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Lifetime, quasi-Fermi level splitting and doping concentration of Cu-rich CuInS2 absorbers

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Abstract

Cu(In,Ga)S2-based solar cells have been shown by Hiroi et al (Hiroi et al 2015 IEEE Journal of Photovoltaics 6 309–312) to achieve higher efficiencies with absorbers processed at high deposition temperatures. Additionally, it is known for CuInS2 cells that the main improvement from higher deposition temperatures is the reduction in the density of deep defects and increased quasi-Fermi level splitting. The increased quasi-Fermi level splitting could result from a reduction in the rate of recombination or from an increase in doping concentration. To investigate which effect is the dominant one, we perform time-resolved photoluminescence measurements and estimate the doping concentration from carrier lifetime and quasi-Fermi level splitting. We find no changes in the effective lifetime, which is in the range of 200 ps. The doping concentration increases from $10^{16}$ cm$^{-3}$ to $10^{17}$ cm$^{-3}$. Our study shows that the increase in quasi-Fermi level splitting with higher deposition temperatures is not due to reduction in non-radiative recombination but due to increased doping concentration.

1. Introduction

Copper indium gallium disulfide, Cu(In,Ga)S2, is among the chalcopyrite materials which promise stable high-efficiency photovoltaic applications. Its bandgap tunability from ~1.55 eV [1] (in pure CuInS2) to ~2.45 eV [1] (in pure CuGaS2) provides suitable values for use as a single-junction solar cell or in tandem with other absorbers for a multijunction solar cell [2, 3]. In comparison to its selenide counterpart, Cu(In,Ga)S2 still suffers from a high open circuit voltage deficit, that is, voltage loss relative to bandgap, ~600 mV compared to ~360 mV in Cu(In,Ga)Se2 [4, 5]. However, Hiroi et al have achieved a high efficiency Cu(In,Ga)S2 solar cell with absorbers processed at high temperature deposition [4, 6]. To understand the influence of the deposition temperature, previously, we have shown, for CuInS2 (without Ga), that the main enhancement from a higher deposition temperature stems from reduced non-radiative recombination in the absorber, because we observed an increased quasi-Fermi level splitting with higher deposition temperature (QFLS) [7, 8]. Additionally, we have shown that for a set deposition temperature, there is an increase in QFLS with higher Cu-excess, i.e., integral composition of [Cu]/[In] > 1 [7, 8]. We could show that the higher QFLS goes along with the reduction of a deep defect [7]. Therefore, it was assumed that the QLFS improvement is due to the reduced density of recombination centres, which would increase the minority carrier lifetime. QFLS gives insight into the quality of the absorber without and before the intricacies of completing the device. As such, it serves as an upper limit for the open circuit voltage in solar cell devices [9, 10].

The minority carrier lifetime is one of the essential parameters used for characterizing doped semiconductor materials for solar cell [11]. It is a measure of device quality by quantifying the rate of recombination and it is directly related to device efficiency [12–14]. Cu(In,Ga)S2 features very short lifetimes of hundred picoseconds [15] when compared to Cu(In,Ga)Se2 where lifetime can range from tens to hundreds of nanoseconds [13, 14, 16]. Longer minority carrier lifetimes indicate a higher concentration of minority carriers and thus a higher electron Fermi level $E_{F,C}$, which in turn increases the QFLS.
The dependence of many device properties and performance on doping concentration makes it an important material property. Established techniques of obtaining the dopant concentration in thin-film solar cells include capacitance—voltage (CV) measurements or Hall measurements [17–19]. Doping concentration has a strong influence on the QFLS of an absorber. In a p-type CuInS₂ absorber, with a higher number of acceptors than donors, any changes in doping concentration would change the position of the hole Fermi level ($E_{F,V}$), thereby changing the QFLS. The effect of changes in Fermi levels with changes in the density if recombination centres or doping level, which in turn results in changes in QFLS, are illustrated in figure 1. In figure 1(a) shows the case of a reduced density of recombination centres: with the Fermi levels split, the position of the electron Fermi level $E_{F,C}$ would shift higher to $E'_{F,C}$, as shown here—and it is assumed that everything else remain unchanged. This would in turn increase the QFLS. Rather, as shown in figure 1(b), as the doping concentration increases and no change in the density of recombination centres, the hole Fermi level ($E_{F,V}$) moves closer to the valence band, thereby increasing the QFLS.

In this paper, the cause of the improvement in QFLS with growth temperature and Cu content for Cu-rich CuInS₂ absorbers by means of photoluminescence measurements is probed [9, 20]. By using information derived from time-resolved and calibrated photoluminescence (PL) measurements, which yield the effective minority carrier lifetime and QFLS respectively, we investigate if the improved QFLS is due to less recombination or higher doping concentration. All PL measurements are excited by a laser that is absorbed within the first nm of the μm thick films, thus an influence of differences in the absorptivity can be excluded.

2. Preparation of samples and experimental produres

The absorber layers studied were deposited by co-evaporation under Cu excess condition i.e., integral composition of [Cu]/[In] > 1, denoted as Cu-rich. The absorbers form stoichiometric CuInS₂ with Cu/In ratio ≈ 1 and copper sulfide (Cu,S) secondary phases [21]. The Cu,S phase was removed by potassium cyanide (KCN) etching leaving an almost stoichiometric absorber [21]. Details of the deposition process can be found in reports by Lomuscio et al [7, 8]. Unlike the selenides, e.g. CuInSe₂, the absorbers do not degrade in air and did not require cadmium sulfide (CdS) coating to prevent degradation [7, 22]. In time-resolved photoluminescence (TRPL) measurement, a laser pulse excites electron-hole pairs in the absorber and the photoluminescence is recorded in time. The TRPL measurements were performed by time-correlated single photon counting (TCSPC) [23]. Excitation was supplied by an 85 ps pulsed laser of 638 nm wavelength at a repetition rate ($f_{rep}$) of 20 MHz. The diameter of the focused beam was ~45 μm. The PL emission was detected with a high-speed photomultiplier with an integrated amplifier. As illustrated in figure 2(a), all measurements were at the PL emission peak ~820 nm, with the integrated monochromator bandwidth of 45 nm to accumulate an adequate number of photons for all the samples at the same measurement condition. The number of excess minority carriers was approximately $7.6 \times 10^{16}$ cm⁻³. This is determined by calculating the number of photons per pulse, assuming that all the photons are absorbed and generate excess carrier pairs, which are then evenly distributed over the absorption length. That is, $\Delta n = \alpha \cdot P_0 / (f_{rep} \cdot A_{beam} \cdot E_{photon})$, where $\Delta n$, $\alpha$, $P_0$, $f_{rep}$, $A_{beam}$ and $E_{photon}$ is the excess minority carriers, absorption coefficient, average laser power, repetition rate, beam area and photon energy respectively. The absorption coefficient of CuInS₂ at the wavelength of the pulsed laser, was estimated as $6.5 \times 10^4$ cm⁻¹ [24]. We aim at low injection conditions, where the excess carrier concentration ($\Delta n$) is less than the equilibrium hole density ($P_0$), i.e. $\Delta n \ll P_0$, because in this case the PL decay time is solely determined by the minority carrier lifetime [25]. On the other hand, in a high injection condition

![Figure 1. Illustration of the positions of the Fermi energy levels with respect to: (a) a reduction of recombination centres (higher electron quasi Fermi level) (b) higher doping concentration (lower hole Fermi level).](image-url)
and the PL decay time is determined by both, minority and majority carrier lifetimes \[11, 25\]. In this work, the excess carrier density is close to the low-injection condition, lower than the typical doping concentration of \(\sim 10^{17} \text{cm}^{-3}\) for Cu-rich CuInS\(_2\) \[26, 27\]. Excitations at lower injection levels were not possible due to the weak luminescence of the absorbers, which led to a low signal to noise ratio. To account for uncertainty in TCSPC, we also measure the instrument response function (IRF) of the set-up. The measured decay curve, \(M(t)\), is a convolution in time \(t\) of the luminescence decay \(D(t)\) and the IRF \(t\), i.e.,

\[
M(t) = \int_0^t \text{IRF}(t')D(t - t')\,dt' \quad [26].
\]

The luminescence decay \(D(t)\) is recovered and fitted using a commercial software from Edinburgh Instruments.

The luminescence decay for an ideal semiconductor is characterized by a single exponential decay \[11\]. However, CIGS absorbers often feature a multi-exponential decay which can be described as an overlay of several decay times \[14\]. In this work, background signal from the dark counts are subtracted, after which the effective lifetime is extracted from the luminescence decay curve by a triple-exponential fit

\[
I_{\text{PL}}(t) = \sum_i A_i \exp \left( -\frac{t}{\tau_i} \right)
\]

where \(I_{\text{PL}}(t)\) is the intensity at a time \(t\) after the laser pulse, \(A_i\) decay amplitude and \(\tau_i\) the decay times for each \(i = 1, 2, 3\). The effective lifetime is then a weighted-average \(\tau_{\text{amp}}\) defined as \(\tau_{\text{amp}} = \sum_i A_i \tau_i / \sum_i A_i\) \[28\]. The weighted-average method takes does not give information of the different decay channels, but it allows for a comparison of samples.

For a calibrated measurement to determine the QFLS, the PL experiment is performed using a 660 nm continuous-wave (CW) laser for optical excitation. Two corrections, namely spectral and intensity, are applied to the raw PL data measured by a steady state excitation. The spectral correction is applied with a commercial calibrated halogen lamp. The intensity correction entails the measurement of the laser beam diameter with a charged-couple device (CCD) camera and the laser power by a photodiode power meter. The incident photon flux is then calculated, and adapted to twice the AM 1.5 solar spectrum photon flux above the bandgap. The room-temperature bandgap for the samples was \(\sim 1.51 \text{ eV}\). An illumination of ‘1 suns’ is used on the samples. The corrected (and now calibrated) spectra are transformed to the energy domain and evaluated using Planck’s generalized law \[29\], which describes the energy dependence of the PL yield as a function of absorptivity, temperature, and QFLS. The QFLS is extracted from a fit of the sufficiently high-energy wing of the PL spectra where absorptivity is assumed to be unity \[9\]. More details on QFLS evaluation can be found in the supplemental detail reported by Babbe et al \[30\].

### 3. Results and discussion

#### 3.1. Effect of changes in growth temperature on the QFLS and effective lifetime

The influence of the integral composition and growth temperature on quasi-Fermi level splitting of Cu-rich CIS absorbers have been reported by Lomuscio et al \[8\]. The results of the different growth parameters and composition on lifetime are presented and discussed here.
To investigate the impact of growth temperature on the rate of recombination, lifetime measurements were carried out on three absorbers with similar Cu/In ratio of 1.8, but different growth temperatures of 550 °C, 590 °C and 650 °C. The decay curves are shown in figure 2(b). It can be seen that, there is no change in the decay curves for the three absorbers. Upon evaluation, the extracted lifetime is about 200 ps. This is an indication of a faster rate of recombination in the CIS absorbers compared to the selenides. Nonetheless, the similarity in the effective lifetime shows that the difference in growth temperature has no significant influence on the rate of recombination of minority carriers in the different absorbers. Details of the QFLS and lifetime of the absorbers are presented in table 1.

From table 1, it is seen that there is a clear increase in QFLS with increasing growth temperature, but the lifetime does not change.

### 3.2. Quasi-Fermi level splitting and effective lifetime on absorbers with different composition

The dependence of QFLS on Cu/In has also been reported by Lomuscio et al [8]. It was shown that there is an increase in QFLS with higher Cu-excess. Here, the Cu-rich absorbers with a Cu/In ratio from about 1.1 to 1.8 are investigated. In figure 3(a), the QFLS and the effective lifetimes are plotted against the corresponding Cu/In ratio. For absorbers processed at 650 °C (black dots), there is a clear increase of more than 40 meV in QFLS with increasing Cu/In ratio, but the lifetime does not show a corresponding increase. In fact, the lifetime scatters around 200 ps. For the high Cu/In ratios different growth temperatures are shown. Again, the QFLS increases with growth temperature, whereas the lifetime scatters around 190 ps.

The origin of this indiscriminate distribution becomes obvious in figure 3(b) where the decay times $\tau_1$, $\tau_2$ and $\tau_3$ are plotted with respect to the QFLS measured on the same sample. The times $\tau_1$ and $\tau_2$ are $\sim 30$ ps and $\sim 200$ ps respectively and not correlated with QFLS. $\tau_1$ and $\tau_2$ are responsible for the main part of the observed decays. $\tau_3$ arises from the decay tail where the influence of noise becomes much more important and thus $\tau_3$ even more randomly distributed between 400 ps and 800 ps. Regardless of the growth temperature or Cu/In of the absorbers studied, the lifetime is always the same. This indicates that, the improved QFLS is not due to reduction in the rate of recombination. Thus, an increase in doping with higher Cu/In ratios or higher growth temperatures must be the reason for the increase in QFLS.

### 3.3. Effect of doping level on the quasi-Fermi level splitting

Here, the effect of doping concentration on QFLS is studied. The estimation of doping concentration from the measurement of the QFLS and the lifetime is described. In a p-type absorber where the majority carrier are holes, the minority carrier can be generated by an external source, and it is possible to estimate the electron...
concentration from the photon flux (ϕ) on the absorber. Since the QFLS is measured under steady state excitation, the generation rate is considered for a steady state light source. For the excitation source, it is assumed that every photon is absorbed and generates an electron-hole pair. Then the excess carrier concentration can be determined from the lifetime. Assuming that the diffusion length of the charge carrier is large enough to achieve a constant carrier concentration over the film thickness, the charge carriers diffuse throughout the thickness (d) of the absorber, then the excess carrier concentration is

$$\Delta n = \frac{\phi \tau}{d}$$

and the charge balance is

$$np = \frac{\phi \tau}{d} N_A$$

with \( n \), \( p \) and \( N_A \) being the electron concentration, hole concentration and doping concentration respectively. Then, the dependence of doping concentration on the quasi-Fermi level splitting is

$$\frac{\phi \tau}{d} N_A = n_i^2 \exp\left(\frac{\Delta F_p}{K_B T}\right)$$

where, \( n_i \) is the intrinsic carrier concentration, \( \Delta F_p \) is the quasi-Fermi level splitting, \( K_B \) is the Boltzmann constant and \( T \) is the temperature in Kelvin. The electron and hole effective masses of 0.16 \( m_0 \) and 1.3 \( m_0 \) respectively, \( m_0 \) being the free electron mass, for CuInS\(_2\) as given by Binsma et al [31] to calculate the intrinsic carrier concentration are utilized. These constants, together with the measured opto-electronic quantities of effective lifetime and QFLS, allows the estimation of the doping concentration of the p-type absorbers.

The calculated doping concentration is plotted against the Cu/In ratio in figure 4. It can be observed that, the plot mirrors the figure 3(a) where QFLS is plotted against Cu/In ratio. We expect this correlation when the lifetime is constant, since then the QFLS is proportional to the logarithm of the doping concentration. For samples A, B and C with similar Cu/In ratio of 1.8, the doping concentration is seen to increase with the growth temperature. To support these series of calculations, doping concentration was also estimated from a CV measurement, performed on finished devices. Due to shunting, it was not possible to do a CV measurement on all the absorbers. However, it was found that, the absorbers processed at 650 °C, with Cu/In ratio higher than 1.4, have doping concentration in the order 10\(^{17}\) cm\(^{-3}\), while those absorbers with Cu/In ratio ~1.3 or lower were in the order of 10\(^{16}\) cm\(^{-3}\). These observations show that, the increase of QFLS with growth temperature or with Cu/In ratio results from higher doping concentration and not from a decrease in recombination rate.

4. Conclusion

In this work, we studied the cause of the improvement in QFLS with higher deposition temperature and higher Cu/In ratio in Cu-rich CuInS\(_2\) absorbers. We showed that, although a higher absorber processing temperature and a higher Cu/In ratio in Cu-rich CuInS\(_2\) absorbers lead to a significant improvement in the QFLS, these parameters do not influence the effective lifetime. Rather, the improvement in QFLS with growth temperature and Cu/In ratio, results from an increase in doping concentration, which expectedly shifts the position of the

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**Figure 4.** Estimated doping concentration on the different absorbers plotted against the Cu/In ratio. The absorbers labelled A, B and C with Cu/In ratio of 1.8 were processed at temperatures of 550 °C, 590 °C and 650 °C respectively.
hole Fermi energy level lower and closer to the valence band. Although we previously saw a lower density of deep defects, the minority carrier lifetime is not affected by the changes in deposition temperatures and Cu/In ratio. As such, to optimize CuInS₂ solar cells for higher efficiency, it is still necessary to reduce the recombination channels that reduces the effective lifetime.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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