Temperature dependence of $Cu_2ZnSn(Se_xS_{1-x})_4$ solar cells

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Abstract
The temperature dependence of open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and relative efficiency of monograin $Cu_2ZnSn(Se_xS_{1-x})_4$ solar cell was measured. The light intensity was varied from 2.2 to 100 mW/cm^2 and temperatures were in the range of T = 175-300K. With a light intensity of 100 mW/cm^2 dV_{oc}/dT was determined to be - 1.91mV/K and the dominating recombination process at temperatures close to room temperature was found to be related to the recombination in the space-charge region. The solar cell relative efficiency decreases with temperature by 0.013 %/K. Our results show that the diode ideality factor n does not show remarkable temperature dependence and slightly increases from n = 1.85 to n =2.05 in the temperature range between 175 and 300K.
Also a new method to study spatial potential fluctuations in compensated absorber materials used in solar cells is introduced. The method is based on the analysis of the temperature dependence of quantum efficiency curves in solar cells. As an example $Cu_2ZnSnSe_4$ monograin solar cells are studied at temperatures between 10 and 300K. It is shown that this absorber material has spatial potential fluctuations with average energetic depth of 25 meV. The room temperature bandgap energy of $Cu_2ZnSnSe_4$ is found to be E_g =1.017 eV.

1. Introduction.

$Cu_2ZnSnSe_4$ (CZTSe) is a p-type semiconductor, which could replace CIS and CIGS absorber in future solar cells. In this compound the expensive and resource-limited In is substituted by Zn and Sn. Latest studies have shown that the bandgap energy of this compound at room temperature is about 1 eV [1-2]. This is also confirmed by theoretical calculations [3]. An ideal thin-film solar cell absorber material should have a direct bandgap of around 1.3–1.4 eV and therefore one needs to adjust the bandgap energy. One possible way to do so is to use solid solutions with an overall stoichiometry of $Cu_2ZnSn(Se_xS_{1-x})_4$. Unfortunately, the fundamental physical properties of these solid solutions are as yet not well understood. The same is true already for CZTSe. Photoluminescence (PL) and Raman studies of this compound [1] showed rather high concentrations of charged point defects. A high defect concentration is typical also for In-rich $CuInSe_2$ and other compensated ternary compounds and usually leads to the formation of spatial potential fluctuations [4, 5]. As a result, the density of states function for valence and conduction bands has an exponential tail. Potential fluctuations usually form potential wells for holes and thus localized states can be formed. These states can be detected by PL emission, which involves recombination of free electrons with holes localized in these tail states. Usually this emission shows asymmetrical PL bands and from the shape of these PL bands the average depth of potential fluctuations γ can be found [4]. Typically in chalcopyrite ternaries γ has a value below 30 meV [4-6]. Our recent PL studies show,

that in CZTSe $\gamma \approx 24$ meV [7]. The hole concentration in this absorber was always lower than 10^{16} cm^{-3} as determined by C-V measurements.
In the present paper we propose a new method to study spatial potential fluctuations in CZTSe. It is based on the analysis of temperature dependent quantum efficiency measurements of solar cells.

2. Results

In summary, from *I–V* measurements we have calculated the monograin $Cu_2ZnSn(Se_xS_{1-x})_4$ solar cell parameters as a function of temperature. For a light intensity of 100 mW/cm^2 the dV_{oc}/dT = - 1.91 mV/K and E_A was close to the bandgap energy of 1.2 eV. The dominating recombination is related to recombination in the space-charge region. The solar cell relative efficiency decreases with temperature with a slope of 0.013 %/K. The diode ideality factor *n* was close to a value of 2 and showed a very small increase with temperature.
Quantum efficiencies of photocurrent generation in $Cu_2ZnSnSe_4$ monograin solar cell were measured between 10 and 300K. It was shown that these curves can be used to determine effective bandgap energies of the absorber. The temperature dependences of the effective bandgap energies and of the integrated quantum efficiency dependencies allow to calculate the average depth of potential wells for change carriers. The such determined value of 25 meV agrees very well with the value determined in photoluminescence measurements. It was shown that the room temperature bandgap energy in $Cu_2ZnSnSe_4$ is E_g =1.017 eV.

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