Photovoltaic Devices Fabricated with CIGS Nanocrystal Inks

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Introduction:

Photovoltaic devices (PVs), which convert sunlight into electricity directly, are a promising energy source because they are renewable and clean. To be widely used, they need high power conversion efficiency (PCE) and low cost. Spray-deposited [1] thin-film $CuIn_{1-x}Ga_xSe_2$ (CIGS) PVs have the potential to achieve this goal.

In this approach, a CIGS layer was deposited as an ink and then thermally annealed under selenium atmosphere—a process called selenization—to achieve high efficiency. The quality of the annealed CIGS nanocrystal film was highly dependent on the selenization conditions. We investigated various parameters related to selenization to improve power conversion efficiency (PCE).

Sel #	Pre-Se. Anneal	Mo Bake	NaCl Bath	PCE [%]	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF*
359	No	No	No	0.071	0.221	-1.163	0.276
360	No	No	Yes	0.096	0.163	-2.287	0.257
361	No	Yes	No	0.230	0.395	-2.088	0.279
362	No	Yes	Yes	0.243	0.334	-2.607	0.279
363	Yes	No	No	1.485	0.477	-10.460	0.298
364	Yes	No	Yes	1.006	0.478	-7.746	0.272
365	Yes	Yes	No	2.760	0.474	-20.075	0.290
366	Yes	Yes	Yes	1.832	0.410	-11.839	0.378

Figure 1: Measurement results of Mo baked, pre-selenization annealed, or NaCl bath soaked samples.

Fabrication Process:

Solar cells were fabricated on soda-lime glass with a layered molybdenum (Mo) / CIGS / cadmium sulfide (CdS) / zinc oxide (ZnO) / indium tin oxide (ITO) structure. One micrometer (μm) of Mo was sputter deposited on soda-lime glass (Delta Technologies), followed by spray deposition of approximately 1 μm of CIGS nanocrystals. The nanocrystal film was annealed in argon (Ar) for one hour between 475°C and 525°C. The substrate was then inserted into a graphite box and annealed under selenium atmosphere at 500°C for ten minutes. CdS was then deposited by chemical bath. A window layer of 50 nm of ZnO and 600 nm of ITO were sputtered to complete the device.

Experiments:

Various pre-selenization treatments of the CIGS nanocrystal films were studied. Devices were annealed in Ar before CIGS deposition (Mo bake), after CIGS deposition (pre-selenization anneal), or soaked in a sodium chloride (NaCl) bath [2]. The Mo bake consisted of annealing a back contact in an argon atmosphere at 475°C for one hour just after Mo deposition. The pre-selenization anneal was carried out at 475°C in Ar for one hour immediately after depositing the CIGS layer.

It is known that sodium plays a role in CIGS crystallization [2] and during these anneals sodium diffuses from the soda-lime to the Mo/CIGS interface. Sodium was also added directly to the CIGS film by soaking the CIGS-coated substrate in a 1 g/L aqueous NaCl bath of for 15 minutes before selenization.

Figure 1 shows the measurement results of samples with these pre-selenization treatments. All photovoltaic device measurements were performed under Air Mass 1.5 illumination. V_{OC} is open circuit voltage and J_{SC} is short circuit current density. *FF* is a fill factor—the ratio of the product of voltage and current at maximum power and the product of V_{OC} and J_{SC}. The Mo bake and pre-selenization anneal both exhibited a positive effect on improving PCE.

The effect of the temperature ramp rate during selenization was also studied. Films were selenized for ten minutes after ramping the temperature at 20, 50, 80 and 110°C/min to 500°C. The nanocrystal films were treated prior to selenization by annealing at 475°C and soaking the films in a NaCl bath.

Device PCEs were 0.008% for 20°C/min, 0.034% for 50°C/min, 0.230% for 80°C/min and 0.251% for 110°C/min. Higher ramp rates produced higher PCE. Scanning electron microscope (SEM) images (Figures 2 and 3) show that the crystalline domains in the selenized CIGS films were larger when ramped at 110°C/min compared to 20°C/min. Films with larger crystalline grains are expected to have decreased recombination of electrons and holes for improved PCE. In addition, the thickness of the molybdenum selenide ($MoSe_2$) layer, generated by converting Mo to $MoSe_2$ during selenization, of 20°C/min was 664 nm, while that of 110°C/min was 373 nm. A thin $MoSe_2$ layer was better, as thicker $MoSe_2$ layers increased the series resistance in the device and degraded PCE.

Next, we investigated different CIGS layer deposition processes. Two processes were used where Process 1 was the conventional method and Process 2 was a new proprietary one. Pre-selenization and NaCl bath were performed in both of Process 1 and 2.

Figure 4 shows the I-V curve of the device fabricated with Process 2. The PCE of Process 2 was 6.564%, while that of Process 1 was 0.191%. Process 2 also improved *FF*—*FF* of Process 2 was 50.6%, while that of Process 1 was 30.1%. These results were supposed to be caused by the high quality of the CIGS layer fabricated with Process 2.

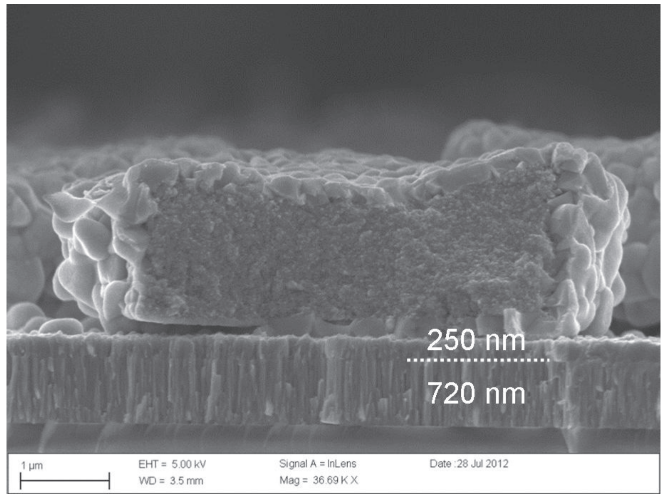

Figure 2: Cross section SEM image of 20°C/min ramp rate sample.

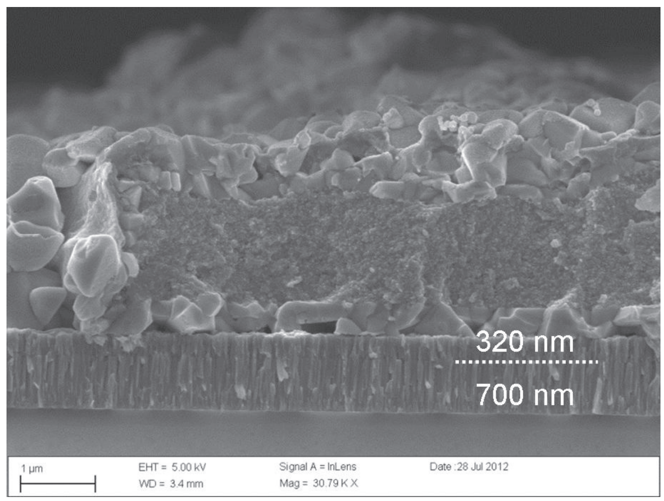

Figure 3: Cross section SEM image of 110°C/min ramp rate sample.

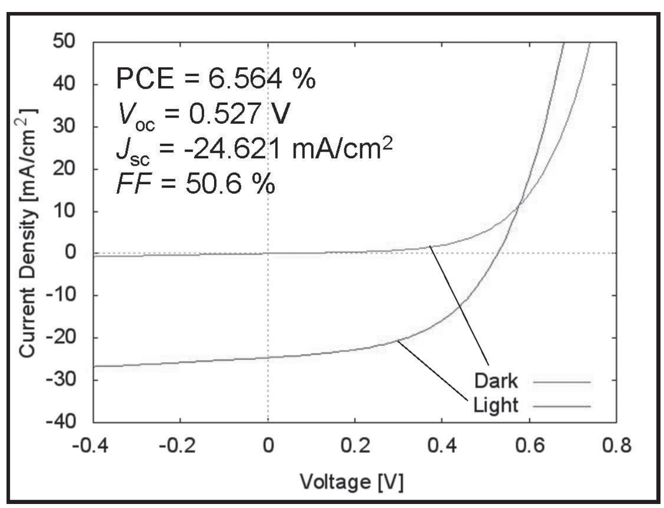

Figure 4: I-V curve of sample fabricated with new proprietary process.

Conclusions:

Spray-deposited CIGS nanocrystal films were selenized to increase PV device efficiency. Various processing parameters were studied. Pre-selenization anneal, molybdenum bake, higher heating ramp rate and new CIGS layer deposition process yielded substantial improvements in device efficiency.

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References:

[1] Panthani, M. G. et al.; Journal of the American Chemistry Society, vol. 130, no. 49, pp. 16770–16777 (2008).

[2] Guo, Q. et al.; Progress in Photovoltaics: Research and Apps (2012).