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Interference effects in photoluminescence spectra of $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films

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Photoluminescence (PL) is commonly used for investigations of $\text{Cu}_2\text{ZnSnS}(\text{e})_4$ [CZTS(e)] and $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) thin film solar cells. The influence of interference effects on these measurements is, however, largely overlooked in the community. Here, it is demonstrated that PL spectra of typical CZTS absorbers on Mo/glass substrates can be heavily distorted by interference effects. One reason for the pronounced interference in CZTS is the low reabsorption of the PL emission that typically occurs below the band gap. A similar situation occurs in band gap graded CIGS where the PL emission originates predominantly from the band gap minimum located at the notch region. Based on an optical model for interference effects of PL emitted from a thin film, several approaches to reduce the fringing are identified and tested experimentally. These approaches include the use of measured reflectance data, a calculated interference function, use of high angles of incidence during PL measurements as well as the measurement of polarized light near the Brewster angle. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4926857>]

I. INTRODUCTION

Both $\text{Cu}_2\text{ZnSnS}(\text{e})_4$ [CZTS(e)] and $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) have been studied extensively for applications in thin film solar cells. Photoluminescence (PL) is a versatile technique commonly used to examine a wide range of properties of these materials, including the optoelectronic quality, band gap, defects, spatial uniformity, and potential fluctuations.^{1–6} In all of these studies, it is critical for the interpretation of the results that the measured spectrum accurately reflects the luminescence emitted by the sample. Several effects can influence the measured PL spectrum, and should be accounted for. An example of a well-known artefact observable in the near infrared and infrared spectral region is absorption lines due to water vapour in the air.^{7,8} In addition to PL contributions from the studied material itself, the interpretation may also need to account for PL associated with secondary phases. As an example, ZnSe is a secondary phase commonly present in CZTSe, resulting in characteristic features in the PL spectrum.⁹ In the present paper, another phenomenon affecting the PL spectrum is demonstrated, namely, that of thin film interference. This effect follows from the coherent superposition of the luminescence emitted and internally reflected by the sample. While interference is well known to affect cathodoluminescence measurements¹⁰ as well as PL measurements for certain material systems, such as InGaN/GaN quantum wells and Si nanocrystals in SiO_2 ,^{10–14} it seems to be largely overlooked in the thin film photovoltaic community. Several reported PL spectra measured on CZTS(e) show multiple peaks, which could of course be related to the material properties.^{15–17} However, one should also consider the impact of interference effects in the interpretation. In this paper, it is demonstrated that thin film interference can strongly affect the PL spectrum of smooth CZTS absorbers. Using an optical model to simulate

the effect, we identify various approaches to reduce the impact of interference on the measured spectrum. The success of each approach is experimentally evaluated.

II. EXPERIMENTAL DETAILS

The absorbers used for this PL study are prepared by annealing reactively sputtered Cu-Zn-Sn-S films in a small volume graphite box containing a stoichiometric excess of elemental S. More details of the preparation are given in Ref. 18. The thickness of the absorber used for the majority of this study is 2.2 μm . The elemental ratios determined by x-ray fluorescence are $\text{Cu}/\text{Sn} = 1.9$ and $\text{Zn}/(\text{Cu} + \text{Sn}) = 0.39$, respectively. A series of CZTS absorbers are prepared using the same baseline process but with different thicknesses of 500 nm, 750 nm, and 1500 nm achieved by varying the sputtering time. The composition of these samples is similar with $\text{Cu}/\text{Sn} = 1.85$ and $\text{Zn}/(\text{Cu} + \text{Sn}) = 0.38$.

A CIGS thin film with a notch profile band gap grading is produced by co-evaporation as described in Ref. 19.

PL measurements are performed in a Renishaw inVia confocal Raman microscope equipped with a silicon CCD detector. All measurements are performed at room temperature, using a 532 nm laser with a power of 0.26 mW for excitation, and a microscope lens with a numerical aperture of 0.13, resulting in an excitation intensity of about 1300 W/cm². The measurements are corrected for the spectral response of the system by application of a correction function obtained using an Avantes calibrated light source.

The total reflectance is measured over a spectral range from 250 nm to 2500 nm, using a Perkin Elmer Lambda 900 double beam spectrometer equipped with an integration sphere. Data are recorded at near normal incidence (8° tilt) with 5 nm steps.

TABLE I. Optical constants of CZTS and Mo determined by ellipsometry.

Energy [eV]	n_{CZTS}	k_{CZTS}	n_{Mo}	k_{Mo}
1	2.38	0.043	2.05	3.74
1.25	2.42	0.055	2.25	2.86
1.5	2.51	0.086	2.55	2.53
1.7	2.53	0.21	2.57	2.49

The complex refractive indices of CZTS and Mo as well as the thickness of the CZTS layer are extracted using spectroscopic ellipsometry. Measurements are performed in several steps on a Woollam VASE instrument, for incidence angles of 65, 70, and 75°. First, with soda lime glass as the growth substrate, the optical constants of Mo and MoS₂ are extracted from measurements on Mo/glass and MoS₂/Mo/glass samples, respectively. Then, the full CZTS/MoS₂/Mo/glass multilayer stack is measured for a CZTS absorber with Cu/Sn = 1.81, Zn/(Cu + Sn) = 0.41, and a layer thickness of approximately 500 nm. The ellipsometric analysis determined the film thickness and optical constants of the sample layers by calculating the spectroscopic quantities from a model and fitting the parameters of the model to match the measured quantities. The model assumes a stack of CZTS/MoS₂/Mo, where the CZTS layer is composed of two sublayers: a compact baselayer with dielectric functions modelled by oscillator dielectric susceptibilities and a porous overlayer constructed from a mixture of air and the baselayer by use of the Bruggeman effective medium approximation.^{20,21} The resulting overall thickness of CZTS is confirmed using SEM cross section measurements. This supported the correctness of the simultaneously estimated dielectric functions. The optical constants for a few selected energies are shown in Table I, while a more detailed ellipsometry study will be published separately.

III. OPTICAL MODEL OF INTERFERENCE IN PHOTOLUMINESCENCE

An optical model taking multiple reflections into account is applied to calculate the interference pattern. The model used in this work is based on the work by Holm *et al.*¹⁰ To model the PL emission, an ensemble of randomly

oriented incoherently radiating electric dipoles is assumed. The emission from the dipoles is averaged over all emission angles and Fresnel reflection coefficients are used to describe the reflection at each interface.¹⁰ Based on this model, an interference function (IF) proportional to the emission probability is calculated. The Appendix contains a detailed description of the IF calculation. The application of this IF to correct for interference effects is not unique. Several similar approaches have been proposed in literature; see, for example, Refs. 10, 14, 22, and 23. Our model was modified to take the front surface roughness into account based on scalar scattering theory.^{24,25} This accounts for the specular and diffuse reflected and transmitted light for interfaces with roughness comparable to or smaller than the wavelength. More details are available in the Appendix.

Using the optical constants determined by ellipsometry, an IF applicable to CZTS is calculated. The interference function can be applied to either correct the measured PL spectrum ($\text{PL}_{\text{true}} = \text{PL}_{\text{measured}}/\text{IF}$) or simulate the PL spectrum using an assumed peak shape ($\text{PL}_{\text{simulation}} = \text{PL}_{\text{peak shape}} \times \text{IF}$). In the following, it is discussed how the model points to approaches to reduce the effect of interference effects on the measured PL spectra.

A. Interference function compared to reflectance

First, we discuss under which circumstances the IF mimics the transmission of the sample. In this case, assuming negligible absorption at the PL emission wavelength, the IF can be approximated by $1 - R$, where R is the sample reflectance. When light is emitted inside the CZTS layer, one can distinguish between two types of interference, namely, wide angle interference as illustrated in Figure 1(c) and multiple beam interference illustrated in Figure 1(d).²⁶ Multiple beam interference is independent of the distribution of the emission centres, while wide angle interference is sensitive to the origin of the luminescence in the layer. Depending on the distribution of active emission centres, either multiple beam or wide angle interference can dominate. If it is assumed that the PL originates from the same region that absorbs the exciting laser light (minority carrier diffusion length < absorption length), the emission profile can be estimated with the Beer-Lambert law applied at the laser

FIG. 1. Comparison of interference function and reflectance (a) assuming an emission profile equal to a Beer-Lambert absorption profile, (b) assuming emission from a Gaussian distribution with a FWHM of 30 nm that is located 300 nm from the layer surface. Schematic illustration of (c) wide angle interference and (d) multiple beam interference.

wavelength: $I(z) = I_0 \exp(-\alpha z)$. For CZTS with $\alpha(532 \text{ nm}) = 6 \times 10^4 \text{ cm}^{-1}$, the majority of the light is absorbed in the top 150 nm of the layer. In this case, the wide angle interference smears out due to the depth distribution of the emission. Figure 1(a) shows that the IF mimics $1 - R$ in this case. If on the other hand the emission originates from a narrower depth distribution, one will expect to observe the influence of wide angle interference. This is illustrated in Figure 1(b), where it is assumed that the emission originates from a Gaussian distribution with a FWHM of 30 nm located 300 nm from the film surface. This situation could occur if the band gap of the absorber has a minimum at some distance from the absorber surface, as seen for the common notch profile of CIGS. In Figure 1(b), it is noticed that IF and $1 - R$ are very different due to the strong effect of wide angle interference in this case. Using the optical constants for CZTS, we find that the influence of wide angle interference vanishes when the luminescence originates from emission centres distributed over a depth of more than 80 nm. In most cases, where the luminescence originates from a wider distribution of depths, the IF can be approximated by $1 - R$. The experimentally obtained reflectance can then be applied to correct for interference effects in case optical properties of the layers are unknown. For normal incidence, a more general condition for applicability of $1 - R$ can be determined by evaluation of $p = H \times (2 \times \pi \times n) / \lambda$, where H is the width of the active emission centre distribution, n is the index of refraction, and λ is the wavelength of the light.¹⁰ If $p \gg 1$, the interference function mimics the transmission spectrum and $1 - R$ approximates IF. In the other extreme $p \ll 1$, wide angle interferences dominate and IF cannot be approximated by $1 - R$.

B. Effect of sample tilt

An approach to reduce interference effects is to measure the sample under various angles. Figure 2 shows the calculated polarization-averaged IF alongside the IF components for s- and p-polarized lights for different tilt angles of the sample. When measuring normal to the sample surface [Figure 2(a)], the s- and p-polarized components have coinciding maxima and minima. The polarization averaged IF is therefore similar to both of the components. If the angle is increased to the Brewster angle for the CZTS/air interface ($\theta_B = \arctan(n_{\text{CZTS}}/n_{\text{air}}) = 67^\circ$, for $n_{\text{CZTS}} = 2.38$), the s- and

p-polarized components are affected differently. It is expected that the fringe contrast is significantly reduced for the p-polarized light due to the suppressed reflectivity of the CZTS/air interface at this angle. On the other hand, one expects the IF for the s-polarized light to remain affected by interference fringes. It should be kept in mind that the Brewster angle is only strictly valid for one wavelength. It is therefore not expected that fringes totally disappear. Figure 2(b) confirms that this is in fact the case. Due to the reduced fringe contrast, it is relevant to measure PL using a polarizer that removes the s-polarized luminescence. This will be discussed in Sec. IV E. Figure 2(c) shows the IF for an even steeper measurement angle of 75° . This angle is not unique but it is chosen since it is realized that an interesting phenomenon happens near this angle. It is noticed that the minima in the s-polarized component coincide with maxima in the p-polarized component and vice versa. Because of this effect, the polarization averaged IF shows significantly lower fringe contrast. This interesting phenomenon can be utilized to measure a photoluminescence spectrum less affected by interference effects. It should be noticed that the angle for this effect is sensitive to the optical constants of the material. This approach might therefore not be applicable to any material.

C. Effect of roughness

Interference effects are only observable for relatively smooth layers. As the roughness increases, the specular internal reflectance and transmittance through the front interface are reduced, and the interference effects diminished. In order to quantify this effect, the roughness is included in the model described in the Appendix. Figure 3 shows the effect of root-mean-square (RMS) roughness on the fringe contrast for a CZTS layer with a thickness of 2200 nm. It is observed that the fringing is very dominant in smooth films with low RMS roughness, like the samples studied here as discussed later. For films with RMS roughness of around 120 nm or more, the fringe contrast reduces significantly, and one would not expect to observe distinguishable fringes in PL spectra.

IV. EXPERIMENTAL RESULTS

In this section, it is demonstrated that the interference effects observed in PL measurements can be accurately described by the theoretical model. The effect of a notch

FIG. 2. Calculated interference function for different measurement tilt angles. (a) Measurement normal to surface, (b) measurement at the Brewster angle of the CZTS/air interface, (c) measurement at 75° .

FIG. 3. Effect of RMS surface roughness on fringe contrast for a CZTS layer with a thickness of 2200 nm.

profile band gap grading as well as the thickness of the absorber layer is shown with examples. It will finally be demonstrated how to reduce the influence of interference on PL measurements.

A. Demonstration of interference in photoluminescence

First, we illustrate the appearance of fringes in the PL spectrum and illustrate that these can be described by the model described in Section III. Figure 4 shows PL spectra of a CZTS absorber measured under three different angles 0°, 50°, and 75° relative to the surface normal. It is noticed that the location and depth of the fringes in the PL spectra shift when the sample is tilted. This is a first indication that the fringes are artefacts, rather than genuine features of the sample's PL spectrum. Included in Figure 4 is the calculated IF for the three measurement angles. The coincidence between the maxima of the IF and the PL spectrum is clear. According to the model, the fringe location shifts since the optical path length in the absorber is increased when the

FIG. 4. Bottom: Room temperature PL spectra collected for different tilt angles relative to the sample surface normal. Top: Interference function calculated for the same tilt angles.

sample is tilted. The observed shift of the fringes when tilting the sample from 0 to 50° is in good agreement with the fringe shift in the calculated IF. The agreement demonstrates that the model accurately reflects the observed phenomenon, and thus that we can confidently attribute the PL fringes to interference. Another interesting observation is that the measurement under the angle of 75° appears less affected by fringes, an observation that is in good agreement with the calculated IF, also showing significantly reduced amplitude of the fringes. This happens since maxima for the s-polarized light coincide with minima for the p-polarized light as explained in Section III.

B. Simulation of PL spectra affected by interference

The IF and $1 - R$ approaches discussed previously are applied in order to further prove the point that the observed fringes are indeed due to interference and to disentangle the material specific PL spectrum. Figure 5(a) shows the measured PL spectrum at normal incidence along with the measured optical reflectance (R). By multiplication of a Gaussian curve with $(1 - R)$, the spectral shape of the measured PL is accurately approximated. To obtain an even closer fit, the reflectance can be multiplied by a factor c that scales the fringe amplitude of the measured reflectance to match the fringe amplitude observed in PL. The match between the measured PL and the PL approximated with this simple model is striking, and confirms that the cause of fringing in PL is the same as the reflection measurement, i.e., interference of reflected light. In this model, it is implicit that the PL spectrum has a Gaussian shape, which is of course an oversimplification. It does however turn out to serve useful for demonstrative purposes and to approximate the true spectrum. In Figure 5(b), we demonstrate an alternative approach to obtain a similar result using the calculated IF instead of measured reflectance data. Since the calculated IF uses optical constants for the layers as input parameters, the success of this approach is very sensitive to the accuracy of these parameters. It is noticed that the fringe contrast is underestimated by the IF. This could be caused by a too high extinction coefficient in the model. Multiplication of the extinction coefficient used in the calculation with 0.7 yields a more convincing fit. One possible reason why this factor is needed could be that the optical constants and PL measurements were performed on different samples. Unless the optical constants and layer thicknesses are very well defined for the particular sample, the measured reflectance gives a better fit in cases with dominating multiple beam interference. It has to be kept in mind that $1 - R$ would not be applicable in case of a strong influence from wide angle interference. An example of this situation is given for a CIGS thin film in Sec. IV C.

C. Wide angle interference in notch profile CIGS

While the interference function of our CZTS absorbers is dominated by multiple beam interference, and thereby resembles $1 - R$, we have observed another situation in band gap graded CIGS absorbers. As shown in Figure 6, the PL spectrum for a band gap graded CIGS absorber on Mo back contact is influenced by interferences which are not in phase

FIG. 5. (a) PL spectrum measured at normal incidence compared to a Gaussian multiplied by the measured reflectance with a correction factor c . (b) The same data using the calculated interference function instead of measured reflectance. In the red curve, the extinction coefficient is multiplied by 0.7.

with the measured $1 - R$. The CIGS absorber was deposited by three-stage evaporation as described elsewhere,¹⁹ giving a double band gap grading with the minimum, or notch, at around 300 nm from the absorber surface. Radiative recombination will be highest in this notch and the distribution of luminescence centres can be approximated by a Gaussian centred at this position. This is qualitatively the situation described in Figure 1(b), where wide angle interference contributes to the total interference.

D. Dependence of layer thickness

The CZTS film thickness has a pronounced effect on the interference pattern. Figure 7 shows PL and reflectance measured on three samples with different CZTS thicknesses. It is noticed that the period of the oscillations in the fringes approaches the width of the PL peak for the thin (i.e., $<1 \mu\text{m}$) samples. The appearance of interference effects becomes less obvious in this case, since one will not observe multiple fringes. The effect of interference is nonetheless still equally important since it affects the shape and position of the measured PL spectrum. The PL spectrum obtained for the 750 nm thick absorber illustrates this point. The spectrum does not appear to be obviously affected by interference at

FIG. 6. PL spectrum of a CIGS thin film with a band gap notch compared to $1 - R$ measured on the same sample.

first sight, but the fact that the PL peak and the local minimum in $1 - R$ coincide alters the peak shape significantly. For samples thinner than 500 nm, the interference effect becomes less significant since fringe spacing becomes wider than the PL peak. The study of very thin layers can therefore be an alternative approach to avoid interference effects. If the sample preparation allows it, one alternative approach would be to deposit much thicker films $>10 \mu\text{m}$. In this case, the fringe separation would be much smaller than the peak width, and the underlying peak shape would be more easily distinguishable.

E. Brewster angle measurement

Given the interference artefact, the main problem for the experimentalist is how to obtain the “true” PL spectrum. First, we attempt to utilize the Brewster angle effect. When measuring near the Brewster angle, the reflection of p-polarized light diminishes, which will theoretically result in reduced interference fringes in the PL. In order to experimentally test this, a polarizer was inserted in the luminescence in order to collect only s- or p-polarized lights emitted by the sample. This is compared to the s- or p-polarized component of the calculated IF. As seen in Figure 8(a), the fringes heavily distort the PL spectrum for the s-polarized light. The measured spectrum can be accurately simulated using the s-polarized component of the IF, illustrating good agreement between the theoretical model and the measured PL. When only collecting the p-polarized luminescence, shown in Figure 8(b), it is noticed that the PL is less affected by interference effects. It is again possible to obtain a similar curve shape by multiplication of a Gaussian with the p-polarized component of the IF. The expected reduction of fringe contrast for p-polarized light is nicely observed in the PL measurement. This result illustrates that measurement at the Brewster angle with a polarizer represents an experimentally viable approach to obtain a PL spectrum less affected by interference effects.

F. Comparison of correction approaches

Several correction approaches have been discussed in this paper. In order to compare these, they are shown side by side

FIG. 7. Normal incidence PL measured for samples with different CZTS layer thicknesses compared to a Gaussian $\times (1 - R)$, where R is the measured reflectance. The legend is the same for all plots.

FIG. 8. PL measured at the Brewster angle (67°), compared to the calculated IF and simulated PL spectra (Gaussian $\times$ IF). (a) Only the s-polarized component of the PL is measured and compared to the s-polarized part of the IF. (b) Similar comparison for the p-polarized component.

in Figure 9. Measurement of the same sample tilted by 75° yields a spectrum with a peak shape very similar to a Gaussian. Under these measurement conditions, the amplitude of the fringes is significantly reduced as shown previously. The spectrum is therefore close in peak shape to the true PL spectrum, unaffected by interference. The attempt to correct the spectrum measured at normal incidence with the IF yields a spectrum that remains somewhat distorted. The IF does not totally remove fringes, presumably due to a deviation between the optical constants used in the model with those of the particular sample. It is also attempted to correct the normal incidence PL using the measured reflectance data. Again, the corrected PL is very similar in shape to the Gaussian, which shows that this peak shape is a reasonable approximation for the emitted PL (in this example). By introduction of a scaling factor c , the corrected spectrum ($PL/(1 - R \times c)$) is even less affected by the interference fringes. This approach, does, however have some issues if the true PL spectrum is not well

approximated by a Gaussian. If the emitted PL contains several peaks, it would be inaccurate to calculate the factor c assuming a single Gaussian. The impact of the interference fringes can therefore be over- or underestimated in an attempt to fit the measurement to a single Gaussian. The final attempt to measure the true PL spectrum shown in Figure 9 is to collect only p-polarized light with the sample tilted to the Brewster angle. This approach reduces but does not eliminate the fringes. None of the methods yields a true spectrum totally unaffected by interference, but all approaches have some merit. All approaches certainly give a spectrum that more accurately reflects the true PL than the uncorrected spectrum heavily distorted by interference.

When applying PL for study of materials, the experimentalist could be interested in various features of the spectrum depending of the details of the investigation, i.e., peak position, width, absolute intensity, or shape of high and low energy tails. The applicability of the proposed approaches depends on the amount of details expected from the measurement. If one is mainly interested in the overall PL yield and an approximate peak position and width, one of the correction approaches can be applied. One has to keep in mind that the shape of the spectrum remains slightly affected by interference. The peak width and position will therefore be susceptible to errors. When applying the correction approaches is it not advisable to analyse the details of the spectrum, such as fitting of tails, since the peak shape may remain slightly distorted.

FIG. 9. Comparison of the uncorrected PL spectrum and different approaches to correct the spectrum for interference effects.

V. DISCUSSION: CONDITIONS FOR PRESENCE OF INTERFERENCE FRINGES IN PHOTOLUMINESCENCE

Now that we have demonstrated the importance of interference effects on PL measurements, we will briefly discuss

the conditions necessary to observe the phenomenon. One may wonder why interference effects in PL measurements have not been discussed for CZTS(e) and CIGS thin film solar cells given the large volume of publications on the topic. The answer could be that for most samples, interference effects are relatively small. A series of requirements must be met in order to clearly observe interference effects.

(1) The sample must be sufficiently smooth. For samples with roughness on a length scale comparable to the wavelength of light, any interference effects will cancel out over macroscopic measurement areas. The roughness of CZTS(e) or CIGS thin films can vary greatly depending on the preparation conditions. The samples used in the present study were prepared with our co-sputtering and annealing baseline process.¹⁸ This process typically yields smooth samples with a RMS roughness around 40 nm as measured by atomic force microscopy (AFM). This is comparable to the reported RMS roughness in the range 30–66 nm for CZTS prepared by sulfurization of Cu-Sn-Zn precursors sputtered from an alloy target.²⁷ Another group obtained significantly rougher CZTS layers with RMS values in the range 85–134 nm using a similar preparation approach.²⁸ Due to the smooth surface of the samples studied here, pronounced interference effects can be seen.

(2) The reflectance at the back contact must be sufficiently high. CZTS(e) and CIGS are typically deposited on optically thick molybdenum coated on glass. A thin layer of MoS(e)₂ is normally formed during absorber preparation,²⁹ with thickness depending on the processing time and conditions. Some processing routes even lead to the formation of voids at the back contact (see, e.g., Refs. 30 and 31). The properties and roughness of the Mo layer can likewise vary to some degree depending on the processing conditions. Since variations in the reflectivity of the back interface are dependent on the processing route, the impact of this factor must be evaluated for each individual case.

(3) In order to observe interference in the spectrum, the emitted PL must not be significantly reabsorbed over the path back and forth through the layer under study. One reason that interference is rarely observed in PL spectra of CIGS is that the energy of the emitted luminescence is close to the band edge of the material, where the absorption coefficient is still high compared to the film thickness (typically $\sim 1\text{--}2\ \mu\text{m}$). Reabsorption of the luminescence will therefore attenuate the backside reflected component and prevent strong interference. In typical CZTS samples, the PL peaks are, however, often observed at energies significantly lower than the band gap determined by QE.² Since the absorption coefficient is lower in this spectral range, the PL is not strongly reabsorbed and reflections from the back contact can reach the front of the sample. It should also be mentioned that interference fringes can be observed in CIGS if the band gap of the layer is graded. If the band gap has a minimum near the surface, the PL emitted into the bulk of the film will not be strongly absorbed and allow for interference.

(4) It is important to consider the width of the PL peak in comparison to the fringe spacing of the interference spacing. As discussed, this is dependent on the sample thickness. The width of the PL peak of course also plays a role. In a situation where the PL peak is much narrower than the

interference fringe spacing, the interference effect would be negligible. This would, for example, be the case when studying excitons or narrow donor acceptor transitions at low temperature.

(5) Finally, it should be mentioned that the particular properties of the experimental setup could impact how interferences are observed. It was, for example, demonstrated that the effect is less pronounced for certain measurement angles. Measurements in a PL setup where the sample is not perpendicular to the collection optics therefore result in different spectra than a setup with collection normal to the surface. One can likewise imagine that the numerical aperture of the setup can be of importance. Confocal PL setups optimized for high spatial resolution often used in literature^{4,6,16} use high numerical aperture microscope objectives. Two opposing effects could play a role when using higher numerical apertures. On one hand, a higher numerical aperture results in a smaller spot size. A lower thickness variation within the probed area is therefore expected and hence more prominent interference fringes. On the other hand, the higher numerical aperture results in a wider angular spread of the collected light and therefore less impact of interference effects. In order to experimentally investigate the impact of these effects, measurements were performed with microscope objectives with numerical apertures in the range 0.13–0.75. Based on the results (not shown), it was concluded that the numerical aperture did not strongly influence the interference fringes observed in the PL spectrum. It is therefore expected that interference effects can be observed in other PL setups with very different numerical apertures.

VI. SUMMARY

It has clearly been demonstrated that interference can drastically affect the PL spectra of CZTS and CIGS absorbers. The low reabsorption of PL emission in CZTS, which enhances interference, can also be seen in band gap graded CIGS. Being aware of this issue is critical for correct interpretation of the measurements. We demonstrate approaches to obtain a PL spectrum less affected by interference effects. First, the spectrum can be corrected using measured reflectance data or a calculated interference function. This approach is moderately successful, but can be improved by introducing fit parameters. The second approach to reduce influence of fringing is to measure the sample at a large angle from the surface normal. The PL spectrum obtained at 75° tilt is only slightly affected by interference, while p-polarized PL collected at the Brewster angle remains more distorted. The PL spectrum of thin (<500 nm) or rough (RMS roughness > 120 nm) absorbers is less affected by interference. For future PL studies, it is recommended to verify whether interference effects could be important for a particular measurement. Tilting the sample when measuring PL and comparing to measured reflectance of the sample are two straightforward approaches.

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APPENDIX: CALCULATION OF INTERFERENCE FUNCTION

1. Interference function for smooth thin films

The approach taken for the determination of the interference function for smooth thin films is developed by Holm *et al.*¹⁰ In the following, we list the equations derived by Holm *et al.*, and define the parameters going into the model. The derivation is briefly explained, but not explicitly shown. See Ref. 10 for the detailed derivation. Since the interference function is compared to the total reflectance from the thin film/substrate structure in the main text of this paper, the equations for calculation of the optical reflectance are included.

First, we define the sample structure and the parameters needed to calculate the both the reflectance and interference function. Figure 10 shows three media 1, 2, and 3 corresponding to air with complex refractive index N_1 , CZTS thin film with complex refractive index N_2 , and thickness d and Mo substrate with complex refractive index N_3 , respectively. The complex refractive index is defined as $N_j = n_j + ik_j$ with $j = 1, 2, 3$, where n is the index of refraction and k is the extinction coefficient.

When calculating the interference function, the collected PL must be related to PL generated inside the layer. It is assumed that the PL is generated from depth z and collected at an angle θ_1 to the surface normal of the thin film. In a confocal setup, the excitation laser is likewise incident at an angle θ_1 . The refraction and reflection angles inside the CZTS film θ_2 can be determined by $\theta_2 = \sin^{-1}(n_1 \sin \theta_1 / n_2)$ from Snell's law.³²

To calculate the interference function and reflectance, the reflection and transmission at each interface must be known. This is described with the Fresnel coefficients defined as³²

$$\begin{aligned} r_{ij}^{(s)} &= \frac{N_i \cos \theta_i - N_j \cos \theta_j}{N_i \cos \theta_i + N_j \cos \theta_j} \\ r_{ij}^{(p)} &= \frac{N_i \cos \theta_j - N_j \cos \theta_i}{N_i \cos \theta_j + N_j \cos \theta_i} \\ t_{ij}^{(s)} &= \frac{2N_i \cos \theta_i}{N_i \cos \theta_i + N_j \cos \theta_j} \\ t_{ij}^{(p)} &= \frac{2N_i \cos \theta_j}{N_i \cos \theta_j + N_j \cos \theta_i}, \end{aligned} \quad (\text{A1})$$

where $r_{ij}^{(s,p)}$ and $t_{ij}^{(s,p)}$ denote the Fresnel reflection and transmission coefficients for s - or p - polarized lights when light is incident from medium i to j . In order to compare the sample reflectance to the interference function, the total reflectance of the structure is calculated. Assuming that the interfaces are smooth and flat, the reflectance amplitude of the structure is³²

$$r^{(s,p)}(\theta_1, \lambda) = \frac{r_{12}^{(s,p)} + r_{23}^{(s,p)} \exp(i\phi)}{1 + r_{12}^{(s,p)} r_{23}^{(s,p)} \exp(i\phi)}, \quad (\text{A2})$$

where ϕ is quantified by $\phi = \frac{2\pi N_2 \cos \theta_2}{\lambda} 2d$. The total reflectance of the thin film stack is then

$$R(\theta_1, \lambda) = \frac{1}{2} (|r^{(s)}|^2 + |r^{(p)}|^2). \quad (\text{A3})$$

In the following, it is briefly described how the interference function is obtained in the work by Holm *et al.*¹⁰ It is assumed that the photoluminescence originates from spontaneous emission of an ensemble of electric dipoles of equal magnitude but randomly oriented. The total radiated power is obtained by summing up the differently oriented dipoles incoherently. In other words, the orientation-dependent amplitude of the radiated field from up-going rays U_0 and down-going rays D_0 for each single dipole is first summed up. The absolute square is subsequently calculated to obtain the fraction of generated power that escapes the film, in other words, the emission probability for each dipole. Full sphere solid angle averaging over an ensemble of randomly oriented dipoles yields the following expression for the emission probability:¹⁰

$$P^{(s)}(\theta_1, \lambda) = \frac{1}{8\pi} \frac{n_2}{n_1} |t_{21}^{(s)}|^2 \frac{|1 + r_{23}^{(s)} \exp(i\delta)|^2}{|1 - r_{21}^{(s)} r_{23}^{(s)} \exp(i\phi)|^2}, \quad (\text{A4})$$

$$\begin{aligned} P^{(p)}(\theta_1, \lambda) &= \frac{1}{8\pi} \frac{n_2}{n_1} |t_{21}^{(p)}|^2 \\ &\times \frac{\left\{ 1 + |r_{23}^{(p)}|^2 + 2 \operatorname{Re} [r_{23}^{(p)} \exp(i\delta)] \cos(2\theta_2) \right\}}{|1 - r_{21}^{(p)} r_{23}^{(p)} \exp(i\phi)|^2}, \end{aligned} \quad (\text{A5})$$

where $\delta = \frac{2\pi N_2 \cos \theta_2}{\lambda} (2d - 2z)$. The expression in Eqs. (A4) and (A5) are equivalent to Eqs. (10) and (11) in the work done by Holm *et al.*¹⁰ but rewritten to suit the terminology of Fresnel coefficients defined in Eq. (A1). The full derivation can be found in the paper written by Holm *et al.*¹⁰

Assuming the distribution of luminescence centres $L(z)$ is homogenous, e.g., $L(z) = 1$, and that the excitation profile $E(z)$ to be proportional to the depth dependent laser intensity $E(z) \propto \exp(-\alpha_{\text{laser}} z / \cos \theta_2)$ with α_{laser} being the absorption coefficient of the CZTS layer at the laser excitation energy. The depth integrated interference function is obtained by integrating Eqs. (A4) and (A5) over the depth of the film

FIG. 10. Schematic illustration of PL generated in the CZTS film and collected at angle θ_1 to the surface normal. U_0 and D_0 denote up-going and down-going rays, respectively.

$$IF^{(s,p)}(\theta_1, \lambda) = \int_0^d L(z)E(z)P^{(s,p)}dz$$

$$= \int_0^d P^{(s,p)} \exp(-\alpha_{\text{laser}}z / \cos \theta_2) dz, \quad (\text{A6})$$

$$IF_{\text{total}}(\theta_1, \lambda) = \frac{1}{2}(IF^{(s)} + IF^{(p)}). \quad (\text{A7})$$

The interference function in Eq. (A7) is finally normalized as follows:

$$IF_{\text{norm}}^{(s,p)}(\theta_1, \lambda) = \frac{\int_0^d L(z)E(z)P^{(s,p)}dz}{\int_0^d L(z)E(z)dz}$$

$$= \frac{\int_0^d P^{(s,p)} \exp(-\alpha_{\text{laser}}z / \cos \theta_2) dz}{\int_0^d \exp(-\alpha_{\text{laser}}z / \cos \theta_2) dz}. \quad (\text{A7}')$$

2. Interference function for rough samples

The effect of roughness is added to the interference function by modifying the Fresnel coefficients according to scalar scattering theory.^{25,33} This approach was used in previous work to model the optical properties of a-Si:H solar cells with rough interfaces.³³ In our model, we consider the air/CZTS interface to be rough with RMS roughness σ_{rms} but the CZTS/Mo interface to be smooth. The specular part of the amplitude reflection and transmission coefficients for the light scattered from the rough surface is given in relation to the Fresnel coefficients defined in Eq. (A1) as the following:

$$r_{12}^{(s,p)\text{spec}} = r_{12}^{(s,p)} \exp \left[-\frac{1}{2} \left(\frac{2\pi\sigma_{\text{rms}}2N_1 \cos \theta_1}{\lambda} \right)^2 \right]$$

$$r_{21}^{(s,p)\text{spec}} = r_{21}^{(s,p)} \exp \left[-\frac{1}{2} \left(\frac{2\pi\sigma_{\text{rms}}2N_2 \cos \theta_2}{\lambda} \right)^2 \right]$$

$$t_{12}^{(s,p)\text{spec}} = t_{12}^{(s,p)} \exp \left[-\frac{1}{2} \left(\frac{2\pi\sigma_{\text{rms}}(N_1 \cos \theta_1 - N_2 \cos \theta_2)}{\lambda} \right)^2 \right]$$

$$t_{21}^{(s,p)\text{spec}} = t_{21}^{(s,p)} \exp \left[-\frac{1}{2} \left(\frac{2\pi\sigma_{\text{rms}}(N_2 \cos \theta_2 - N_1 \cos \theta_1)}{\lambda} \right)^2 \right]. \quad (\text{A8})$$

The interference function for samples with rough surfaces are obtained by following the procedures given for the smooth samples by replacing the Fresnel coefficients in Eqs. (A4) and (A5) with the expressions in Eq. (A8).

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