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Characterization of Cr Doped CuGaS₂ Thin Films Synthesized By Chemical Spray Pyrolysis

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ABSTRACT. Addition of an impurity or intermediate band in a semiconductor can extend its optical functionalities to novel application such as intermediate band solar cells (IBSCs). For this purpose, the optical and electronic characterization were performed on Chromium (Cr) doped (1-4%) chalcopyrite CuGaS₂ (CGS) thin films synthesized by chemical spray pyrolysis technique on glass substrates. The structural and chemical characterization studied in the past confirmed that the prepared films are in tetragonal chalcopyrite structure with polycrystalline nature [1]. In the present study, electronic transitions studied by photo-modulated reflectance (PR) measurements showed widened bandgaps when Cr was added, and agrees well with our calculation based on density functional theory (DFT). Native defect-related transitions typically observed within the bandgap of the host CGS semiconductor were reduced in the Cr added films. This observation is consistent with photo-luminescence (PL) spectra measured at room temperature. An additional signature of an impurity band emerged in the PR transitions for Cr-added samples. Analysis of spin-resolved density of state calculation suggests that the IB originates from spin-polarized bands.

Introduction. Addition of an intermediate band (IB) such as an impurity band can extend the functional limit posed by the conventional two-band character of semiconductor materials. For example, the concept of intermediate band solar cells (IBSC) makes use of an intermediate step to excite electrons from the valence band (VB) to the conduction band (CB) by two-step photon absorption (TSPA) of long wave-length photons that otherwise transpire through the material [2]. Detailed balance calculation predicts conversion efficiency of 65.1% for a three band solar cell (e.g. VB, IB, CB) under maximal solar concentration which is much higher than the conventional solar cell consisting two bands (e.g. VB and CB) [3]. The key operational demonstration of TSPA both at low [4] and room temperature [5-7] has been presented in a few IB systems of thin films and nanostructures despite much enhancement is needed in the magnitude of the TSPA driven current for practical application.

The quest for three band system have been spanned over various IB materials in recent years such as thin films of highly mismatched alloy (HMA) III-V dilute nitrides and II-VI oxides [5,8-10], deep impurity doped hosts [6], and nanostructures using quantum dots [11], quantum rings [12], etc. Key factors that drive IB formation process are different in each approach, and consist of host electronic structures, structural dimensionality, nature of the impurity atoms, etc. In HMA thin films, isoelectric impurities atoms with much different affinity and size in III-V and II-VI hosts modifies electronic structures remarkably with distinct three band features [13-15]. Low-dimensional structures such as QD array produce distinct mini-bands due to quantum-size effect [2]. Fabrication of large number in density and stacks of QD array can promote the needed optical absorption for IR-generated currents. In order to improve the IBSC efficiency, host materials with much wider band gap such as AlGaAs or InGaP are required [16].
For solar cells, Cu-based chalcopyrite semiconductors attract research interests mainly due to their higher absorption coefficients suitable for thin-film application. Of particular, the direct bandgap of CuGaS₂ or ‘CGS’ in short lies in the green region of the visible spectrum at room temperature [17]. It can be a suitable IB host since its bandgap of 2.4eV is relatively wide, and can accommodate impurity or IB bands sufficiently deep to avoid thermal escape of photo-generated carriers staying at the IB bands. Doping of transition metals in CGS has been predicted to be a potential candidate for IB solar cells [18]. Earlier reports for doping of transition metals such as Fe [19], V [20], Mn [21], Cr [22], Zn, Ti [23] to the CGS hosts have been predicted for the creation of IB. The valency match and the less distortion in lattice make the transition and rare earth elements to a suitable dopant for a chalcopyrite lattice.

Recently, we have reported that chemical spray pyrolysis deposition technique can be employed fabricating Cr doped CGS thin films on glass substrates maintaining polycrystalline qualities [1]. The addition of chromium didn’t produce any observable lattice changes in X-ray diffraction, presumably due to similar ionic radii and electron affinity. The pyrolysis technique is employed to extend its application to cost effective large scale production. In this paper, at first, we study the optical properties using photo-modulated reflectance (PR) and photoluminescence (PL) characterizations at room temperature. Next, electronic band structure and density of state analysis are performed based on density functional theory (DFT). Sub-bandgap transitions in PR and modification in PL in Cr added CGS thin films have been discussed in terms of the calculation.

**Experimental.** Thin films were synthesized by chemical spray pyrolysis technique on glass substrates. The precursor solution for the host CGS synthesis consists 0.1 M of copper acetate, gallium chloride and of thiourea dissolved in deionised water. For Cr doping, the molar concentration of chromium chloride was varied between (1-4 wt%). The follow-on mixture solution was deposited on glass substrates by the chemical spray pyrolysis technique. Temperature of the glass substrates was maintained at 250 °C. Obtained thin films thickness is in the range of ~ 2 μm. The thin films were single phase as confirmed by X-ray diffraction, and presence of Cr ions were characterized by X-ray photoelectron spectroscopy. Details of the synthesis and physical characterization is published elsewhere [1].

Photo-modulated reflectance (PR) spectroscopy was performed at room temperature utilizing a mechanically chopped 405 nm line of a 15 mW solid-state laser. The applied laser intensity for PR measurements was kept constant at 33 mW/cm². Details of the PR system is explained elsewhere [6]. Photo-luminescence (PL) spectroscopy was performed at room temperature utilizing 405 nm line of a 30 mW solid-state laser. In order to improve the PL signals by suppressing wave-guiding effect of the glass substrate, PL signal collection was made under total reflection condition monitored by reflectivity from glass in a secondary photo detector. The electronic structures were calculated based on density functional theory (DFT) of siesta code using GGA exchange-correlation functionals [24].

**Photo-modulated reflectance (PR) characterization.** PR spectra of the samples are shown in Figs. 1. The structures in the high energy regions are related to the host bandgap \( E_g \) \( (VB\rightarrow CB) \) transitions. The \( E_g \) values and width \( (\Gamma) \) of the transitions were retrieved using a third derivative low electric field model [25], which are 2.47 eV and 0.22eV for the present CGS film without Cr addition. The \( E_g \) and \( \Gamma \) values are 2.87 eV and 0.03 eV for 1% Cr, and 2.87 and 0.09 eV for 4% Cr-added samples, respectively. The high width values \( \Gamma \) indicate the presence of compositional and spatial inhomogeneity in the thin films. On the other hand, Cr addition extend the bandgaps of the host material from 2.47 eV to 2.87 eV. The long tails below the bandgaps are commonly observed in materials when compositional inhomogeneity is prominent. Inside the host bandgap, as shown in Fig. 1(a), there appears two additional transistions \( E_{D1} \) and \( E_{D2} \) involving defect bands of CGS native defects. With Cr addition, transition strength of both of the defect bands in Fig. 1(b) are much suppressed. This leads to an overall improvement of the PR background in the bandgap region, and observation of PR transistons \( E_{IB} \) below the \( E_g \) location in the Cr added thin films in Fig. 1(b). This transition feature
(VB→IB) indicates the emergence of an impurity band (IB) inside the gap. The energy position $E_{IB}$ is around 2.25 eV.

![PR spectra of CuGaS$_2$ thin films](image1)

**Fig 1.** Room temperature PR spectra of CuGaS$_2$ thin films without and with Cr impurities. PR features are assigned to two native defects $E_{D1}$ and $E_{D2}$ at low energy region, and an impurity bands $E_{IB}$ and bandgaps $E_g$ at high energy region. Least squares fits are drawn for the bandgaps.

**Photoluminescence (PL) studies.** Fig. 2 shows the PL spectra for CGS thin films with different level of Cr dopants. The sharp line at about 1.53 eV is grating-scattered light of the diode-pumped laser (405 nm or 3.06 eV). Another narrow peak at 1.91 eV also originates from the scattered light. Although in standard case optical filters are set to cancel scattered light out, such a measure was not taken in the present experiments in order to allow PL detection from hosts’ high bandgaps.

At low energy region, the 1.53 eV line overlapped with a native defect peak, assigned $E_{D1}$ in PR, and only faintly observed in the CGS without Cr. In the mid energy region, the broad and strong PL peak at the energy around 1.8 eV matches well with the PR assigned peak $E_{D2}$. This PL signals, in accordance with past reports on MOVPE grown samples [26], can be attributed to a defect band due to low Cu/Ga ratios (<0.84). A similar band is also observed in thin films produced under S-poor conditions, and annealing under S-overpressure has been shown effective to remove the defects [27]. In the present spectra, the $E_{D2}$ locations are nearly constant with minor red-shifts by around 20 meV in the Cr added samples. The PL intensities of the defect bands are observed reduced with increasing Cr in consistent with a similar trend in PR transition strengths of the defects, and can be attributed to a partial passivation of the native defects due to Cr addition. At the high energy region in Fig. 3, weak PL signals can be observed at around 2.33 eV for the CGS thin film without Cr, and nearly matches with PR assigned $E_g$ peak although around 100 meV away at 2.43 eV. This slight difference can be ascribed to the presence of long-low-energy tails observed in PR. Past report show that PL signals often are generated from tail states where strong photo-carrier trapping and re-trapping occur, and give rise to S-shape behaviour in temperature-dependent PL peak traces [28]. An improvement in material homogeneity can reduce this gap. The Cr-added samples did not produce $E_g$ related PL at photon energy up to 2.6 eV beyond which the direct beam of excitation laser affects PL background significantly, and perhaps buries the $E_g$ signals of Cr added samples underneath.

The inset of Fig. 2 shows the enlargement of the PL magnitude at the high energy region in which response from the IB band expected. Weak peaks can be observed for the Cr added samples nearly at the host $E_g$ location. Since PR analysis also suggests about the presence of the $E_{IB}$ nearby, it is difficult to differentiate the assignment of the peaks.
**Fig. 2.** Room-temperature PL spectra for the thin films with different Cr contents. PL peaks are assigned to transitions two native defects $E_{D1}$ and $E_{D2}$ at low energy region, and bandgaps $E_g$ at high energy regions.

The inset 2 shows the enlargement of the PL magnitude between 2.2 – 2.6 eV in which response from the IB band expected.

**Band structure analysis.** In order to analyse the electronic structure, band structures were calculated by first principles theoretical calculations based on density functional theory (DFT). The $2\times2\times1$ super-cell considered in the present work is a 64-atom system consisting four units of conventional 16-atom chalcopyrite tetragonal cells stacked along the x- and y-axes. The corresponding symmetry of the super-cell is the space group $81: P4\overline{3}$. In the supercell, one Ga atom was replaced with the Cr atom accounting to the impurity concentration is about 1.56% in total, and 6.25% in Ga sites (or, $x = 0.0625$). This value is comparable to that used in the present experiments.

Calculations have been performed with the SIESTA code [24], an ab initio periodic density-functional method, self-consistent in the local density approximation. Norm-conserving, nonlocal pseudopotentials and linear combination of atomic orbitals have been used. The exchange-correlation effects of the valence electrons were described through the generalized gradient approximation (GGA), within the Perdew-Burke-Ernzerhof (PBE) functional. The Monkhorst-Pack scheme was set $6\times6\times6$ for the pure case, and $3\times3\times3$ for the doping cases for Brillouin zone sampling. In order to get accurate results, we optimized atomic coordinates, which were obtained by minimizing the total energy and atomic forces. The relaxation run was considered converged when the force on the atom was less than 0.04 eV/Å. Before relaxation, experimental values of CGS lattice constants were set, $a=5.3512$ Å and $c/2a=0.98$ [29]. Then we calculated the electronic structures for each optimized model.

Fig. 3 show the band structures along the high symmetrical directions of the Brillouin zone for the CGS and Cr doped crystals. As observed, the band structure of Cr-doped CGS is nearly same to the non-doped one, except that the band-gap is widened and an intermediate band appears in the bandgap. More importantly, the Fermi level exists inside the intermediate band. This suggests that the IB band is partially filled, which is a key requirement in order to realize an operational IBSC via TSPA process. The lowest band gap between the VB and CB is located at Γ point, and it’s a direct bandgap with a value of 0.64 eV for the non-doped and 0.88 for the Cr-doped crystals. Although experimental values of our CGS is around 2.4 eV [1], such an underestimation of the calculated bandgaps is an inherent feature of the DFT method.
Fig 3. The bulk electronic band structure for CuGaS₂ (left) and CuGaCrS₂ (right) in the DZ-GGA calculations after dynamical relaxation. Spin orientation was set random. The Fermi level of the compound has been set at the energy zero. The diagram is displayed in the main directions of the corresponding first Brillouin zone.

Density of states analysis (DOS). The IB band was confirmed by analysing the DOS of the Cr doped CGS. Spin resolved total density of states (DOS) over all atomic orbitals are shown in Fig. 4. The Fermi level has been set at the energy zero. The partially filled IB mainly contains up-spin states while the down spin states maintains the conventional two-band character. These situations fulfil a key requirement in order to realize efficient two-step photon absorption (TSPA) process.

There is another spin-band around 0.40 eV below the conduction band (CB). The PR retrieved $E_{IB}$ location is of similar order deeper from the CB, and can be ascribed to the spin-band in Fig. 4. However, further verification is needed to confirm the origin. Because a wide separation of the IB band can limit the thermal excitation of IB electrons and can promote photo-excitation via TSPA, this upper IB band can be made optically active for TSPA if suitable filling of the band can be designed.
Fig 4. Spin resolved total density of states (DOS) over all atomic orbitals in CuGaS$_2$ with Cr doping. The Fermi level has been set at the energy zero.

Summary. The key finding of the present study is the observation of sub-band gap optical response for Cr doped CGS thin films, and its assignment to an intermediate band by means of theoretical band structure evolution.

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