



## How different are CZTS grain boundaries ?

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### ARTICLE INFO

#### Article history:

Received 8 September 2020

Accepted 27 October 2020

### ABSTRACT

No, defects are not always bad. Vacancies, antisites, or impurities are in general trapped at the grain boundaries and contribute to scattering (of charge carriers). In general, grain boundaries reduce the performance (efficiency of the solar cell). However, there are certain materials where the defects enhance performance. CdTe, CuInSe<sub>2</sub> (CIS), Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) are a few examples. The present work involves CAFM studies on CZTS films deposited to Si and soda-lime glass substrate to explore the underlying physics behind unique grain boundary physics in CZTS. Discussions are made in the light of the reactions that take place on CZTS surface and corresponding energy band diagrams are drawn

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Do single crystalline semiconductors outperform their polycrystalline counterparts in photovoltaic performance? In general yes, however, this is *not always true*. There is a certain class of materials where polycrystalline materials show more efficiency than their single crystalline counter parts e.g.: CdTe, CuInSe<sub>2</sub> [1], etc. Grain boundaries (GBs) is what makes the difference between single crystalline and polycrystalline materials. The fact that polycrystalline form of CdTe and CuInSe<sub>2</sub> solar cells have more efficiency points at anomalous grain boundary physics in these materials [2]. When a part of In in the lattice of CuInSe<sub>2</sub> is replaced by Zn and the other part by Sn Cu<sub>2</sub>ZnSnS<sub>4</sub> structure is realized [3]. Zn, Sn are relatively more abundant in the earth's crust compared to In, and in this aspect CZTS is commercially significant compared to CIS. The fact that poly CdTe and CuInSe<sub>2</sub> have more efficiency makes these materials unique and inexpensive for scaling up, however, does CZTS display this property? The present work is an answer to this question.

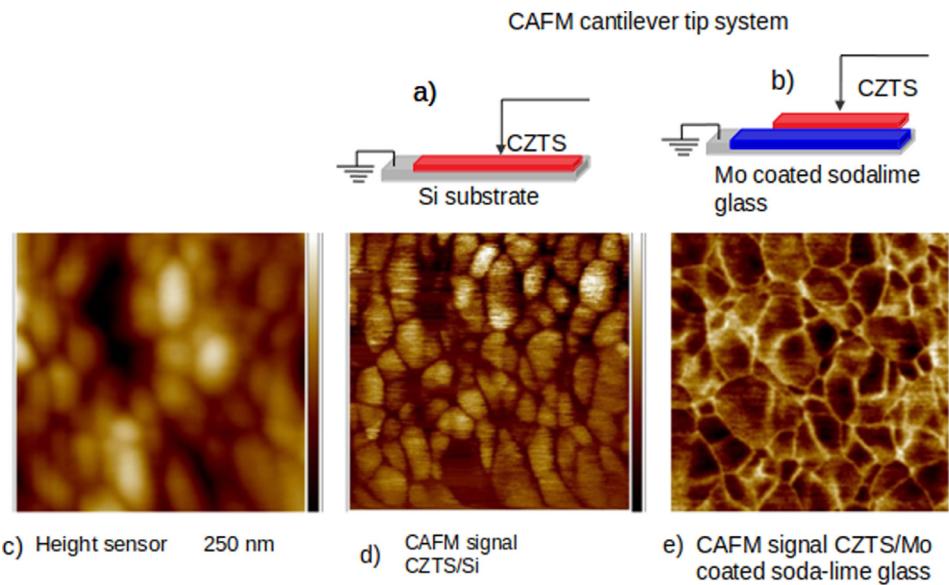
In CdTe, the GBs as such do not show any unique GB physics, however, they are passivated by annealing in CdCl<sub>2</sub> atmosphere. Cl substitutes for Te, which donates one electron to the conduction band, and moves the Fermi level nearer to the conduction band [4]. It also pushes the mid-bandgap states into the valence band and hence "cleansing" the gap and reducing the recombination, thus enhancing the CdTe/CdS device performance. Thus it is the external passivation of the GBs in CdTe that leads to unique GB physics. However, the situation chalcogenide CuInSe<sub>2</sub> is different. Yanfa yan et al., reported that in chalcogenides, this property

is due to (i) hole reflector model and (ii) passivation of GBs by diffusion of sodium from soda-lime glass substrate [5]. There are several studies on CuInSe<sub>2</sub> (or CuInGaSe<sub>2</sub>) both theoretical and experimental. Some studies support the hole reflector model based on the defects trapped at the grain boundaries [6], whereas strong experimental evidence have been reported by various other groups that support the passivation of the grain boundaries model [7,8]. There have been some reports on CZTS grain boundary physics which prove that it is passivation of Gbs by Na, K diffusion that leads to electrically benign grain boundaries [9–12]. The effort of this work is to put all the points together with experimental evidence, to see a) if or not the hole reflector is a right explanation for the observed anomalous grain boundary physics in CZTS or b) is it the only external passivation of grain boundaries that contributes to the high efficiency polycrystalline solar cells, c) what kind of reactions take place at the surface due to diffusion of Na from the substrate and support the results with fundamental physics associated with the materials. Hence a proper design of the samples is important to decouple both the effects, i.e., the hole reflection, and external passivation of grain boundaries model. Since there is no diffusion of any impurities or alkali elements from Si substrate, CZTS films are deposited on Si to study part a) and CZTS deposited on Molybdenum (Mo) soda-lime glass for part b).

CZTS films with a little Cu-poor and Zn rich conditions were prepared using hydrazine free nano-ink by drop-casting it on Si and Mo coated soda-lime glass substrates and heated it at 250 °C for 5 mins to drive away organic solvents and then heated at 500 °C for 1 h in N<sub>2</sub> atmosphere. High pure copper (II) acetate monohydrate (Sigma Aldrich), zincacetate (Alfa Aesar), tin chloride penta hydrate (Sigma Aldrich), and elemental sulphur (SigmaAldrich) dissolved in oleylamine (Sigma Aldrich) were used as precursors for

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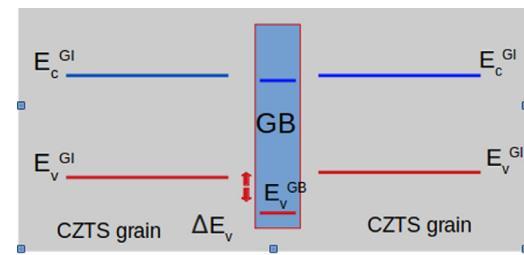
**Fig. 1.** a), b) Schematic of CAFM tip and sample system for CZTS on Si and Mo coated soda-lime glass substrates respectively, c) topography image, d), e) current maps recorded on a) and b) respectively

the synthesis of nano-ink. In the present work, CZTS nano-ink was prepared from the hot-injection technique [3,13,14]. Thin films on Si as well as Molybdenum (Mo) coated soda-lime glass substrates were prepared. Conductive atomic force microscopy (CAFM) studies were carried out using Bruker dimension edge model scanning probe microscopy. Topography and current sensing images were recorded simultaneously. SCM-PIT (Platinum, Yrridium coated Si tip) tip was used for CAFM studies.

CAFM corresponds to the contact mode of recording topography as well as current images. All images were recorded on 250 nm x 250 nm area of CZTS. Fig. 1a and 1b corresponds to a schematic of tip-sample systems of CAFM studies on CZTS coated on 1a) Si substrate and 1b) on Mo coated soda-lime glass substrate, the films are under the CAFM tip. Grey color represents substrates in both the cases (a) Si, b) soda-lime glass), red color represents CZTS and blue represents Mo. Fig. 1c corresponds to the height sensor image, while Fig. 1d, 1e correspond to current map images of CZTS on Si and Mo coated soda-lime glass substrates respectively.

From the CAFM results, in Fig. 1d) the current image for CZTS deposited on Si, currents at the interior of the grain, and grain boundaries can be observed. The scale on the right side of each image shows the variation in the current. Dark regions correspond to lower currents, while bright regions correspond to relatively high current. Grain boundaries correspond to low current, while the interior of the grains has high currents. The relation between the current at the interior of the grains and grain boundaries to hole-reflector model will be the content of the discussion that follows

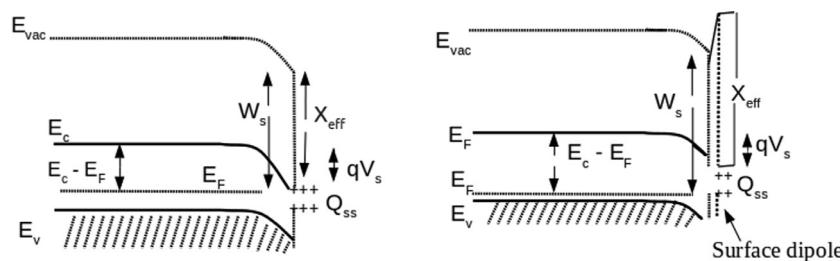
CZTS is a polar semiconductor. Polar semiconductors have a surface charge that creates instability and to obtain stability, neutralizing the surface charge is essential. Hence polar semiconductors undergo a structural rearrangement that involves the creation of defects, that are energetically less costly to neutralize the charge on the surface [15]. CZTS is intrinsically a p-type semiconductor where the valence band edge is made up of Cu 3d electrons and the conduction band edge is made of S 3P electrons. The defects that are created to neutralize the charge involve  $V_{Cu}$  and  $Zn_{Cu}$  defects which are trapped at the grain boundaries. Since the valence band is made of Cu 3d electrons and Cu vacancies are trapped at grain boundaries the p-d repulsion between the S 3p electrons and Cu 3d electrons pushes the valence band edge at the GBs a little lower, creating a valence band offset [16,17], as shown in Fig. 2.



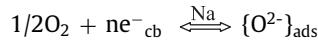
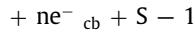
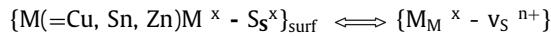
**Fig. 2.** Valence band offset between grain interior (GI) and grain boundary (GB) of CZTS. Valence band and conduction band energy levels  $E_v$  and  $E_c$  on either side of grain boundary are shown.  $\Delta E_v$  - Valence band offset, GB - grain boundary, GI - grain interior

Cu vacancies are known to form a shallow acceptor level in CZTS and hence CZTS is a p-type semiconductor [18,19]. The holes see a potential barrier at the GB and get repelled from the GB, hence the electrons do not find the holes at the grain boundaries which reduces the recombination (at the GBs) and hence unique grain GBs in these materials happen by hole reflection from GBs. In case the hole reflector model is what explains the unique grain boundary physics in CZTS then it is supposed to show this nature even in the absence of Na or K presence at GBs. If the Cu vacancies trapped at the grain boundaries creates valence band offset then the holes generated at the grain boundaries should get reflected from the GBs, and the current map images from CAFM should show high current at the grain boundaries, however the results are indifferent to what is anticipated. These results rule out the possibility of the hole reflector model contributing unique grain boundary physics in CZTS.

Similarly, CAFM studies were carried out on CZTS deposited on Mo coated soda-lime glass substrate. In this case, the CAFM images show relatively bright regions at grain boundaries that correspond to high currents. However, here the catalytic role Na that diffused to GBs from the substrates plays a crucial role. The chemical reactions that take place on the surface of CZTS and the effect of Na diffusion on the reactions help us gain insights into the CAFM results on the soda-lime glass substrate. Kroger-Vink notation is used to understand the Na induced reaction in CZTS [20].



**Fig. 3.** Energy band diagrams that schematically show the effect of  $O_2^-$  released by catalytic of Na on  $O_2$  molecule on band bending, surface charge and electron affinity before and after surface oxidation effect.  $E_{vac}$  vacuum energy level,  $E_c$  conduction band level,  $E_v$  valence band level,  $E_F$  fermi level,  $X_{eff}$  is the effective electron affinity,  $Q_{ss}$  is the charge in the surface states,  $W_s$  is work function at the surface,  $qV_s$  is the band bending



$M$  represents metal (Cu, Zn, Sn), subscript corresponds to the site occupied, ' $M$ ' by the metal  $M$ , ' $s$ ' corresponds to sulphur site, ' $surf$ ' and ' $cb$ ' represent surface and conduction band respectively. The superscripts represent the charge. ' $x$ ' corresponds to neutral charge, while ' $+$ ' corresponds to positive charge and ' $n$ ' is an integer that denotes the amount of positive charge. Sulphur in CZTS is in bond with metals Cu, Zn, Sn in the lattice. Since the high efficient CZTS solar cells involve the active layer that is synthesized/deposited under Cu-poor and Zn-rich conditions [21], in the present case also, the samples are prepared under such conditions, this may confine  $M$  in the above reactions to either Zn or Sn. Sulphur is very volatile material and during sulphurization it is highly possible that sulphur vacancies may be created [22]. When sulphur vacancies are created ( $V_s$ ) electrons are contributed to the conduction band, reducing the p-type doping of CZTS [23], this is shown in reaction 1. Sodium that diffuses from soda-lime glass to the active layer is trapped at the grain boundaries, this sodium breaks the  $O_2$  (physisorbed on the surface) molecule at grain boundaries into O atoms, this O ( $O^{2-}$ ) and can attract positively charged sulphur vacancies, these are represented in reactions 2 and 3. This is shown in reaction 3.  $O_s$  creates a shallow acceptor level that drives CZTS p-type [23]. The changes in the band diagram as a result of the above reaction are shown in Fig. 3a and 3b

Sodium catalytic action breaks  $O_2$  mole into atoms leaving  $O^{2-}$  on the surface at the grain boundaries. The effect of such reaction on band bending, surface charge ( $Q_{ss}$ ), effective electron affinity are schematically shown in the band diagram. When S vacancies are eliminated it reduced band bending at the grain boundaries. Difference in band bending in the presence and absence of S vacancies are shown in Fig. 3a and 3b respectively, given by  $qV_s$ . Also,  $O_s$  dopes CZTS p-type and also forms an acceptor level. This is shown by the Fermi level ( $E_F$ ) shift closer to the valence band. When O forms bond with metal M, a bond is formed which does not exist before and this creates a surface dipole that increases the effective electron affinity (when extra charge adds to the surface more energy needs to be spent to remove the electron from the conduction, this increase in electron affinity). The formation of dipole at the surface is shown in Fig. 3b.

Thus our experiments support that it is the catalytic action of Na that is actually passivating grain boundaries at CZTS, leading to unique grain boundary physics. However, can the hole reflector model be ruled out?, as it cannot explain the unique property in kesterites. Before any conclusive statements are made, it is neces-

sary to look at bigger picture and take a stand on this. Whether hole reflector model or formation of ordered defect compounds in ternary chalcogenides, both are related to the intrinsic nature of polar semiconductors to attain charge neutrality explained by the equation  $\Delta H_f(\alpha + \beta) = \Delta H_f(\alpha) + \Delta H_f(\beta) + \Delta H_{int} + \Delta H_{ord}$  [24]. It is a very interesting field of inquiry to investigate into why hole reflector model has not been experimentally proven, even if ordered defect compounds have been studied in ternaries (though not in quaternary CZTS). In  $CuInSe_2$ , formation ODC ( $CuIn_3Se_5$ ), gives rise to type inverion and hence homoepitaxy [25,26]. In addition to  $CuIn_3Se_5$  ternary chalcogenides have various other compounds such as  $CuIn_5Se_8$ ,  $Cu_2In_4Se_8$  etc., that can be generated by a general formula discussed by Zhang et al [24]. In our previous work we have reported that on Cu-poor and Zn-rich samples, no evidence to support the formation of order defect compounds was observed [27]. However, it is very important to understand what is form of ODCs in CZTS? May be if the actual form of ODCs in CZTS are explored then: a) ODCs invoke type inversion at the surface improves the efficiency, they may validate hole reflector model (reduced the grain boundary scattering), c) this along with alkali catalyzed passivation of grain boundaries might be important factors to improve the efficiency. Hence a systematic study in this direction is important to properly assess the materials properties and models.

Nanocrystalline CZTS films were deposited on Si as well as Mo coated soda-lime glass substrates. From the CAFM results, relatively bright regions (corresponding to high currents) were observed at grain boundaries for CZTS/Mo/soda-lime glass substrate and the other way for CZTS/Si system. This is attributed to the catalytic action of Na or  $O_2$  (in case of CZTS/Mo/soda-lime). The reactions at the surface of CZTS are explained by Kroger-Vink notation and equivalent band energy diagrams are presented.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgment

The authors thank Department of Science and Technology (DST), New Delhi for facilitating the establishment of "Nano Functional Materials Technology Center" (Grant: SRNM/NAT/02-2005) at IIT Madras. The authors MSR and SKS are thankful for financial help obtained through the DST project (DST/TM/SERI/2K11/111).

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