INFLUENCE OF ANNEALING IN SULFUR FLUX ON CZTS FORMATION BY USING MOLECULAR BEAM EPITAXY SYSTEM

Yosuke Shimamune, Kazuo Jimbo, Genki Nishida, Masanari Murayama, Akiko Takeuchi, Hironori Katagiri

National Institute of Technology, Nagaoka College, Japan

Cu₂ZnSnS₄ (CZTS) thin film is attractive for solar cell material because of its high absorption coefficient of 10⁴ cm⁻¹ and suitable band gap energy of 1.5eV for light absorbing layer. CZTS thin film is generally formed by the different two process of precursor formation and sulfurization. Those are processed in the different two equipment respectively. We reported that CZTS was formed by co-evaporation of Cu, Zn, Sn and S on the Mo/SLG substrate followed by annealing in S-flux in a single system of Molecular Beam Epitaxy (MBE)[1]. On those films, secondary phase of Cu₂₋₄S is also found and detected amount has a strong dependency on substrate temperature while annealing in S-flux. In this study, correlation between CZTS and Cu₂₋₄S and the influence of Cu₂₋₄S on the solar cell performance are reported.

CZTS is formed by co-evaporation of Cu, Zn, Sn and S on 25mm x 25mm Mo/SLG substrate at temperature of 320°C for 100min followed by annealing in S-flux at substrate temperature of 400°C for 0, 30, 60 and 120min in MBE system. The formed films were analyzed by the X-ray fluorescent spectroscopy (XRF, ZSX mini II, Rigaku Corp.) and Raman mapping (CPRIS-11-532A, S.T.JAPAN INC.). And solar cells were fabricated on those CZTS/Mo/SLG followed by forming stacking layers consisting of CdS by chemical bath deposition, Al doped ZnO by RF sputtering and Al by thermal evaporation. Current density-voltage (J-V) measurement were performed under the standard testing condition (AM1.5, 100mW/cm²).

Figure 1(a) and (b) show the photographs of the typical sample surface and solar cell formed on sample shown in figure 1 (a), respectively. Figure 1 (c) and (d) are 1x1 mm² shots mapping of Raman intensities originated from CZTS at 340 cm⁻¹ and Cu₂₋₄S at 477 cm⁻¹, respectively. It is found that CZTS and Cu₂₋₄S have variation within substrate area and it is thought to be induced due to heater proximity to substrate or crucibles location. The intensities of Raman peaks are averaged within cell size of ~4x4 mm² for direct comparison between Raman intensity and cell performance. Figure 2 shows the cell size level correlation of CZTS and Cu₂₋₄S Raman intensities and power conversion efficiency η of solar cell. By annealing in S flux, CZTS intensities become stronger and Cu₂₋₄S become weaker. Detected XRF intensities of Cu and S were almost constant even after annealing. These results suggest that Cu₂₋₄S phase transition to CZTS phase occurs while annealing. With decreasing Cu₂₋₄S well, power conversion efficiency η raises and is improved with increasing CZTS intensity. This means further optimization of annealing process will introduce better performance solar cell.

Figure 1: Photographs of the surface of typical sample surface(a) formed by 60min annealing and solar cell(b). And intensity distribution of Raman peaks originated from CZTS at 340 cm⁻¹(c) and Cu₂₋₄S at 477 cm⁻¹(d). Brightness shows the spectra intensities. (Bright:Strong, Dark:Weak).

Figure 2: Cell size level correlation of CZTS Raman shift spectra intensities and Cu₂₋₄S spectra intensities (solid marker) and power conversion efficiency η of solar cell (open marker).