Optical Characterization of Defects in High-efficiency $(Ag,Cu)(In,Ga)Se_2$

Siming Li
National Renewable Energy Laboratory
Golden, USA
siming.li@nrel.gov

Rouin Farshchi
MiaSolé Hi-Tech Corp.
Santa Clara, USA
rouin.farshchi@googlemail.com

Michael Miller
The Ohio State University
Columbus, USA
miller.7831@osu.edu

Aaron R. Arehart
The Ohio University
Columbus, USA
arehart.5@osu.ed

Darius Kuciauskas
National Renewable Energy Laboratory
Golden, USA
darius.kuciauskas@nrel.gov

***Abstract*—We applied time-resolved photoluminescence (TRPL) spectroscopy to study optimized chalcopyrite $(Ag,Cu)(In,Ga)Se_2$ thin films. The device shows power conversion efficiency of 18.7%. The metastable defect V_{Se}-V_{Cu} within ACIGS at E_V+0.98 eV is detected in sub-bandgap TRPL excitation spectra. TRPL lifetime of 50 ns is limited by the density of mid-gap defects such as Cu_{Ga} or Cu_{In}. The similarity of TRPL dynamics before and after light soaking indicates the optimized ACIGS thin film is less metastable because the density of V_{Cu}-V_{Se} defect is reduced to below 10^{15} cm^{-3}. This study indicates that ACIGS has improved cell efficiency and reliability characteristics.**

Keywords—metastability, photoluminescence, ACIGS, thin film, solar cells

I. Introduction

Recently, silver (Ag) alloyed chalcopyrite $Cu(In, Ga)Se_2$ (ACIGS) has been investigated due to its lower melting temperature and wide-bandgap. Literature shows that the density of deep defects such as In_{Cu} or Ga_{Cu} in ACIGS could be reduced after Ag substituting for Cu.[1] However, its PV performance can be altered by the stress of heat and light soaking.[2] The metastable effect is from (V_{Se}-V_{Cu}) divacancy complex, which could be converted from a shallow donor to a shallow acceptor and additional deep recombination center under illumination according to Lany-Zunger model. [2, 3] The metastable effect may introduce additional uncertainty in device performance causing problems in device design. [4] Therefore, understanding the effect of metastability in ACIGS is critical to the design of efficient solar cells.

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II. Experimental

A. Device Characterization

Our samples were fabricated by MiaSolé using industrial processes as described in [5]. The solar cell devices (structure ZnO/CdS/ACIGS) had efficiency 18.7% with V_{OC} = 780 mV, J_{SC} = 31.5 mA/cm^2, and FF = 77%. For optical spectroscopy, ZnO was removed by etching and CdS/ACIGS absorber were studied.

B. Optical and Electrical Characterization

TRPL and photoluminescence (PL) were used to study ACIGS defect properties. Fully digital capacitance-based deep level optical spectroscopy (DLOS) was used to obtain the density of (V_{Se}-V_{Cu}) divacancy complex at E_V +0.98 eV.

III. Result and Discussion

Fig.1 shows ACIGS PL emission spectra at 300 K. Integrated intensity-dependent PL follows a power law of $I_{PL} = I_P^k$, where I_{PL} and I_P are the intensity of photoluminescence and laser power. The inset shows k ≈ 2 indicating excitonic transition.

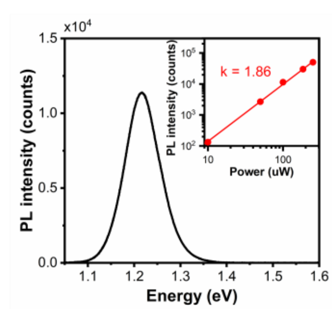

Fig.1. PL emission spectra of ACIGS when the thin film was photoexcited at 633 nm using 100 µW laser power. The inset shows the PL intensity as a function of excitation intensity with k value of 1.86.

To characterize shallow defect state, we measured the sub-bandgap excitation spectra with TRPL at room temperature, shown in Fig.2a. The excitation spectrum is obtained by applying tunable optical pump to photoexcite the defect within the bandgap, as shown in Fig.2b. The signal around 0.98 eV is assigned to V_{Se}-V_{Cu} defect, which has been reported previously in CIGS. [6] The Gaussian analysis indicates the full width at half maximum (FWHM) of the defect band,118 meV, and standard deviation (σ), 50 meV.

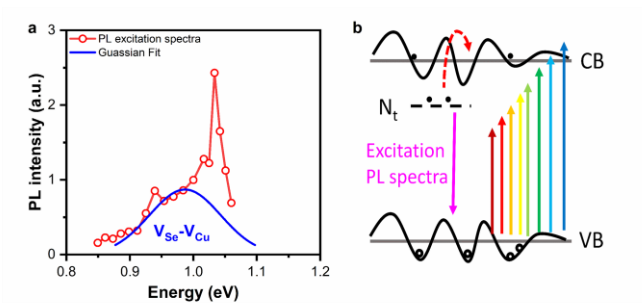

Fig.2. (a) TRPL excitation spectra at 300 K. The blue is the Gaussian fit. (b) Illustration of TRPL excitation spectra measurement.

The (V_{Se}-V_{Cu}) divacancy complex has been recognized as metastable defect, which relates to metastability of CIGS device performance. According to Lany-Zunger model, the defect could be converted from a shallow donor to a shallow acceptor and additional deep recombination center under illumination.[3]

We applied TRPL to characterize recombination, and Fig. 3 shows PL intensity as a function of time. The figure exhibits PL intensity on a logarithmic scale, and the magnitude of PL intensity is proportional to $B \times N_A \times n$, where B is the radiative recombination coefficient, N_A is majority carrier concentration within p-type absorber, and n is the minority carrier concentration from photoexcitation. The fast decay within 1 ns is due to carrier diffusion from the initial generation profile into the bulk.

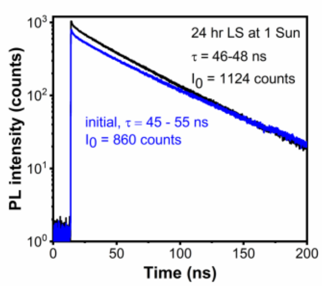

Fig.3. The TRPL on ACIGS before and after 24 hours 1-sun illumination. The sample was photoexcited at 640 nm and 0.9 $\mu J/cm^2$ for both measurements.

The TRPL lifetime with slow time constant of 45-55 ns is determined by the concentration of mid-gap defects, which is due to $Cu_{In/Ga}$ substitutional defects. [7] Using estimated electron capture cross-section 1-50x10^{-14} cm^2,[2] the mid-gap defect density is in the order of 10^{13} cm^{-3}.

To understand the metastability of this absorber, we exposed the sample under 1-sun illumination for 24 hours, and then measured by TRPL again, as shown in the same figure. The PL intensity in the p-type absorber is determined by net acceptor density, as previously discussed. Under light soaking, the metastable defects are active in ACIGS and this effect leads to the conversion of shallow donor to a shallow acceptor so that the magnitude of PL intensity is increased around 30% due to the increased acceptor density.

Simultaneously, the conversion of metastable defect gives additional deep recombination center after light soaking.[3] By comparing the TRPL lifetime in Fig. 3, the TRPL lifetime is reduced around 10% by increasing mid-gap defect density. A. J. Ferguson, *et al*. compared the metastability behavior in two types of ACIGS, and they found that dark heat and light soak induced change of ACIGS device performance and TRPL dynamic is more sensitive to the absorber with high selenium vacancy-related defect density.[2] Therefore, it is possible that the higher reported stability of the absorber in this study is due to the low density of (V_{Se}-V_{Cu}) defect in the order of 10^{14} cm^{-3} from DLOS.

IV. Summary

We employed steady-state PL and TRPL to characterize mid-gap defect and metastable defect in an optimized ACIGS thin film, and measured the change in TRPL dynamic upon light soaking. We found that acceptor concentration is increased 30% after illumination at 1 sun for 24 hours, and the mid-gap trap state density stays approximately the same, ~10^{13} cm^{-3}, which indicates the optimized ACIGS thin film is less metastable. This attributed to E_V+0.98 eV trap concentration reduce to <10^{15} cm^{-3}. The similarity of TRPL dynamic before and after light soaking indicates a more stable ACIGS absorber with the low density of V_{Cu}-V_{Se} defect.

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