

# Influence of Cu content on the physical characteristics of $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$ thin films for intermediate band solar cells

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## Abstract

Intermediate band semiconductors can increase the efficiency of photovoltaic solar cells via sequential absorption of photons in a wider range of the solar spectrum. The introduction of Cr substituting Ga atoms in the chalcopyrite  $\text{CuGaS}_2$  is proposed to create a suitable intermediate band, investigating the influence of the Cu/Ga ratio on the structural, morphological, optical, and electrical characteristics. For this purpose,  $\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  thin films (with  $x$  ranging from 0.8 to 1.2) are prepared by modulated evaporation from elemental sources and analyzed comparatively by X-ray diffraction, Raman spectroscopy, atomic force microscopy, spectrophotometry, and Hall effect measurements. The incorporation of Cr produces an in-gap absorption that is independent of the Cu/Ga ratio. The mean crystallite size, surface roughness, and electrical conductivity increase with the Cu content in both  $\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$ .

## Introduction

Chalcopyrite  $\text{Cu}(\text{In},\text{Ga})(\text{Se},\text{S})_2$  (CIGS) thin films are being developed as photovoltaic absorbers for large-scale applications [1, 2], with great versatility because their direct bandgap can be tuned between 1.0 eV for  $\text{CuInSe}_2$  and 2.2 eV for  $\text{CuGaS}_2$  [3]. In these traditional photovoltaic semiconductors, electrons are directly excited from the valence band (VB) to the conduction band (CB) by absorbing photons, and thus, a low photocurrent is expected for pure  $\text{CuGaS}_2$  owing to its wide bandgap energy. Nevertheless, the introduction of transition metals substituting Ga atoms in the host material can give rise to a new intermediate band (IB), being with the Ti- and Cr-substituted systems the being most suitable to provide the desired properties [4, 5]. The formation of such IB is due to the hybridization of 3d valence electrons of the transition metals inserted in  $\text{CuGaS}_2$ , producing an enhancement in the absorption coefficient [6]. They can introduce a partially filled IB that enables three-photon transitions (from the VB to the IB, from the IB to the CB, and also from the VB to the CB), which allows for higher photocurrents without sacrificing the photovoltage [7]. Therefore,  $\text{CuGaS}_2$  is an ideal host material for intermediate band solar cells and can take advantage in exploiting CIGS-related technologies for high-performance photovoltaic devices.

It is known that Cu concentration has a great influence on the structural and electronic properties of CIGS films [8, 9]. Cu-rich conditions are generally used to achieve better chalcopyrite crystallization [10], but avoiding the segregation of secondary phases like  $\text{Cu}_x\text{S}$  or  $\text{Cu}_x\text{Se}$ , which are detrimental for the electrical performance [11]. About the techniques for material characterization and/or quality control, X-ray diffraction (XRD) is commonly used to identify the chalcopyrite structure and other crystalline phases in the semiconductor films [12]. Furthermore, the study of the vibrational properties via Raman spectroscopy is effective in analyzing both chalcopyrite and secondary phases in poor crystalline samples [12–14].

Stoichiometric  $\text{CuGaS}_2$  (that is with Cu/Ga  $\sim$  1.0) is usually chosen as host material for Ti or Cr incorporation, varying the Ti/Ga or Cr/Ga atomic ratio in the 0.02–0.14 range to create an intermediate band that is analyzed by optical measurements [7, 15–17]. Differences in the Cu/(Ti + Ga) or Cu/(Cr + Ga) ratios are generally produced with the Ti or Cr insertion, but the influence of the Cu proportion in the intermediate band compound is not clearly established. Nevertheless, it can be relevant for the structural, morphological,

and electrical characteristics that influence also the photovoltaic performance [18].

In this work,  $\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  thin films were deposited onto conventional soda-lime glasses by modulated evaporation from elemental sources. The Cu/Ga atomic ratio was varied from Cu-poor ( $x = 0.8$ ) to stoichiometric ( $x = 1.0$ ) and Cu-rich ( $x = 1.2$ ) regions in order to analyse-analyze comparatively the effect of Cu content on pure and Cr-substituted chalcopyrites. Superior crystalline quality of the Cu-rich samples is determined by XRD and Raman spectroscopy, while atomic force microscopy shows that the surface roughness increases with the mean crystallite size. Carrier concentration and electrical conductivity are also increasing with the Cu content. The effectiveness of Cr incorporation is proven by the optical detection of in-gap absorption for the various  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  layers.

## Experimental procedure

$\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  thin films were prepared by modulated flux deposition in a custom-designed evaporation chamber [19, 20] containing a rotating holder that transports soda-lime glass substrates cyclically around different areas: Cu, Ga, and Cr beam sources, heating lamps, and reactive sulfur region. Before use, the substrates were degreased with neutral soap, rinsed with deionized water, and dried in air. Once inside the evaporation chamber, the substrates were rotated at 30 rpm and heated at 450 °C during the deposition processes. This is the optimum temperature for single-phase chalcopyrite formation, typically used without softening effects on soda-lime glasses [1, 7]. The temperatures of the elemental sources were adjusted to obtain layers with different Cu/Ga ratios ranging from 0.8 to 1.2, as was established by compositional measurements with a Fischer X-ray fluorescence (XRF) analyzer. The evaporation time was fixed to gain a film thickness  $t = 300 \pm 10$  nm, which was verified by post-deposition measurements with a Dektak 3030 profilometer.

The crystallographic properties were examined by XRD with radiation Cu K $\alpha$ 1 ( $\lambda = 1.54056$  Å) using a Philips X'pert instrument with a Bragg–Brentano  $\theta$ – $2\theta$  configuration. Crystalline phases were identified by comparison with the cards from the Joint Committee of Powder Diffraction Standards (JCPDS). The degree of crystallinity was evaluated according to the Scherrer formula [3], which indicates that for a polycrystalline material the full width at half maximum of a diffraction peak is inversely proportional to the effective crystallite size.

The microstructure was analyzed with a B&W Tek system consisting of a BAC151B microscope and an i-Raman spectrometer, using as the excitation source a green laser of wavelength 532 nm and power 40 mW as the excitation source, with 21  $\mu\text{m}$  spot diameter on the sample. The topography was examined by atomic force microscopy (AFM) with a Park XE-100, taking digital images that allow to quantify the surface roughness.

The electrical conductivity, carrier concentration, and mobility were determined with an ECOPIA Hall Measurement System. Before electrical measurements, the samples were placed on a holder with four gold-plated spring-loaded pins, using Van der Paw configuration. Conductive Ag paste is added to improve pin contact to the layer. For optical characterization, transmittance ( $T$ ) and reflectance ( $R$ ) data were recorded with a double beam spectrophotometer Perkin–Elmer Lambda 9 in the wavelengths-wavelength range  $\lambda = 0.3$ – $1.5$   $\mu\text{m}$ , taking the bare glass substrate as  $T = 100\%$  reference. The beam spot size is about  $0.5$   $\text{cm}^2$ , placed in the middle of the  $2 \times 2$   $\text{cm}^2$  sample area.

## Results and discussion

The samples are named according to their elemental composition, as it is summarized in Table 1. All  $\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  films exhibit a tetragonal crystalline structure, according to the XRD patterns depicted in Fig. 1. The diffraction peaks around  $29.0^\circ$  and  $48.1^\circ$  are indexed to the (112) and (220) reflections of the chalcopyrite  $\text{CuGaS}_2$  [21], where each S anion is tetrahedrally coordinated to two Cu cations and two Ga cations. The intensities ratio,  $I(112)/I(220)$  in the Fig. 1 inset, has a minimum value for the stoichiometric layers (with Cu/Ga = 1.0) and increases in the other cases, more for the Cu-rich than Cu-poor samples. The availability of two different cations and the low defect formation energies allow massive

surface reconstructions, which make the polar {112} planes more stable than the non-polar {110} surfaces in the chalcopyrite structure [22, 23]. Depending on the composition of the crystallite, the cation terminated (112) surface is stabilized mostly by the formation of Cu vacancies ( $V_{Cu}$ ) in the Cu-poor case or by  $Cu_{Ga}$  antisites on the Cu-rich case [22]. The incorporation of Cr produces a slight displacement of the diffraction peaks toward the low-angle direction, similar to that observed in other works [17]. This indicates some lattice expansion, due to the ionic radius of  $Cr^{3+}$  that is slightly larger than  $Ga^{3+}$  [5].

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**Fig. 1** XRD patterns of  $Cu_xGaS_2$  and  $Cu_xGaCr_{0.1}S_2$  thin films with various  $x = Cu/Ga$  proportions. The inset shows the value of the intensities ratio

**Table 1** Compositional data obtained by XRF measurements for the various samples, with an experimental error of  $\pm 1$  at%

Sample	Cu (at%)	Ga (at%)	Cr (at%)	S(at%)
$Cu_{0.8}GaS_2$	22	26	0	52
$Cu_{1.0}GaS_2$	25	24	0	51
$Cu_{1.2}GaS_2$	28	23	0	49
$Cu_{0.8}GaCr_{0.1}S_2$	21	25	3	51
$Cu_{1.0}GaCr_{0.1}S_2$	25	24	2	49
$Cu_{1.2}GaCr_{0.1}S_2$	27	22	3	48

From each XRD pattern, the crystalline parameters ( $a$ ,  $c$ ) have been obtained from the measured interplanar spacings,  $\frac{1}{d_{hkl}} = \frac{1}{\lambda} \sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}$ , using the following equation for the tetragonal structure [24]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Besides, the mean crystallite size has been determined by the Scherrer formula:[3]

$$S_{(hkl)} = \frac{K\lambda}{\beta_i \cos \theta_i} \quad (2)$$

where  $\lambda$  is the X-ray wavelength,  $\beta_i$  is the full width at half maximum of the diffraction peak located at the  $\theta_i$  angle, and  $K$  is a constant that can take values from 0.6 to 2.0 depending on the crystallite shape and other considerations. In this paper, a value  $K = 0.9$  (which assumes cubic crystallites) is used to compare with related works [3, 24], taking into account that the calculated  $S_{(hkl)}$  values represent estimates.

Figure 2 shows the evolution of the crystal lattice characteristics as a function of the Cu/Ga ratio. For the  $Cu_xGaS_2$  films, the  $a$ -parameter decreases in the range  $a = 5.416$ – $5.352$  Å when the Cu proportion increases from  $x = 0.8$  to  $x = 1.2$ , while the  $c$ -parameter remains practically unchanged ( $c = 10.715 \pm 0.005$  Å). It is known that intrinsic point defects (like  $V_{Cu}$  or  $Cu_{Ga}$ ) cause variations of the anion position in the middle of the cation tetrahedron. In particular, Cu vacancies produce a displacement of anions into the direction of the Ga atoms, decreasing the average Ga–S bond length ( $R_{Ga-S}$ ) and increasing the lattice parameter  $a = (R_{Cu-S})^2 - (R_{Ga-S})^2$  [25]. Otherwise,  $Cu_{Ga}$  defects decrease the  $a$ -value, owing to the larger ionic radius estimated for Cu than Ga [25]. Then, the obtained results are consistent with a diminution of  $V_{Cu}$  defects and/or increment of  $Cu_{Ga}$  defects when the Cu proportion increases.  $Cu_xGaCr_{0.1}S_2$  samples evidence analogous evolution of the  $a$ -parameter with the Cu content, but also an increment in the  $c$  values, achieving a maximum  $c = 10.805$  Å for the layer with  $x = 1.2$ . These structural data are according to ab initio calculations [26], which indicate that the partial substitution of Ga by Cr in the host chalcopyrite produces small diminution in the  $a$ -lattice parameter and increment in the  $c$  dimension, with the subsequent enlargement of the tetragonal distortion ( $c/a$ ) value [26]. About the crystallite sizes, Fig. 2 shows that Cu-poor samples have small (112) and (220) facets, being  $S_{(112)} = S_{(220)} = 9 \pm 1$  nm for the layers with  $x = 0.8$ , independently independent of the presence or absence of Cr. Both facets enlarge in the most stoichiometric

films, being  $S_{(112)} = S_{(220)} = 13 \pm 1$  nm for  $\text{Cu}_{1.0}\text{GaS}_2$  and  $S_{(112)} = S_{(220)} = 10 \pm 1$  nm for  $\text{Cu}_{1.0}\text{GaCr}_{0.1}\text{S}_2$ . A further increment of the Cu content (to  $x = 1.2$ ) almost duplicates the  $S_{(112)}$  value, but now in detriment of  $S_{(220)}$ . This is attributed to the unique versatility of the  $\{112\}$  planes to accommodate structural defects, like  $\text{Cu}_{\text{Ga}}$  antisites in the Cu-rich samples [22].

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**Fig. 2** Evolution of the tetragonal lattice parameters (**a**, **c**) and the mean crystallite sizes ( $S_{(112)}$ ,  $S_{(220)}$ ) as a function of the Cu/Ga ratio

Raman spectroscopy is also a useful tool for structural characterization of thin films. Figure 3 includes the Raman spectra of the samples with various Cu/Ga ratios. These spectra were fitted with Lorentzians, as shown for the layer with Cu/Ga = 0.8 in the figure. The maximum intensity peak appears at  $300 \text{ cm}^{-1}$  and has been assigned to the  $A_1$  mode.[26] It arises due to the in-plane motion of S atoms, while the cations are stationary, and is the most intense mode among those expected for the chalcopyrite structure [27, 28]. Films with a higher Cu content exhibit a higher scattering intensity ( $I_1$ ) which is related to the crystallite size enlargement observed by XRD. The additional peaks detected at 256, 336, and  $370 \text{ cm}^{-1}$  are usually assigned to a combination of  $B_2$  and E modes [29], because these modes fall too close to each other to be resolved [30]. The high-frequency signals at 336 and  $370 \text{ cm}^{-1}$  are related to vibrations of the Ga–S bond, whereas the peak at  $256 \text{ cm}^{-1}$  is attributed to Cu–S bond vibrations [13, 15, 28]. The absence of peaks related to possible impurities or Cu–Au type ordering [27] is clear evidence of the single-phase nature of these chalcopyrite films. No significant variations in the peaks position and width have been detected for the layers prepared at different Cu/Ga proportions with or without Cr. Nevertheless, the ratio between the most intense peaks ( $I_1/I_2$  in the Fig. 3 inset) is found increasing with the mean crystallite size ( $S_{(112)}$  in Fig. 2). In fact, the intensity of the  $A_1$  mode has been used for monitoring the crystalline quality of other chalcopyrite films [31].

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**Fig. 3** Raman spectra corresponding to the  $\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  thin films with various  $x = \text{Cu/Ga}$  proportions. The inset shows the value of the intensities ratio

The surface morphology and the corresponding root-mean-square roughness ( $r$ ), determined by AFM for the various samples, are represented in Fig. 4. This shows that Cu-poor layers are constituted by small grains giving smooth surfaces, with  $r = 6$  nm for  $\text{Cu}_{0.8}\text{GaS}_2$  and  $\text{Cu}_{0.8}\text{GaCr}_{0.1}\text{S}_2$ . The increment of the Cu content promotes the formation of larger grains that clump together to form cauliflower-like clusters, in the same way as seen in analogous chalcopyrite films [10]. The surface roughness increases with the grain size, which can be favorable for solar cell applications. The density of grain boundaries should be low (large grains) to reduce the recombination rate and improve the photovoltaic performance [10]. Besides, a rough surface will trap more light and allows allow reducing the absorber film thickness [32]. The highest roughness corresponds here to  $\text{Cu}_{1.2}\text{GaS}_2$ , with  $r = 14$  nm, while  $\text{Cu}_{1.2}\text{GaCr}_{0.1}\text{S}_2$  gives a slightly lower value of  $r = 12$  nm. Limit in the Cu content is established ( $\text{Cu/Ga} \leq 1.2$ ) to prevent  $\text{Cu}_x\text{S}$  phase segregation [19]. A linear relationship between the roughness and the grain size is observed for the present samples, in agreement with the evolution of the (112) crystallite sizes obtained by XRD [3]. The distribution in a larger scale is illustrated in Fig. 5 for the Cu-rich layers, showing how the small grains are grouped in cauliflower-like clusters that are typical of chalcopyrite thin films [3, 24, 33].

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**Fig. 4** AFM images taken for the various  $\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  layers on  $2 \mu\text{m} \times 2 \mu\text{m}$  areas. The root-mean-square roughness ( $r$ ) is included for each sample

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**Fig. 5** AFM images for the Cu-rich layers on 10 μm × 10 μm areas

The electrical characteristics of the various samples are resumed in Fig. 6, where the carrier concentration ( $N$ ), mobility ( $\mu$ ), and conductivity ( $\sigma$ ) are plotted as a function of the Cu/Ga ratio. From the figure, it is evident that the carrier concentration has greater effect than mobility on the conductivity of the films, which are all p-type. The lowest conductivity values correspond to Cu-poor layers,  $1.3 \times 10^{-4}$  S/cm for  $\text{Cu}_{0.8}\text{GaCr}_{0.1}\text{S}_2$  and  $2.0 \times 10^{-3}$  S/cm for  $\text{Cu}_{0.8}\text{GaS}_2$ , being with the holes density of  $3.8 \times 10^{13}$   $\text{cm}^{-3}$  and  $4.9 \times 10^{14}$   $\text{cm}^{-3}$ , respectively. In similar Cu-poor  $\text{Cu}(\text{In,Ga})\text{Se}_2$  layers, it is known that the doping level increases by Na diffusing-diffusion from the soda-lime glass, a fact that is not discarded for the present samples. However, for Cu-rich compositions, the intrinsic doping level is so high that the presence or absence of Na has no influence [8]. The carrier concentration increases with the Cu content, up to  $10^{17}$ – $10^{18}$   $\text{cm}^{-3}$  for  $\text{Cu/Ga} = 1.0$  and to  $10^{19}$ – $10^{20}$   $\text{cm}^{-3}$  for  $\text{Cu/Ga} = 1.2$ . The same behavior has been reported for analogous  $\text{CuGaS}_2$  and  $\text{CuGaS}_2:\text{Cr}$  thin films [16, 33, 34], which is due to the influence of the material stoichiometry on the electrically active intrinsic defects. Several studies have shown that the compound defect consisting of  $2(\text{V}_{\text{Cu}})^- + (\text{Ga}_{\text{Cu}})^{2+}$  is energetically favorable in  $\text{CuGaS}_2$ , but it does not contribute toward the overall carrier density [22, 35]. The carrier concentration is mainly due to  $\text{V}_{\text{Cu}}$  and  $\text{Cu}_{\text{Ga}}$  defects, which provide one and two holes, respectively, and, therefore, the material can be p-type doped within a wide compositional range [35].  $\text{Cu}_{\text{Ga}}$  is a low formation energy defect in the Cu-rich material [36], where it provides carrier concentrations typically above  $10^{17}$   $\text{cm}^{-3}$  [24, 33]. Otherwise, Ga-rich samples show free carrier densities around  $10^{13}$   $\text{cm}^{-3}$ , which is attributed to the presence of isolated donor-like  $\text{Ga}_{\text{Cu}}$  defects [36, 37]. The incorporation of Cr onto a Ga site is favored in Ga-poor (that is Cu-rich) conditions, where  $\text{Cr}_{\text{Ga}}$  has to compete with  $\text{Cu}_{\text{Ga}}$  antisites. Thus, the decrease in free carrier density for  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  in comparison with equivalent  $\text{Cu}_x\text{GaS}_2$  samples indicates the change of some  $\text{Cu}_{\text{Ga}}$  acceptor defects to  $\text{Cr}_{\text{Ga}}$  antisites that are electrically neutral.

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**Fig. 6** Evolution of the carrier concentration, mobility, and conductivity as a function of the Cu/Ga ratio. The error bars (represented as the 30% of the mean value) are in the same order than the printed points

The optical transmittance ( $T$ ) and reflectance ( $R$ ) obtained for the  $\text{Cu}_x\text{GaS}_2$  and  $\text{Cu}_x\text{GaCr}_{0.1}\text{S}_2$  films as a function of the radiation wavelength are represented in Fig. 7, where each measured spectrum has been averaged from the respective maxima and minima envelop curves in order to eliminate the interference effects [38]. They indicate that the thickness  $t$  of the absorber layer is small enough to allow light reflected at the absorber/substrate interface (attenuated by the film absorption) to interfere with light reflected at the absorber/air interface, with analogous effects in transmittance. Then, the absorption coefficient ( $\alpha$ ) was calculated by the expression [6]:

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**Fig. 7** Optical transmittance and reflectance (averaged to eliminate interference effects) as a function of wavelength for the various samples. The average calculation is illustrated by showing the spectra measured for  $\text{Cu}_{0.8}\text{GaS}_2$  (solid lines) and  $\text{Cu}_{0.8}\text{Cr}_{0.1}\text{GaS}_2$  (dashed lines)

$$\alpha = \frac{1}{t} \ln \left[ \frac{1 - R}{T} + \frac{4TR}{(1-R)^2} \right] \quad (3)$$

The corresponding absorption spectra versus radiation energy are analyzed in Fig. 8. All samples have a same behavior in the high-energy region, where the photon absorption is due to the interband optical transition. These experimental data show a good fit to the expression  $a = A (E - E_g)^{1/2}$ , which corresponds to a direct transition from the valence band ( $E_V$ ) to the conduction band ( $E_C$ ) [3], as it is illustrated in the Fig. 8b. The calculated bandgap energy is  $E_g = E_C - E_V = 2.20 \pm 0.02$  eV, without significant dependence on the film composition. This is according to the bandgap energies reported for other polycrystalline CuGaS<sub>2</sub> and CuGaS<sub>2</sub>:Cr samples, which are typically in the 2.15–2.45 eV range [3, 7, 16, 17, 39], lower than for CuGaS<sub>2</sub> single crystal [40]. Otherwise, the film composition has a great influence on the sub-gap absorption characteristics. The lowest sub-gap absorption, compatible with small Urbach tails [8], is observed for Cu<sub>0.8</sub>GaS<sub>2</sub>. The increment of the Cu content produces an additional absorption around 1.9 eV in Cu<sub>1.0</sub>GaS<sub>2</sub> and Cu<sub>1.2</sub>GaS<sub>2</sub>, which is attributed to an acceptor level located 0.3 eV above the valence band. Theoretical calculations have given a charge transitional level located at  $E_V + 0.5$  eV for Cu<sub>Ga</sub> states in CuGaS<sub>2</sub> [37], experimentally identified by photoreflectance and photoluminescence measurements [41]. Cu<sub>Ga</sub> is a low formation energy defect that is expected to predominate in Cu-rich material and also in near-stoichiometric layers when the free-carrier density is above  $10^{17}$  cm<sup>-3</sup> [37]. Upon addition of Cr, the transition strength of the defect band is much suppressed and a broader absorption band appears [41], as seen in Fig. 8a. The sub-gap absorption plotted in the Fig. 8b inset shows two levels located at  $E_1 = 1.70 \pm 0.02$  eV and  $E_2 = 2.00 \pm 0.02$  for the Cu<sub>x</sub>GaCr<sub>0.1</sub>S<sub>2</sub> samples. Such optical characteristics can be assigned to the creation of an intermediate band by effective Cr incorporation [17, 41].

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**Fig. 8 a** Optical absorption coefficient,  $a$ , as a function of the radiation energy,  $E$ , for the various thin films. **b** Bandgap energy calculation and detail of the sub-gap energy levels determination from the respective  $a^2$  vs.  $E$  plot

Figure 9 illustrates the observed changes in the bands structure, due to Cu<sub>Ga</sub> defects in pure CuGaS<sub>2</sub> and Cr states in Cu(Ga,Cr)S<sub>2</sub>. For CuGaS<sub>2</sub>, the VB maximum is contributed by the Cu-3d and S-3p states and the CB minimum is derived from the Ga-4 s and S-3p states [17, 42]. After inserting Cr, additional levels appear because of structural changes. The Cr<sup>3+</sup> ([Ar] 3d<sup>3</sup>) ions substitute the Ga<sup>3+</sup> ([Ar] 3d<sup>10</sup>) in a tetrahedral crystal field environment, where the fivefold degenerated 3d orbital of Cr will split into two main manifolds: lower twofold degenerate e<sub>g</sub> states and upper threefold degenerate t<sub>2g</sub> states [43]. These partially filled and isolated Cr-3d states introduce an intermediate band that is represented in Fig. 9 according to the bibliography [42, 43]. Two of the 3d<sup>3</sup> electrons fill the majority spin e<sub>g</sub> states, and the third one lies in the t<sub>2g</sub>-type band, which is crossed by the Fermi level [43]. Electrons in the lower occupied IB states can transfer to the CB by absorbing photons with energy about 2.0 eV. Besides, electrons excited from the VB to the upper empty IB states can transfer to the CB through a non-equilibrium transition, by absorbing a second photon with energy around 1.7 eV. Such an in-gap band that supports the promotion of electrons from the VB to the CB through a two-photon absorption procedure has gained a great attention for thin film solar cells with enhanced efficiency [7].

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**Fig. 9** Scheme showing the bands-band structure for CuGaS<sub>2</sub>: defects-free (a) or with Cu<sub>Ga</sub> defects (b) and for Cu(Ga,Cr)S<sub>2</sub> (c)

## Conclusions

Chalcopyrite Cu<sub>x</sub>GaS<sub>2</sub> and Cu<sub>x</sub>GaCr<sub>0.1</sub>S<sub>2</sub> thin films ( $0.8 \leq x \leq 1.2$ ) are obtained by modulated evaporation,

with direct interbands transition  $E_g = E_C - E_V = 2.20 \pm 0.02$  eV in all cases. Cr incorporation is proven effective in creating a partially filled intermediate band that is independent of the Cu/Ga ratio. Otherwise, the crystalline quality, morphology, and electrical properties can be tuned by the Cu content.

All the Cu-poor layers (with  $x < 1.0$ ) are constituted by small crystallites (9 nm of mean size) that give smooth surfaces with low electrical conductivity ( $10^{-4} - 10^{-3}$  S/cm) due to small hole densities ( $10^{13} - 10^{14}$  cm $^{-3}$ ). The increment in the Cu content enhances the crystallization of (112) facets including Cu<sub>Ga</sub> antisites, which produce some shrinkage in the  $a$ -lattice parameter, whereas Cr<sub>Ga</sub> antisites created by the Cr incorporation enlarge the  $c$  dimension. Each Cu<sub>Ga</sub> antisite can provide two holes, while the Cr<sub>Ga</sub> antisites are electrically neutral. Thus, the Cu-rich layers (with  $x = 1.2$ ) achieve the highest hole densities ( $10^{19} - 10^{20}$  cm $^{-3}$ ), decreasing in this interval with the Cr incorporation due to the substitution of some Cu<sub>Ga</sub> by Cr<sub>Ga</sub> antisites. Besides, the surface roughness increases with the (112) crystallite size.

The rise in the holes density goes together with an increment of the sub-gap absorption by an acceptor level located at  $E_V + 0.3$  eV, attributed to the Cu<sub>Ga</sub> states in Cu<sub>x</sub>GaS<sub>2</sub>. The addition of Cr produces a broader sub-gap absorption band, with two maxima located at  $E_C - 2.0$  eV and  $E_C - 1.7$  eV for all Cu<sub>x</sub>GaCr<sub>0.1</sub>S<sub>2</sub> layers. This indicates the presence of a partially filled intermediate band, which allows electrons in the lower occupied IB states to transfer to the CB (by absorbing photons with  $E \sim 2.0$  eV), and also electrons excited from the VB to the upper empty IB states can be transferred to the CB (by absorbing a second photon with  $E \sim 1.7$  eV). These Cu<sub>x</sub>GaCr<sub>0.1</sub>S<sub>2</sub> films are suitable for improving the capture of the solar spectrum in advanced photovoltaic devices.

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