Effect of Annealing Temperature in H_2S-free Sulfurization Method for CIS Fabrication

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I. INTRODUCTION

Sulfides such as $CuInS_2$ (CIS) have the potential to have a band gap close to the ideal energy gap ($E_g \approx 1.5$ eV) and can serve as the wide band gap material for tandem solar cell. However, common sulfurization methods employ flammable and toxic H_2S gas. Therefore, a safer method for the sulfurization process such as using sulfur vapour in inert gas (N_2) atmosphere is preferable. In this work, we evaluated the effect of various sulfurization temperatures in the latter method on the physical properties of the deposited CIS.

II. EXPERIMENTAL METHOD

Cu-In precursor layer is deposited on a Mo-coated SLG substrate through co-evaporation method. The precursor is slightly Cu-rich with Cu/In ratio of about 1.23:1. Afterwards, the precursor is set in a graphite container with 16 mg of sulfur powder. The container is placed in a quartz annealing furnace with non-vacuum N_2 atmosphere for the sulfurization process. The quartz furnace is heated to vaporize the sulfur and cause a reaction with the precursor. The heating temperature is varied from 300°C to 600°C (ΔT=100°C/min) and annealed for 20 minutes for each temperature set up. Higher temperature is expected to promote better crystal growth. After the annealing, the samples are naturally cooled in the furnace. The typical molar composition of the CIS sample annealed at 500°C is Cu:In:S = 1.14:1:1.83.

III. RESULT AND DISCUSSION

The cross-sectional SEM measurement of the Cu-In precursor layer showed a uniform Cu-In layer with good adhesiveness on the CuIn/Mo interface. Although In grains were visibly scattered on the surface resulting in an In-rich surface, the EDS analysis confirmed a Cu-rich (54.7% Cu) precursor bulk.

The XRD measurements of the Cu-In precursor layer and the CIS samples sulfurized at different temperatures are shown in Fig. 1. The peak for $CuInS_2$ can be observed at 27.8° for all CIS samples. However, the $CuInS_2$ peaks at 46.2° and 54.9° are only visible for the samples sulfurized at ≥ 400°C. The intensity of the peaks increased with temperature but stayed stable after 500°C. In the experiment, sulfurization at temperatures ≤ 400°C resulted in some solid sulfur remnant in the container. Therefore, it is suspected that at temperatures ≤ 400°C , the sulfurization reaction was not completed. The presence of Cu_2In peak on 29.41° for the 300°C case indicated precursor-like characteristic. More $CuInS_2$ peaks with stronger intensities were found compared to the $Cu_{2-x}S$ peaks.

In Fig. 2, the relationship between Cu_2S formation and sulfurization temperature can be observed. The dark areas in the figure depicted the $Cu_{2-x}S$ phase on the CIS surface. Considering both figures, it can be concluded that $CuInS_2$ is formed earlier in the reaction than $Cu_{2-x}S$. The lack of In_2S_3 suggested that the $CuInS_2$ phase is formed directly from the Cu-In precursor. The $Cu_{2-x}S$ is suspected to form during the cooling process from the excessive S vapour instead of during the film growth. This could explain the lower amount of $Cu_{2-x}S$ in the high temperature samples, since most S should have reacted with the precursor during the growth.

The EDS result of the CIS samples indicated S-rich bulk (>45%) with quite high percentage of Cu (>25%). The composition for samples sulfurized at temperatures higher than 500°C are relatively unchanging. In addition, sulfurization at 500°C and higher might cause a decrease in the adhesiveness of the CIS/Mo interface (porous structure) presumably because of MoS formation.

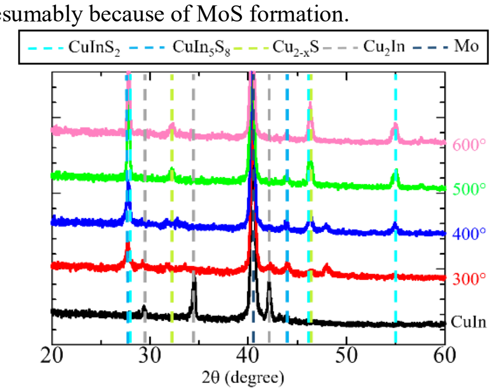

Fig. 1. XRD evaluation of the Cu-In precursor and CIS samples.

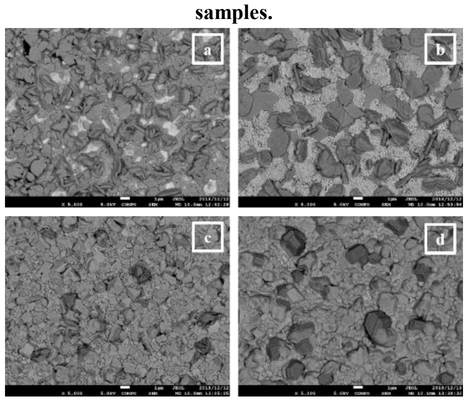

Fig. 2. Surface SEM of CIS sulfurized at (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C.

IV. CONCLUSION

$CuInS_2$ (CIS) was deposited through a safer sulfurization method without H_2S by using vaporized sulfur powder in an inert atmosphere. $CuInS_2$ was formed in all samples with optimum temperature higher than 500°C. A decrease of $Cu_{2-x}S$ formation on the CIS surface with temperature increase was observed from the SEM images. Porous structure in the CIS bulk and MoS on the CIS/Mo interface was observed on the high-temperature-sulfurization sample.

V. ACKNOLEDGMENT

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