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Study of Post-growth Se-annealing on the Properties of $CuGaSe_2$-layers Grown by Three-stage Evaporation Process

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Abstract

Duration of post-growth Se-annealing after three-stage co-evaporation of $CuGaSe_2$ film has been varied. Effect of Se-annealing time has been studied on the electrical properties of the $CuGaSe_2$ layer. Performance of the fabricated solar cells has been studied in correlation to the Se-annealing time.

1. Introduction

chalcopyrite $Cu(In,Ga)Se_2$ is one of the most promising materials to realize high-efficiency thin film solar cell, mainly due to its high optical absorption, and cost effective growth procedure. Quaternary CIGS is a pseudo-binary alloy of ternary $CuInSe_2$ and $CuGaSe_2$. Band gap of the $CuInSe_2$ is 1.04 eV, while it becomes 1.68 eV for its $CuGaSe_2$ counterpart. Thus, band-gap of the CIGS can be controlled by varying the Ga-content, x = [Ga]/([Ga]+[In]) = Ga/III in the material. In case of the single junction solar cell, the ideal band-gap of the absorber layer to achieve the highest conversion efficiency under AM 1.5 sunlight is speculated theoretically to be around 1.4 eV [1]. Therefore, $CuGaSe_2$ with the band-gap of 1.68 eV can be considered as a leading material to enable the highest possible efficiency. Moreover, the larger band-gap makes the $CuGaSe_2$ an ideal absorber material for the top cell in the photovoltaic tandem device together with $CuInSe_2$ as the bottom cell absorber.

Nevertheless, so far, $CuGaSe_2$ solar cells with a CdS buffer have achieved efficiency of around 11 % for the thin film [2]. Therefore, to achieve the optimized material quality of the $CuGaSe_2$ material which is compatible for highest possible efficiency, an extensive study of this material with various compositions is indispensable. In this paper, we have changed the post-growth Se-annealing time to study the effect of Se-annealing on the properties of $CuGaSe_2$ absorber layer.

2. Experimental

Polycrystalline $CuGaSe_2$ thin films with the typical thickness of 2 μm were grown over Mo-coated soda lime glass (SLG) substrates through a three-stage co-evaporation process using molecular beam epitaxy system [3]. Mo back contact layers of 800-nm thickness were deposited by sputtering method with an Ar gas pressure of 0.3 Pa. Evaporation of $CuGaSe_2$ was done at a base pressure of approximately ~10^{-6} Pa from three Knudsen–cells (K-cells) that were the respective Cu, Ga, and Se sources. Growth temperature of the first stage was kept at 400°c during co-evaporation of Ga and Se to form Ga_2Se_3 layer. Temperature was increased to 520°c at the second and third stage when Cu, Se and Ga, Se co-evaporation was done respectively. After the third stage of growth, sample-temperature was decreased at a rate of 9°c/min down to 250°c in a Se atmosphere that we defined as Se-annealing. During Se-annealing Cu, and Ga shutter remained closed, whileon;y Se-shutter was kept open. Several $CuGaSe_2$ samples with different Se-annealing time were grown. The composition of the grown $CuGaSe_2$ films was measured by electron probe micro-analysis (EPMA) at 15 kV of acceleration voltage. Solar cell fabrication was completed by the deposition of a CdS buffer layer through chemical bath process followed by the deposition of i-ZnO/Al:ZnO bi-layer by sputtering and finally Al by thermal evaporation which is used as front contact. To avoid any surface oxidation effect during positron annihilation experiment, $CuGaSe_2$ film was etched with KCN solution followed by the deposition of 25nm thick CdS layer by chemical bath process. Thus, the sample structure for the positron annihilation experiment becomes: CdS/$CuGaSe_2$/Mo/SLG.

Doppler broadening spectra of the annihilation radiation were measured as a function of the incident positron energy *E* using a continuous-current-type positron beam located at the University of Tsukuba. The spectra were characterized by the *S* parameter, defined as the fraction of annihilation events in the energy range of 510.24 - 511.76 keV. The relationship between *S* and *E* was analyzed by VEPFIT, a computer program developed by van Veen et al. [4].Electrical properties were studied by the van der Pauw Hall measurement method at room temperature. Photovoltaic properties of the solar cells were analyzed by ESS-1000 solar simulator at room temperature.

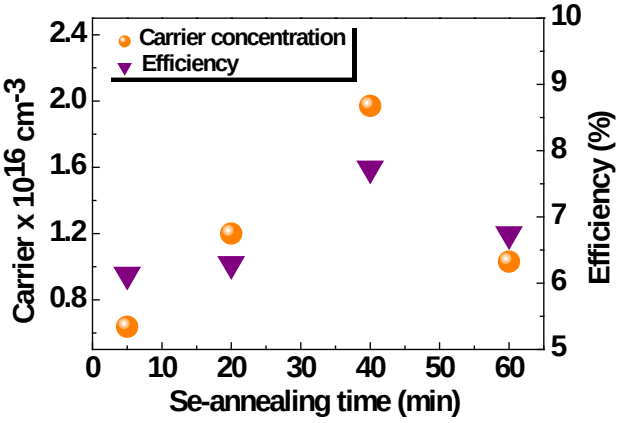

Fig. 1 Carrier concentration and photovoltaic performance of $CuGaSe_2$ films as a function of post-growth Se-annealing time.

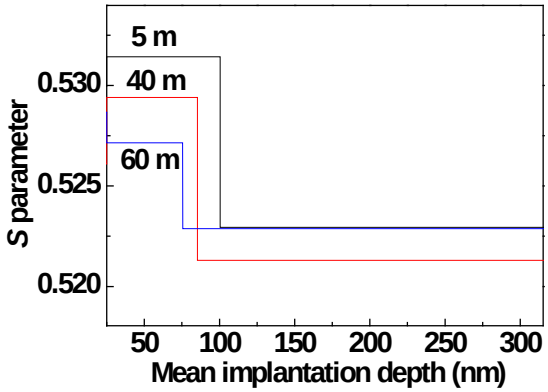

Fig. 2 Depth distributions of *S* parameter obtained from analysis of the *S*-*E* curves for several $CuGaSe_2$ samples with different Se-annealing time (5 min, 40 min, and 60 min).

3. Results and Discussions

Shown in Fig. 1 is the carrier concentration of all the $CuGaSe_2$ films grown with different post growth Se-annealing time. Photovoltaic-efficiency fabricated with the corresponding $CuGaSe_2$ absorber layer has also been plotted on the same figure. All the samples showed *p*-type conductivity. With increasing Se-annealing time, hole concentration increased and resistivity decreased. It can also be considered that with shorter annealing time, Se-deficiency should generate anion vacancy, V_{Se}, which would act as donor. So, V_{Se} is one of the candidates for decreasing hole concentration with decreasing Se annealing-time. It has been also proposed that anion vacancy of V_{Se} drives out Cu and forms dipole complex, V_{Se} - V_{Cu}, due to shorter annealing time. These donor type defects are responsible for lower carrier concentration in the samples with shorter annealing time. It is apparent that solar-cell performance is correlated to the carrier concentration in the absorber layer.

To understand more clearly about the effect of the post-growth Se-annealing time on the $CuGaSe_2$ layer, we have performed positron-annihilation measurement for few $CuGaSe_2$ samples. Figure 2 shows the depth distributions of *S* parameter for samples grown with post-growth annealing times of 5, 40, and 60 min. The *S* value for the defect-rich region decreased with increasing annealing time, which we attribute to decreased defect-concentration. Volume of the near surface defect-rich zone also decreased with increasing annealing time. However, for the samples with 40 min annealing time, vacancy type defect was further decreased in the bulk region, while for the sample with 60 min annealing time defect in the bulk region is higher than the sample with 40 min annealing time. This observation is consistent with the observed increased in the resistivity and decrease in the hole carrier concentration in the sample with 60 min annealing time.

Previously, it was proposed using positron annihilation technique that at the end of $CuGaSe_2$ growth, a defect-rich region mainly composed of vacancy-type defects has been formed at the surface of the film [5]. These defects can be diffused to the bulk of the sample depending on the sample composition. The diffusion of vacancy-type defects can also be affected by the post-growth Se annealing to control the defect-distribution along the depth of the sample. Thus, Se-annealing affects both the surface as well as bulk of the film.

4. Conclusions

In conclusion, Effect of Se-annealing time has been studied on the defect formation and distribution of defects in the $CuGaSe_2$ layer. Performance of the fabricated solar cells has been studied in correlation to the Se-annealing time. Post-growth Se-annealing has been found to be crucial to control the defect distribution along the depth of the film, thereby, affecting the fabricated device-performances.

Acknowledgements

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