The device performance improvement by reducing the secondary phase of $Cu_{2-\delta}Se$ in $Cu(In_{1-x},Ga_x)Se_2$ (CIGS) solar cells

Xia Hao[1*], Hideki Hagiya[1], Takeaki Sakurai[1], Yukiko Kamikawa[2], Shogo Ishizuka[2], Akimasa Yamada[2], Hajime Shibata[2], Shigeru Niki and Katsuhiro Akimoto[1]

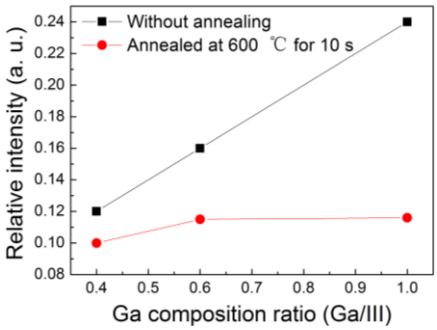
[1]*Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan*

[2]*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan*

[*]*E-mail: hao.xia0808@gmail.com*

$Cu(In,Ga)Se_2$ (CIGS) is a mixed crystal semiconductor of $CuGaSe_2$ (CGS) and $CuInSe_2$ (CIS), the bandgap can be varied from 1.04 ~1.68 (eV) by changing the composition ratio of In/III and Ga/III. Theoretically, bandgap engineering can be made to achieve an Eg of 1.4 eV for optimized performance of CIGS based solar cells. However, the bandgap of the best researched CIGS solar cell with the conversion efficiency of 22.3 %, is 1.08 eV. [1] The peak of theoretical efficiency and experimental efficiency is not consistent and the open circuit voltage tend to be saturated with the increased Ga content. In our previous work, we have found that the degradation of the efficiency, especially for CIGS solar cells with high Ga content which are fabricated by 3-stage process may be related to the presence of the secondary phase $Cu_{2-\delta}Se$.[2] For this reason, in order to achieving higher efficiency, it is of great importance to eliminate $Cu_{2-\delta}Se$ phase. Considering that the reason of the formation of $Cu_{2-\delta}Se$ might be the diffusion deficient of Ga and/or In, in this work we report a post annealing treatment to reduce the secondary phase and improve the device performance.

The CIGS polycrystalline thin film was grown on Mo coated soda-lime glass substrate by 3-stage process in a molecular beam epitaxy (MBE) system and the copper content was roughly fixed at approximately Cu/(In+Ga)=0.9. To form cell structure, CdS layer was deposited on CIGS by chemical bath deposition (CBD). Then the highly resistive i-ZnO and n-ZnO:Al layers were successfully deposited by magnetron sputtering. Various annealing treatments were carried out after the CIGS deposition to find the optimized condition. The Raman spectra were recorded by using 532-nm excitation laser source and a CCD detector. The *J-V* characteristics of the devices were measured with an Advantest R6245 *J-V* source meter under standard condition.



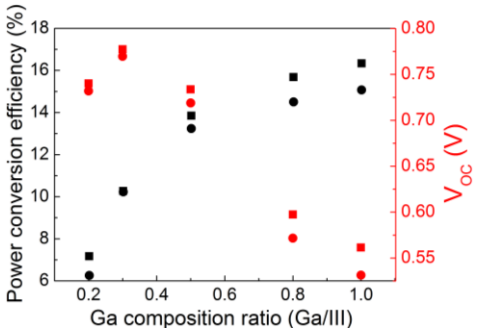


Fig. 1. (left) The relative Raman peak intensities in device with and without annealing. Fig. 2. (right) annealing effect on V_{OC} and Efficiency of devices with various Ga contents. (Filled squares stand for the annealed samples while circles are for those without annealing, V_{OC} and Eff are marked in black and red,

We first attempted to anneal CIGS thin films directly after the deposition of the 3rd stage, by maintaining the substrate at a temperature of 520 ℃ for 30 mins in Se atmosphere. The Raman result suggests that the relative intensity of $Cu_{2-\delta}Se$ peak decreased, but not so efficiently. The annealing temperature was then increased to 550 ℃ by using an electrical furnace. Raman spectra suggested that the intensity of $Cu_{2-\delta}Se$ peak first decreased with the increasing annealing time followed by an increase. It indicates that the long annealing time is not fitful for realizing a decrease in $Cu_{2-\delta}Se$. Therefore, a fast annealing was carried out by using a flash lamp at 600 ℃ for 2 mins was then performed. The relative Raman intensity profile for both cases with and without lamp annealing was shown in Fig. 1. $Cu_{2-\delta}Se$ was significantly removed. And the photovoltaic performances for both devices were summarized in Fig. 2. The power conversion efficiencies for the controlled CIGS solar cells are all improved. In conclusion, rapid post annealing of CIGS thin films is an effective way to reduce the secondary phase of residual $Cu_{2-\delta}Se$ and therefore contributes to the efficiency improvement of the solar cells.

References:

[1] http://www.solar-frontier.com/eng/news/2015/C051171.html

[2] X. Hu, et al, Jpn. J. Appl. Phys., **53**,068008 (2014)