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Detailed photoluminescence studies of thin film Cu$_2$S for determination of quasi-Fermi level splitting and defect levels

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We have studied chalcocite (Cu$_2$S) layers prepared by physical vapor deposition with varying deposition parameters by calibrated spectral photoluminescence (PL) and by confocal PL with lateral resolution of λx ≈ 0.9 μm. Calibrated PL experiments as a function of temperature T and excitation fluxes were performed to obtain the absolute PL-yield and to calculate the splitting of the quasi-Fermi levels (QFLs) μ = E$_{f,n} - E_{F,p}$ at an excitation flux equivalent to the AM 1.5 spectrum and the absorption coefficient σ(ℏω), both in the temperature range of 20 K ≤ T ≤ 400 K. The PL-spectra reveal two peaks at E$_{\#1}$ = 1.17 eV and E$_{\#2}$ = 1.3 eV. The samples show a QFL-splitting of μ > 700 meV associated with a pseudo band gap of E$_g$ = 1.25 eV. The high-energy peak shows an unexpected temperature behavior, namely, an increase of PL-yield with rising temperature at variance with the behavior of QFL-splitting that decreases with rising T. Our observations indicate that, contrary to common belief, it is not the PL-yield, but rather the QFL-splitting that is the comprehensive indicator of the quality of the excited state in an illuminated semiconductor. A further examination of the lateral variation of opto-electronic properties by confocal PL and the surface contour shows no detectable correlation between Cu$_2$S grains/grain boundaries and the PL-yield or QFL-splitting. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4850955]

I. INTRODUCTION

Chalcocite (Cu$_2$S) is an abundant and non-toxic p-type semiconductor and a suitable candidate for thin film solar cells. The Cu$_2$S/Cd$_{1-x}$Zn$_x$S heterojunction was the first reported thin film solar cell device, which reached an open-circuit voltage of $V_{oc} \approx 600$ meV and power conversion efficiencies of η ≈ 10%. Nonetheless, due to the complex phase diagram of the Cu$_2$S compound, there is a variety of different phases and stoichiometry configurations stable at room temperature, and with different and sometimes contradicting properties. The reported band gaps of 1.05 eV up to 2.5 eV (Refs. 7 and 8) have been observed as a direct and indirect transitions. It was shown that only the chalcocite phase is suitable for photovoltaic applications, because copper poor Cu$_2$-S shows a degenerating doping due to the high number of Cu vacancies decreasing the fill factor, short-circuit current, open-circuit voltage, and thus the power conversion efficiency. The chalcocite phase shows band gaps of about 1.2 eV close to the ideal band gap according to the Shockley-Queisser limit, and can be found in 3 configurations: low-chalcocite for $T < 377$ K, high-chalcocite for 377 K < $T < 709$ K, and cubic-chalcocite for $T > 709$ K with the low-chalcocite phase the most stable one. The phase transition from low to high-chalcocite is important, since the preparation and/or annealing of the film often occurs at temperatures in the high-chalcocite regime, while experiments and application of fabricated solar cells are performed at room temperature.

Research on the historical Cu$_2$S/CdS solar cell has been abandoned due to long term stability problems from degradation of the Cu$_2$S layer in air, but also from inevitable diffusion of copper ions into the CdS layer due to the unusually high mobility of the Cu atoms. Nevertheless, alternative solar cell concepts like the Cu$_2$S/ZnO-heterostructure, for which an attainable power conversion of η = 17.8% has been predicted, the ZnO/Cu$_2$S/Cu$_2$O p-i-n structure, and the Cu$_2$S/Ti$_2$O heterojunctions are feasible. The advantages of the first two structures are a slow diffusion of copper ions into the ZnO-layer, while Siol et al. showed that there is no cation diffusion into the Cu$_2$S layer. Cu$_2$S also got back into focus for nano-particles and nano-rods as light absorbing material revealing new approaches to potential applications.

In our study, we present results on excitation-density and temperature dependent photoluminescence (PL) on the mm- and on the μm-scale on low- and high-chalcocite. PL is a contact-less technique to determine the radiative recombination of photo-generated excitation states and to get access to opto-electronic properties like the absorption A(ℏω), the splitting of quasi-Fermilevels (QFLs) μ, and to acquire information about the energetic position and dynamics of defect levels within the band gap as well as the laterally fluctuation of the opto-electronic properties and allows us to distinguish between different phases. Since the QFL-splitting of a semiconductor can be interpreted as the upper limit of the open-circuit voltage of a finally fabricated solar cell, $V_{oc} = \mu/\epsilon$, with the elementary charge e, PL measurements provide a technique for analyzing the suitability of absorbers before they are used as solar cells.

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II. EXPERIMENT & SAMPLES

To determine the absolute emitted photoluminescence, the PL setup has been calibrated by use of a tungsten filament lamp. The samples were illuminated with a 532 nm Nd:YAG laser with varying excitation intensities of $10^{-3}$ to $10^4$ AM 1.5 solar spectrum equivalent and under stationary injection conditions. The diameter of the excitation amounts to 4 mm. For cooling the sample to 12 K, a closed-cycle He cryostat was used and the samples were heated against the cooling up to 400 K. The emitted photoluminescence was collected by a lens optic and directed into a monochromator for spectral dispersion and detection by a Si photodiode. The relative PL measurements were obtained with a reflective collimator in front of the entrance slit attached to a multimode fiber, which was fed into an Optical Multichannel Analyzer (OMA) with a (100 x 1340) pixel large Si-CCD array (cooled down to $-120^\circ$C) and a 512 pixel long InGaAs-CCD line (cooled down to $-100^\circ$C), respectively.

For laterally resolved maps, we used a confocal microscope setup. The sample was mounted on a piezo stage and illuminated with $\lambda = 532$ nm at room temperature and an excitation intensity equivalent to $10^4$ suns. The excitation and the collection were performed with a 60 x microscope objective with a numerical aperture of $NA = 0.65$ resulting in a lateral resolution of $\Delta x \approx 0.9 \mu m$. The emitted PL signal was coupled into a multimode fiber and coupled into a spectrometer with a 512 pixel InGaAs CCD line.

The optical transmission was recorded with a Varian Cary 5E UV-VIS-NIR two beam spectrophotometer in the region from 300 nm to 2500 nm with a wavelength-resolution of 1 nm. To obtain the reflection and transmission of the same position on the film, we used the so called VW method. In this work, we focus on three Cu$_2$S samples on boro-aluminosilicate glass substrates (Corning Eagle XG) prepared at the TU Darmstadt by physical vapor deposition (PVD), namely, with a substrate temperature of $T_{sub} = 90^\circ$C during the deposition process and a low deposition rate of 10 Å/min at a crucible temperature of $T = 1100^\circ$C. The samples are denoted as LTA (low temperature annealing), MTA (medium temperature annealing), and HTA (high temperature annealing) and have been annealed for 60 min at temperatures of $T_{ann} = 160^\circ$C, $T_{ann} = 230^\circ$C, and $T_{ann} = 290^\circ$C, respectively. All samples have thicknesses $d$ of about 500 nm. The source material was Cu$_2$S powder from abcr GmbH & Co. KG with a purity of 99.5% (metals basis). The Cu$_2$S films have been examined by XRD measurements at the TU Darmstadt and show a stoichiometry of Cu:S = 2:1 with a monoclinic structure. A full description of the preparation process and the structural properties of the films can be found in a separate publication.

A. Structural properties

Fig. 1 shows two SEM micrographs of a sample prepared with the same parameters as sample HTA, but on ITO instead on glass. The measurements were obtained at the TU Darmstadt and show on the very large scale aggregations of elemental copper (bright dots in Fig. 1(a)) and on the very small scale cracks (dark lines in Fig. 1(b)) in the film due to thermal strain during the annealing and cooling of the film. AFM images show a very smooth surface ($\sigma_{rms} = (13.7 \pm 0.5)$ nm) and grain sizes of several hundred nanometers. Here,

$$\sigma_{rms} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (h - \bar{h})^2} \quad (1)$$

denotes the roughness with mean height $\bar{h}$ and the number of pixels $N$. The cracks are not visible in the AFM map, but the large structures with a size of $\approx 1 \mu m$ are likely the aggregations of elemental copper. Samples LTA and MTA show a roughness of $\sigma_{rms} = (12.8 \pm 0.5)$ nm and $\sigma_{rms} = (6.3 \pm 0.5)$ nm, respectively.

FIG. 1. SEM micrographs of a Cu$_2$S layer of (a) a large-scale section with elemental copper aggregations on top of the film and (b) a small-scale section revealing small cracks in the film. (c) AFM map and (d) histogram of height deviation of a ($10 \times 10$) $\mu m$ large region of sample HTA.
B. Optical properties

Results of optical analyses show transmissions between 30% and 60% for samples MTA and HTA in the region between 1000 nm and 2500 nm with interference fringes due to the thin film and a flat surface (Fig. 2(a)). In the transparent region, the envelope of the transmission decreases slightly, which has been reported in other publications.37 The reason for the decrease of the transmission is not known, but one can speculate whether it is due to other phases of Cu₄S, although Marshall and Mitra37 contribute the absorption in the low-energy regime to free carriers and impurities. Parreira et al. have shown that the transmission in the low-energy regime can be increased by an additional annealing after deposition in air.38 Sample LTA shows a significant smaller transmission of less than 10% in the low-energy regime, what is likely a result of a low annealing temperature of 160 °C. The comparison between the transmission and reflection spectra in Fig. 2(b) reveals a mismatch of the interference peak positions. This is either an effect of an inhomogeneous refractive index along the depth of the Cu₂S film or an inhomogeneous film thickness. Hence, the multiple reflected and the multiple transmitted waves undergo a different optical path resulting in a slightly shifted position of the interference maxima and minima, see Fig. 2(b). From the reflection spectra in Fig. 2(b) reveals a mismatch of the interference peak positions. This is either an effect of an inhomogeneous refractive index along the depth of the Cu₂S film or an inhomogeneous film thickness. Hence, the multiple reflected and the multiple transmitted waves undergo a different optical path resulting in a slightly shifted position of the interference maxima and minima, see Fig. 2(b). From the transmission \( T(h\omega) \) and the reflection \( R(h\omega) \), the absorption \( A(h\omega) \) is calculated by \( A(h\omega) = 1 - R(h\omega) - T(h\omega) \). From the absorption, we define the pseudo or optical band gap \( E_{\text{opt}} \), what in our case the energy, at which the absorption \( A(h\omega) \) is less or equal to \( \exp(-1) \). With the thickness \( d \) of the film, it is possible to calculate the absorption coefficient (Fig. 2(b)) with the inverted Lambert-Beer relation

\[
\alpha(h\omega) = -\ln[1 - A(h\omega)]/d. \tag{2}
\]

From the \( \chi^2 \) over \( E_{\text{photon}} \) plot in Fig. 2(d), we can extract the direct band gap at \( E = (1.15 \pm 0.1) \) eV, which has been already observed for a Cu₄S film.39 The optical band gap is \( E_{\text{opt}} = (1.249 \pm 0.001) \) eV. The absorption coefficient is larger than \( 10^4 \) in the absorbing regime, but also relatively high in the sub-gap regime, what can be contributed to the absorbing copper aggregations. For \( E_{\text{photon}} > 2.5 \) eV, the transmission in Fig. 2(a) is constant and larger than the noise level of the spectrophotometer, indicating a residual transmission due to cracks in the film.

C. Temperature dependent photoluminescence

According to Planck’s generalized law, the emitted photon flux \( Y_{\text{PL}}(h\omega) \) of a semiconductor into the solid angle \( \Omega \) can be written as

\[
Y_{\text{PL}}(h\omega) = \frac{\Omega}{4\pi^2 h^2 c^2} \frac{A(h\omega) \times \langle h\omega \rangle^2}{\exp \left[ \frac{h\omega - \mu}{k_B T} \right] - 1}, \tag{3}
\]

with the photon energy \( h\omega \), the speed of light in vacuum \( c_0 \), the absorptivity \( A(h\omega) \), Boltzmann’s constant \( k_B \), the temperature \( T \) of the electronic system,40 and the splitting of quasi-Fermi levels \( \mu = E_{\text{fb}} - E_{\text{fp}} \). The main assumptions here are stationarity, a distribution of excess carriers according to quasi-Fermi level statistics with momentum and energy relaxation times much smaller than the recombination time and QFL-splitting constant along the depth.31 With the known photon flux \( Y_{\text{PL}}(h\omega) \), we easily calculate \( \mu \) from the high-energy regime, where \( A(h\omega) \approx 1 \). Moreover, the absorption is derived by the use of

\[
\ln A(h\omega) = \ln \left[ \frac{Y_{\text{PL}}(h\omega)}{C \times \langle h\omega \rangle^2} \right] - B(h\omega; \mu, T), \tag{4}
\]

with a constant \( C \) containing the solid angle and the photon density of states and the Bose-term \( B(h\omega; \mu, T) \) containing the temperature \( T \) of the electronic system and the QFL-splitting \( \mu \). Calibrated temperature-dependent PL-spectra (Fig. 3(a)) reveal two peaks, denoted as \#1 and \#2 with different temperature behavior 40 K \( \leq T \leq 340 \) K. While the low-energy peak at \( E_{\#1} = 1.17 \) eV vanishes with increasing temperature, the high-energy peak starts to grow at \( E_{\#2} = 1.29 \) eV and undergoes a red-shift for temperatures \( T > 120 \) K while the low-energy peak shows a small blue-shift. The high-energy PL-peak \#2 at room temperature lies at an energetic position of \( E_{\#2} = 1.22 \) eV. In contradiction to common PL measurements of semiconductors like GaAs,32 Si,33 CuInSe₂, or Cu₂ZnSnS₄34 compounds, the PL-yield of peak \#2 increases with increasing temperature by one order of magnitude between 20 K and 300 K. While for sample HTA the low-energy peak \#1 is more dominant at low temperatures compared to sample MTA and the high-energy peak \#2 cannot be identified, sample MTA shows a smaller PL-yield at \( T = 300 \) K and a smaller PL-yield of peak \#1 at

![FIG. 2. (a) Transmission spectrum of samples LTA, MTA, and HTA. (b) Transmission and reflection spectra of sample HTA. (c) Absorption coefficient of sample HTA. (d) Determination of a direct band gap for sample HTA.](image-url)
Peratures

Eopt

T

a high-energy starts to grow and undergoes a red-shift for temperatures different temperatures; the blue line denotes the absorption at cal band gap fits better to Einstein’s relation

FIG. 3. (a) PL-spectra of sample HTA for temperatures from T = 20 K up to T = 340 K. A low-energy peak vanishes for increasing temperatures, while a high-energy starts to grow and undergoes a red-shift for temperatures T > 120 K. (b) Comparison of PL-spectra of samples MTA and HTA at temperatures T = 20 K, T = 100 K, and T = 300 K. (c) Absorption A(hω) for different temperatures; the blue line denotes the absorption at T = 300 K, the horizontal line denotes A = exp(-1). (d) Calculated optical threshold Eopt as function of temperature with different model functions of the temperature behavior. (e) Temperature-dependent Urbach energy and (f) QFL-splitting of sample HTA with linear fits.

T = 20 K with a well recognizable peak #2 (Fig. 3(b)). The PL signal of sample LTA is not determinable with our experimental setup, which only can measure samples with a minimum QFL-splitting of μmin ≈ 400 meV. This leads to the conclusion, that the quality of the photoexcited state is lower compared to samples MTA and HTA, what is in accordance with the low transmission in the sub-gap region of sample LTA. From the absorption spectra in Fig. 3(c) we derived the temperature dependent optical band gap Eopt. The empirical Varshni equation

Eg(T) = E0 − βT²/(ΘD + T),

fits to E0 = (1.322±0.003) eV the T = 0 K band gap, β = (1±8) × 10⁻³ eV/K, and ΘD = (999±1049) K an remarkable high and inaccurate Debye temperature. The optical band gap fits better to Einstein’s relation

Eg(T) = E0 − κ/(exp[ΘE/T] − 1),

with E0 = (1.326±0.003) eV the T = 0 K band gap, κ = (0.075±0.025) a constant describing the electron-phonon coupling, and ΘE = (198±55) K the average phonon temperature. For both fits, we find the same T = 0 K band gap of E0 ≈ 1.325 eV.

We derived the Urbach energy Eu from the absorption coefficient in the sub-gap regime according to

\[ \alpha(h\omega) \propto \exp\left[\frac{\hbar \omega}{E_u}\right], \]

(with describes the long-range disorder in the semiconductor due to impurities, although it has also been interpreted as a quantity for the exciton-phonon coupling in semiconductors. For sample HTA the temperature dependent Urbach energy is comparatively small and rises with increasing temperature from 5 meV at 60 K to 15 meV at 200 K with a slope of ∂Eu/∂T = 0.07 meV/K.

The QFL-splitting (Fig. 3(f)) decrease with increasing temperature and shows an astonishing value of μ ≈ 730 meV at room temperature and an excitation intensity equivalent to the AM 1.5 spectrum. There is a small shift between the set cryostat temperature and the temperature from the fit due to a small signal-to-noise ratio and an insufficient spectral resolution in the high-energy regime. The extrapolated QFL-splitting of μ ≈ 1.32 eV at T = 0 K can be interpreted as the band gap at T = 0 K and in accordance with the band gaps calculated from the optical threshold. In Table I, the interpolated QFL-splittings and band gaps for both samples are shown. Although sample MTA shows a significant smaller PL-yield at T = 300 K, the QFL-splitting is nearly the same as of sample HTA.

For temperatures T > 20 K, the PL-peak shifts by the order of 1.75 kBT per temperature behavior of a donor-acceptor (DA) pair transition, while for temperatures 12 K ≤ T ≤ 20 K the slope of the PL maximum over T is kBT/2, as shown in Figs. 4(a) and 4(b), being an indication for a free-to-bound transition. For transitions of a free electron or hole to a bound donor (Ed) or acceptor (EA) the blue-shift of the maximum energy is expressed by

\[ E_{PL} = E_g - E_{D/A} + k_B T/2, \]

with the binding energy Ed/A of the donor or the acceptor and the free hole or electron in the corresponding band, respectively. Using Eq. (8), we can extrapolate to \( E_g - E_{D/A} = 1.175 \text{ eV at } T = 0 \text{ K} \) and with the knowledge of the band gap derived from QFL-splitting at T = 0 K we find

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \mu_{\text{cryo}}/\text{meV} )</th>
<th>( \mu_{\text{fit}}/\text{meV} )</th>
<th>( \mu_{\text{cryo}}/\text{meV} )</th>
<th>( \mu_{\text{fit}}/\text{meV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTA</td>
<td>701±19</td>
<td>733±10</td>
<td>1291±11</td>
<td>1318±6</td>
</tr>
<tr>
<td>HTA</td>
<td>724±10</td>
<td>734±6</td>
<td>1319±4</td>
<td>1326±3</td>
</tr>
</tbody>
</table>

TABLE I. QFL-splitting μ at T = 300 K and band gap (defined as μ(T=0 K)) of samples MTA and HTA extrapolated from the temperature-dependent QFL-splitting as function of the temperature of the cryostat Tem and the temperature of the fitting procedure Tfit.
$E_{D/A} = 125 \text{ meV}$ the position of an acceptor or donor site in the band gap. For temperatures between $30 \text{ K} \leq T \leq 80 \text{ K}$ we assign peak #1 to a DA pair transition, which evolves by recombination between an excited localized donor-acceptor pair, which binds due to an attractive Coulomb potential. The energy $E_{\text{coul}}$ of the DA-pair writes\cite{45}

$$E_{\text{coul}} = \frac{e^2}{4\epsilon_r \epsilon_0 r}, \quad (9)$$

with distance $r$ between the donor and the acceptor, vacuum permittivity $\epsilon_0$, and relative permittivity $\epsilon_r$ of the semiconductor. Since we do not know the defect density we estimate the distance between the donor and the acceptor. The average distance of DA-pairs in CuGaSe$_2$ was estimated to $d > 40 \text{ nm}$ resulting in a Coulomb energy of $E_{\text{coul}} < 3 \text{ meV}$\cite{46}. For a DA-pair transition the maximum of the PL-spectrum occurs at energy

$$E_{\text{PL}} = E_g - (E_A + E_D) + E_{\text{coul}}. \quad (10)$$

The temperature dependence of the DA-pair recombination follows the relation:\cite{45}

$$Y_{\text{PL}}(T) = \frac{1}{1 + T^{3/2} \sum_{i=1}^{m} C_i \exp \left[ -E_{\text{act},i}/k_B T \right]}, \quad (11)$$

with the number of states $m$, the activation energy $E_{\text{act},i}$ of the donor or the acceptor state, respectively, and a constant $C_i$ describing the probability of the transition. The thermal quenching occurs due to thermal emission of electrons and holes into the conduction or the valence band, respectively.\cite{45} Using Eq. (11) from the experimental results shown in Fig. 4(a), we can extract the activation energies $E_1 = (0.3 \pm 0.1) \text{ meV}$ and $E_2 = (11 \pm 1) \text{ meV}$. Both activation energies can be fitted quite well to the experimental data (Fig. 4(c)), although the decrease of the PL-yield of peak #1 as function of temperature covers less than one order of magnitude. It is noted, that the small energy of $E_1 \approx 0.3 \text{ meV}$ with its large relative error is necessary for the fit between $12 \text{ K} \leq T \leq 20 \text{ K}$.

The increase of the PL-yield of peak #2 (see Fig. 4(d)) with increasing temperature can be explained with the concept of negative thermal quenching (NTQ), which has already been reported on GaAs, ZnO or ZnS films.\cite{47-49} Phenomenologically, NTQ occurs, if an intermediate state emits into another state with radiative recombination due to thermal excitation, leading to an increasing radiative recombination with increasing temperature. According to Shibata\cite{50}, the temperature dependent $Y_{\text{PL}}(T)$ can be described by a combination of several transitions with thermal quenching and negative thermal quenching

$$Y_{\text{PL}}(T) = \frac{1 + \sum_{i=1}^{m} T^{3/2} C_i \exp \left[ -E_i/k_B T \right]}{1 + \sum_{j=1}^{n} T^{3/2} D_j \exp \left[ -E_j/k_B T \right]}, \quad (12)$$

with $m$ the number of states, which show negative thermal quenching, $n$ the number of states, which show positive thermal quenching and two constants $C_i, D_j$ describing the probability of the transitions and the activation energies $E_i, E_j$ of the transition with negative thermal quenching and positive thermal quenching, respectively. Using Eq. (12) with $m = 1, n = 1$, we can extract two activation energies of $E_{\text{act},1} = E_1 = 7 \text{ meV}$ and $E_{\text{act},2} = E_1' = 53 \text{ meV}$. The fit in Fig. 4(d) does not cover all measured temperatures, because we observed a dramatic drop of the PL-yield for temperatures $T > 360 \text{ K}$. This decrease is due to the phase transition of the Cu$_2$S from the low-chalcoite to the high-chalcoite phase, which we confirmed by a measured decrease of the electric conductivity associated with this phenomenon.\cite{51,52}

The maximum position of peak #2 undergoes a blue-shift of a few meV with a slope of $0.9 \text{ k}_B T$ up to $T = 150 \text{ K}$ and undergoes a strong red-shift of more than $100 \text{ meV}$ for higher temperatures. Interestingly, the red-shift of peak #2 begins when peak #1 is not visible anymore. While the strong red-shift surely can be assigned to the temperature dependence of the band gap, the blue-shift for low temperatures shows features of a DA-pair or free-to-bound recombination.

### D. Excitation intensity dependent photoluminescence

With increasing photogeneration of DA-pairs, the average distance between the DA-pairs decreases resulting in an increase of the energy $E_{\text{coul}}$ of the DA-pair. This leads to a blue-shift of the PL and in particular the maximum in Fig. 5(a) can be described by\cite{53}

$$E_{\text{PL}}(I_{\text{exc}}) = E_{\text{PL}, 0} + \beta \log_{10} \left[ I_{\text{exc}}/I_0 \right], \quad (13)$$

![FIG. 4. (a) Energetic position of the low-energy peak #1 and the high-energy peak #2 at different temperatures. (b) Slope of the PL-Maximum over $T$ for both peaks and different temperature regimes. PL-yield as function of $T$ for (c) peak #1 with fit according to Eq. (11) and (d) peak #2 with fit according to Eq. (12).](image-url)
The exponent $k$ for both peaks as function of $T$ and different excitation regimes is shown in Figs. 5(c) and 5(d). To calculate the intensity-dependence, the PL was measured as function of the excitation intensity for 12 different intensities and $k$ was obtained piecewise over three intensities according to Eq. (14). From the PL-yield as function of excitation intensity we obtain an exponent $k \approx 1$ at $T = 15$ K, also indicating a free-to-bound transition. Interestingly, $k$ is rising from $k = 0.7$ to $k \approx 1$ with increasing excitation energy at $T = 80$ K, what might be an effect of the coexisting band-to-band transition and a saturation of the DA level.

**E. Lateral variation of opto-electronic properties**

Since grain boundaries and varying compositions of the film influence the opto-electronic quality of the film we recorded the laterally fluctuation of the photoluminescence and determined for each pixel the integrated PL-yield, QFL-splitting and the Urbach energy $E_u$. Furthermore, Grabitz et al. showed that the overall solar cell efficiency decreases with increasing inhomogeneity. The maps of the lateral variation of opto-electronic properties, listed in Table III. Histograms of the QFL-splitting and the optical threshold $E_{opt}$.

FIG. 5. Energetic position of (a) the low-energy peak #1 and (b) the high-energy peak #2 for different intensities at different temperatures. Slope $k$ of the PL-yield over energy plot for different intensities and temperatures for (c) the low-energy peak #1 and (d) the high-energy peak #2.

FIG. 6. (a) PL spectra and (b) absorption spectra of pixels with different opto-electronic properties, listed in Table III. Histograms of (c) the QFL-splitting and (d) the optical threshold $E_{opt}$. 

with excitation intensity $I_{exc}$, minimum excitation intensity $I_0$, $\beta$ a few meV and the binding energy $E_{PL,0}$ of DA-pairs in thermal equilibrium. In this case, the peak shifts with increasing excitation with $\beta = (3 \pm 1)$ meV at a temperature of $T = 15$ K as well as at a temperature of $T = 80$ K. For the $T = 15$ K measurement, we extract a binding energy of $E_{PL,0} = (1.169 \pm 0.001)$ eV while for the $T = 80$ K measurement, the binding energy is $E_{PL,0} = (1.175 \pm 0.001)$ eV and thus $(6 \pm 2)$ meV larger than for $T = 15$ K. Peak #2 does not change its position at all with increasing excitation intensity. The energetic red-shift at very high excitation is an effect of the increasing heat deposition, as shown in Fig. 5(b).

For all different types of transitions, the PL-yield follows a power law with increasing excitation intensity:

$$Y_{PL}(I_{exc}) \propto I_{exc}^k.$$  

The exponent $k$ can give access to the type of the recombination kinetics. For band-to-band recombination at moderate excitation, $k = 2$ is expected, but at high excitation, one would expect $k = 1$ for the band-to-band transition. For excitons, $k < 2$ is expected while for a DA-pair recombination and free-to-bound transitions one would expect $k < 1$. Nevertheless, depending on temperature and excitation $k$ can have values $0 < k < 2$ for nearly every type of transition, since several recombination processes may superimpose. Thus, additional information is needed to identify the observed transition. Beside the exponent $k$ the PL-yield as function of temperature and the energetic position of the PL maximum as function of temperature and excitation energy can give a hint to the underlying recombination process.

The exponent $k$ for both peaks as function of $T$ and different excitation regimes is shown in Figs. 5(c) and 5(d). To extract a binding energy of $15$ K measurement, we extract a binding energy of $E_{PL,0}$ which is obtained from the absorption spectrum $E_{opt}$ and the Urbach energy $E_u$. Furthermore, Grabitz et al. showed that the overall solar cell efficiency decreases with increasing inhomogeneity. The maps of the lateral variation of opto-electronic properties, listed in Table III. Histograms of the QFL-splitting and the optical threshold $E_{opt}$. 

FIG. 5. Energetic position of (a) the low-energy peak #1 and (b) the high-energy peak #2 for different intensities at different temperatures. Slope $k$ of the PL-yield over energy plot for different intensities and temperatures for (c) the low-energy peak #1 and (d) the high-energy peak #2.

FIG. 6. (a) PL spectra and (b) absorption spectra of pixels with different opto-electronic properties, listed in Table III. Histograms of (c) the QFL-splitting and (d) the optical threshold $E_{opt}$.

with excitation intensity $I_{exc}$, minimum excitation intensity $I_0$, $\beta$ a few meV and the binding energy $E_{PL,0}$ of DA-pairs in thermal equilibrium. In this case, the peak shifts with increasing excitation with $\beta = (3 \pm 1)$ meV at a temperature of $T = 15$ K as well as at a temperature of $T = 80$ K. For the $T = 15$ K measurement, we extract a binding energy of $E_{PL,0} = (1.169 \pm 0.001)$ eV while for the $T = 80$ K measurement, the binding energy is $E_{PL,0} = (1.175 \pm 0.001)$ eV and thus $(6 \pm 2)$ meV larger than for $T = 15$ K. Peak #2 does not change its position at all with increasing excitation intensity. The energetic red-shift at very high excitation is an effect of the increasing heat deposition, as shown in Fig. 5(b).

For all different types of transitions, the PL-yield follows a power law with increasing excitation intensity:

$$Y_{PL}(I_{exc}) \propto I_{exc}^k.$$  

The exponent $k$ can give access to the type of the recombination kinetics. For band-to-band recombination at moderate excitation, $k = 2$ is expected, but at high excitation, one would expect $k = 1$ for the band-to-band transition. For excitons, $k < 2$ is expected while for a DA-pair recombination and free-to-bound transitions one would expect $k < 1$. Nevertheless, depending on temperature and excitation $k$ can have values $0 < k < 2$ for nearly every type of transition, since several recombination processes may superimpose. Thus, additional information is needed to identify the observed transition. Beside the exponent $k$ the PL-yield as function of temperature and the energetic position of the PL maximum as function of temperature and excitation energy can give a hint to the underlying recombination process.

The exponent $k$ for both peaks as function of $T$ and different excitation regimes is shown in Figs. 5(c) and 5(d). To extract a binding energy of $15$ K measurement, we extract a binding energy of $E_{PL,0}$ which is obtained from the absorption spectrum $E_{opt}$ and the Urbach energy $E_u$. Furthermore, Grabitz et al. showed that the overall solar cell efficiency decreases with increasing inhomogeneity. The maps of the lateral variation of opto-electronic properties, listed in Table III. Histograms of the QFL-splitting and the optical threshold $E_{opt}$. 

FIG. 5. Energetic position of (a) the low-energy peak #1 and (b) the high-energy peak #2 for different intensities at different temperatures. Slope $k$ of the PL-yield over energy plot for different intensities and temperatures for (c) the low-energy peak #1 and (d) the high-energy peak #2.

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FIG. 6. (a) PL spectra and (b) absorption spectra of pixels with different opto-electronic properties, listed in Table III. Histograms of (c) the QFL-splitting and (d) the optical threshold $E_{opt}$.
algorithm, which fits piecewise and overlapping slopes in the high-energy regime of the PL spectrum and returns the fitting parameters with both a small fit error and a small deviation to room temperature.57

As it can be seen in Fig. 7 and Table II, sample MTA shows a better homogeneity regarding the integrated PL-yield, the optical threshold and the Urbach energy than sample HTA. The ratio of the maximum PL-yield to minimum PL-yield is 6.8 for sample HTA and 1.8 for sample MTA, what is likely an effect of less cracks in the film due to a smaller annealing temperature. Otherwise, the integrated PL-yield is smaller compared to sample HTA and small elongated structures are recognizable, which are larger than the grains which can be seen in the AFM map. The mean optical band gap \( E_{\text{opt}} = (1.248 \pm 0.013) \text{ eV} \) for sample HTA is the same as determined with the photospectrometer and macroscopic PL-measurement. The optical band gap of sample MTA is about 15 meV smaller.

The maps also reveal that pixels with a high integrated PL-yield do not necessarily show a higher \( \mu \) (pixel 2), although the Pearson correlation coefficient \( r_{X,Y} \) between the integrated PL-yield and \( \mu \) is \( r_{\text{PL},\mu} = 0.8 \). A higher \( \mu \) is slightly correlated to a higher optical band gap \( E_{\text{opt}} \) (pixel 1) with \( r_{\mu,E_{\text{opt}}} = 0.3 \). Regions with a smaller \( \mu \) show a small PL-yield, a large \( E_{\text{opt}} \) and a significant smaller band gap (pixel 6) although the variation of the band gap might be altered by the Urbach energy. The anti-correlation between Urbach energy and the optical band gap is \( r_{E_u,E_{\text{opt}}} = -0.6 \) indicating that regions with reduced band gap show a larger structural disorder, indicating the occurrence of two different Cu2S manifestations in the film.

The slope of the Bose-term of pixels (1)–(5) is nearly the same, so that we exclude a wrong fitting procedure. The PL-spectra in Fig. 6(a) only show a small variation with respect to the underlying PL-yield or QFL-splitting. Otherwise, the absorption spectra in Fig. 6(b) also show a correlation between the Urbach energy and the QFL-splitting of \( r_{\mu,E_u} = -0.4 \). There is no correlation between \( E_{\text{opt}} \) and the integrated PL-yield (\( r_{\text{PL},E_{\text{opt}}} \approx 0 \)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \int Y_{\text{PL}} ) / arb.units</th>
<th>( \Delta \mu ) / meV</th>
<th>( E_{\text{opt}} )/eV</th>
<th>( E_u )/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTA</td>
<td>146±10</td>
<td>2.4</td>
<td>1233±4</td>
<td>16.5±0.2</td>
</tr>
<tr>
<td>HTA</td>
<td>265±51</td>
<td>5.8</td>
<td>1248±13</td>
<td>17.1±0.5</td>
</tr>
</tbody>
</table>

**TABLE II**: Lateral variation of opto-electronic properties for samples MTA and HTA.

**FIG. 7**: 50 \( \mu \text{m} \times 50 \mu \text{m} \) large regions showing the lateral inhomogeneities of (a) the integrated PL-yield and (b) the QFL-splitting \( \mu \) of sample MTA. (c) Lateral variation of the integrated PL-yield, (d) the QFL-splitting \( \mu \), (e) the optical band gap \( E_{\text{opt}} \) and (f) the Urbach energy \( E_u \) of sample HTA. The black circles denote the pixels, which are shown in Table III.

**TABLE III**: Electro-optical properties of the pixels on sample HTA marked in the maps in Fig. 7 and Figs. 6(a) and 6(b).

<table>
<thead>
<tr>
<th>Pixel</th>
<th>( \int Y_{\text{PL}} ) / arb.units</th>
<th>( \Delta \mu ) / meV</th>
<th>( E_{\text{opt}} )/eV</th>
<th>( E_u )/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.8</td>
<td>11.9</td>
<td>1.273</td>
<td>16.99</td>
</tr>
<tr>
<td>2</td>
<td>35.1</td>
<td>4.7</td>
<td>1.255</td>
<td>17.05</td>
</tr>
<tr>
<td>3</td>
<td>30.6</td>
<td>–0.8</td>
<td>1.251</td>
<td>16.71</td>
</tr>
<tr>
<td>4</td>
<td>24.4</td>
<td>–3.6</td>
<td>1.246</td>
<td>17.12</td>
</tr>
<tr>
<td>5</td>
<td>17.1</td>
<td>–8.5</td>
<td>1.265</td>
<td>17.05</td>
</tr>
<tr>
<td>6</td>
<td>7.6</td>
<td>–30.5</td>
<td>1.229</td>
<td>19.06</td>
</tr>
</tbody>
</table>
III. SUMMARY

We investigated Cu$_2$S films with respect to their optical, structural and opto-electronic properties. Structural experiments reveal a smooth surface, which shows aggregations of elementary copper and small cracks as a result of the deposition and annealing process, respectively. Nevertheless, the annealing is important for the opto-electronic quality of the film, as the PL-yield as well as the QFL-splitting of the examined samples increase with the annealing temperature. The direct band gap of the films is $E_g$ equals 1.15 eV while the optical band gap $E_{opt}$ determined from the photoplotrometer and PL experiment are 1.25 eV. Temperature and intensity dependent PL measurements of a thin film Cu$_2$S layer show both an astonishing high QFL-splitting of $\mu \approx 730\text{meV}$ at room temperature and AM 1.5 condition indicating a high quality of the semiconductor confirming its potential as solar cell absorber material.

The temperature behavior of the band-to-band transition can be explained with the model of negative thermal quenching and the underlying band-near defect level is likely the reason for a high PL-yield at room temperature, while the defect peak at low temperatures shows features of a DA-pair transition. We want to emphasize that although the PL-yield of sample HTA increased with increasing temperature and thus seemed to increase the “quality” of the photoexcited electron-hole pair, it is the QFL-splitting, which is the best indicator of the excitation state and which decreases with increasing temperature. Temperature and intensity dependent PL measurements reveal several defects in the band gap, which act as recombination path for the excess charge carriers in the bands. Laterally resolved PL maps indicate the occurrence of two different Cu$_2$S manifestations with slightly different opto-electronic properties.

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1Q. Xu, B. Huang, Y. Zhao, Y. Yan, R. Noufi, and S.-H. Wei, Appl. Phys. Lett. 100, 061906 (2012).
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