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Improvement of Film Quality in CIS Thin Films Fabricated by Non-vacuum, Nanoparticles-based Approach

Yiwen Zhang[1, 2], Manabu Ito[2], Akira Yamada[1] and Makoto Konagai[1]

[1] Department of Physical Electronics, Tokyo Institute of Technology
2-2-12-S9-906 Ookayama, Meguro-ku,
Tokyo 152-8552, Japan
Phone: +81-3-5734-2669 E-mail: zhang.y.ae@m.titech.ac.jp
[2] Technical Research Institute, Toppan Printing Co., Ltd.,
4-2-3 Takanodaiminami, Sugito-machi, Saitama-ken, 345-8508, Japan

1. Introduction

$CuInSe_2$ (CIS) and its alloys with gallium and sulfur are considered as an ideal photovoltaic absorber layer for thin film solar cell due to their favorable electrical properties and long term stability. The conversion efficiency of over 20%, which is the highest efficiency of thin film solar cells, have been developed by co-evaporation method using these materials [1]. By the conventional vacuum-based methods however, it is difficult to reduce the cost of solar cell, because of their drawbacks such as the complexity in process, high production costs and difficulty in scaling up.

Recently, the non-vacuum, nanoparticles-based approach, which is applied on fabrication of CIS absorber layer, has received more attention. The main reason is that this approach provides a possibility to overcome the shortcomings of vacuum-based method, and to fabricate large area CIS solar cell with low cost. But earlier work growing CIS film from selenide used high-melting CIGS precursor particles which fail to result in a uniform, dense absorber film of large-grained CIGS [2, 3]. Here we have developed a new approach to fabricate a high quality CIS thin film. The fabrication was carried out through using copper selenide (Cu-Se) nanoparticles, indium selenide (In-Se) nanoparticles, with thiourea which play a role both as binding agent of nanoparticles and accelerant of CIS crystal growth.

2. Experimental

The Cu-Se and In-Se nanoparticles were synthesized at low temperature according to the similar procedure in the literature [3]. Here, CuI and InI_3 were used to react with Na_2Se under nitrogen atmosphere to prepare Cu-Se and In-Se nanoparticles. The thiourea dissolved in organic solvent was then added into the Cu-Se and In-Se nanoparticles. The Cu/In/Se/S resulting ratio was 0.9/1/1.8/1. The mixture was coated onto the Mo-coated sodalime glass substrate, followed by immediately dried and partially decomposed on a preheated hot plate. The selenization treatment was performed under substrate temperature of 550˚C. Finally, a complete solar cell structure was obtained by depositing the other layers including CdS buffer layer, ZnO window layer and Al electrodes by conventional methods. These samples were characterized by optical microscope, XRD, SEM and I-V measurement.

3. Results and discussion

Cu-Se and In-Se nanoparticles were successfully synthesized by low temperature colloid method. The size of Cu-Se, In-Se nanoparticles is about 30nm (Fig.1 (a)) and 50nm (Fig.1 (b)), respectively.

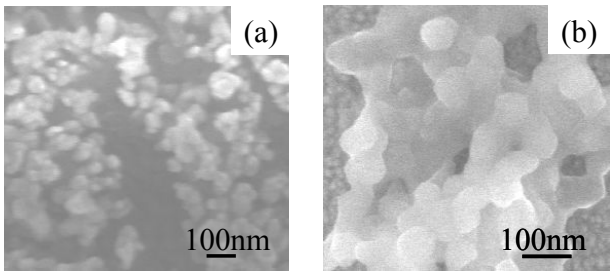


Fig.1 SEM images of nanoparticles synthesized by low temperature colloid method: (a) Cu-Se nanoparticles (b) In-Se nanoparticles

The optical microscope images of various samples were showed in Fig.2. It was observed that the film fabricated by CIGS nanoparticles exhibited visible porosity on the external surface. On the contrary, the film fabricated by using thiourea as binding agent, exhibits smooth surface and no visible porosity was observed. It suggests that the thiourea play an important role to bind the nanoparticles into a dense layer and smoothing the surface during the coating process. Proposed formation mechanism of dense layer is illustrated in Scheme 1. Without thiourea, the nanoparticles easy aggregated together to produce porosity and loose layer. The addition of thiourea contribute to prevent the aggregation of nanoparticles during coating process and the thiourea diffused into the void between the nanoparticles to produce dense layer with smooth external surface.

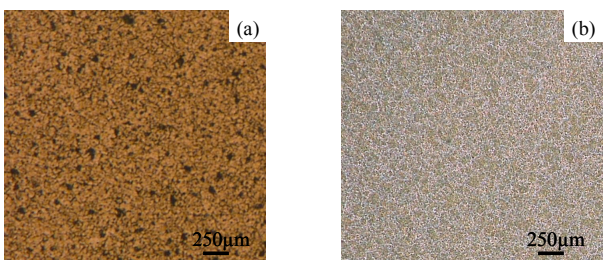
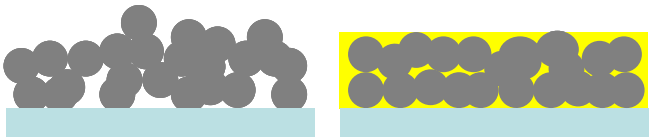


Fig.2 The external surface coated by (a) CIGS nanoparticles and (b) Cu-Se, In-Se nanoparticles with thiourea



(a) (b)

Scheme.1 The CIS layer fabricated by (a) CIGS nanoparticles and (b) Cu-Se, In-Se nanoparticles with thiourea

X-ray diffraction measurement was performed to confirm the film quality of crystallinity after selenization treatment. Fig.3 shows the XRD patterns of various samples. The CIS film fabricated by using Cu-Se, In-Se nanoparticles with thiourea shows higher intensity compared to the film, which fabricated by CIGS nanoparticles according to procedure in the literature [3]. It suggests that starting from Cu-Se, In-Se nanoparticles with thiourea should aid the crystal growth during selenization treatment process.

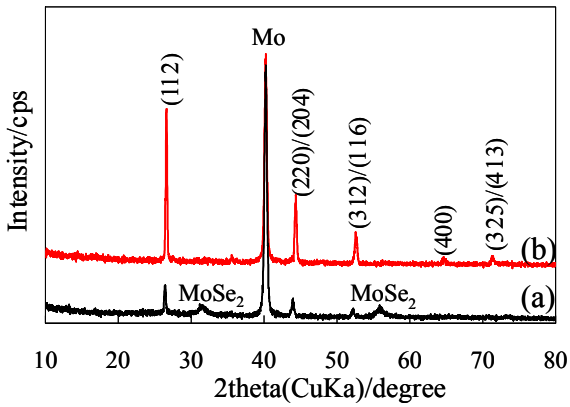


Fig.3 CIS film after selenization treatment fabricated by (a) CIGS nanoparticles and (b) Cu-Se, In-Se nanoparticles with thiourea

The effect of this approach that using Cu-Se, In-Se nanoparticles with thiourea was also proved by cross-sectional SEM images as shown in Fig.4. The dense large-grained CIS film was successfully prepared by using Cu-Se, In-Se nanoparticles with thiourea after selenization treatment, compared to the porosity and small-grained CIS film fabricated by only using CIGS nanoparticles.

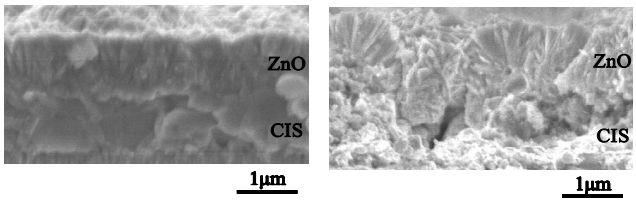


Fig.4 The cross-sectional SEM images of CIS film fabricated by (a) CIGS nanoparticles and (b) Cu-Se, In-Se nanoparticles with thiourea

The solar cell performance was measured under AM 1.5 irradiation. The Jsc of the solar cell, which fabricated by using Cu-Se, In-Se nanoparticles with thiourea, was 15.98mA/cm^2, higher than the solar cell fabricated by CIGS nanoparticles, which was 7.37mA/cm^2.

4. Conclusions

A new approach for quality improvement of CIS film has been developed. To the best of our knowledge, this is the first time that thiourea has been applied as a binding agent and accelerant of crystal growth for the fabrication of high quality CIS film. The fabricated CIS film exhibited dense large-grained layer compared to the same type CIS film which fabricated by CIGS nanoparticles. The increased Jsc of solar cell confirmed the effect of the new approach. These characteristics suggest that the CIS film fabricated by new approach might be useful practically as photovoltaic absorber layer for CIS solar cell.

Acknowledgements

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References

[1] M.A.Contreras, B.Egaas, K.Ramanathan, J.Hiltner, A.Swartzlander, F.Hasoon and R.Noufi, *Progress in Photovoltaic*, 7(4), (1999) 311.

[2] D.L.Schulz, C.J.Curtis,R.A.Flitton, H.Weisner, J.Keane, R.J.Matson, K.M.Jones, P.A.Parilla, R.Noufi and D.S.Ginley, *Journal of Electronic Materials* 27 (5) (1998) 433.

[3] S.Ahn, K.Kim and K.Yoon, *Current Applied Physics* 8 (2008) 766.