters shown in Table III suggests that the performance of solar cells fabricated from low-purity elements is close to the control sample. Another factor that can account for some of the differences are the differences in the chemical composition of the two absorbers (random variables introduced by growth apparatus, Ga variation). Indeed, our preliminary results are encouraging, and the topic deserves to be investigated in detail.

Table III. Properties of CIGS solar cells made from high-purity and low-purity elements.

Sample details	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (%)	Eff (%)
High Purity (Control)	0.671	33.1	77.3	17.2
Low Purity	0.624	34.5	72.1	15.5

2.4 Three-Stage Process at High Rates

Deposition time is an important factor in processing absorbers. Our standard absorber deposition takes 40 min to complete. To find out whether the same level of cell performance can be achieved at shorter deposition times, we doubled the rates of all the elements during the three-stage run. Deposition time was reduced to 20 min. The results of high-rate deposition are inferior, and the major loss is in the V_{oc} as shown in Table IV. It is likely that the out-diffusion of Ga is limited by the reaction rate of the binary selenides during the second stage.

Table IV. Effect of deposition rate.

Sample details	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (%)	Eff (%)
Normal run	0.671	33.1	77.3	17.2
High rates	0.572	32.7	73.0	13.7

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