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Chemical Insights into the Instability of Cu_2ZnSnS_4 Films during Annealing

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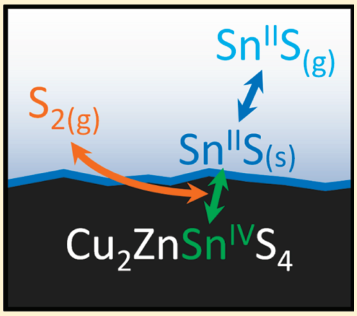
ABSTRACT: Cu_2ZnSnS_4 (CZTS) shows great potential for cheap, efficient photovoltaic devices. However, one problem during synthesis of CZTS films is the loss of Sn as a result of decomposition and evaporation of SnS. This paper uses kinetic models to show that the mechanism of the decomposition reaction probably occurs in at least two stages; first, a loss of sulfur which causes dissociation of the structure into binary sulfides, and only then the evaporation of SnS. Knowledge of the reaction mechanism helps to identify the driving force for decomposition as arising from the relative instability of Sn(IV) in CZTS against reduction; this theory is backed up by thermodynamic data. The volatility of SnS further exaggerates the decomposition by rendering it irreversible. This insight, alongside experimental data, allows prediction of the annealing conditions required to stabilize CZTS surfaces. A fundamental incompatibility of CZTS with high-temperature, vacuum-based processing is exposed, distinguishing it from related indium-containing compounds. This offers an explanation as to why the most efficient CZTS devices to-date all arise from “two-stage” fabrication processes involving low temperature deposition followed by annealing at high pressure, and provides key information for designing successful annealing strategies.



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■ INTRODUCTION

$Cu_2ZnSn(S,Se)_4$ films show potential for efficient, sustainable photovoltaic devices, with record device efficiencies of around 10%.[1] In terms of the pure sulfide material Cu_2ZnSnS_4 (CZTS), the best results so far are around 7%.[2,3] Several of the key properties of CZTS, for example band gap and carrier type, are analogous to those in the related and well-studied indium containing material $CuInS_2$, from which CZTS is derived conceptually by isoelectronic substitution. One aspect in which CZTS is very different from $CuInS_2$, however, is in its stability, in particular, the stability of the film surface under typical high-temperature (>500 °C) processing conditions. In CZTS, losses of Sn have been observed in many cases during film synthesis, and have been attributed to the evaporation of SnS from the film.[4,5] Recently, Redinger et al. showed that SnS losses from CZTS films were reversible, with films of Cu_2S and ZnS being converted to CZTS in the presence of sulfur and SnS vapor.[6] In the same study, they also highlighted the dramatic impact that surface decomposition can have on device performance.

The ability of decomposition products to vaporise is a particular problem for surfaces, because the products can be transported away from the reaction site, rendering the reaction irreversible. The quality of the CZTS film surface is crucial for the function of a photovoltaic cell, since this surface forms one-half of the heterojunction that separates photogenerated carriers. The difficulty of detecting surface-localized decomposition coupled with the vital importance of surface quality make the understanding of surface decomposition in CZTS especially relevant in the effort to improve device efficiency.

Our aim was to investigate more deeply the problem of CZTS surface decomposition. This paper is structured as follows: In the following paragraphs, we use a theoretical approach to form kinetic models for two possible decomposition pathways. In part A of the Results section, the kinetic models are compared against some experimental measurements and the most realistic model is chosen. Part B of the results sections deals with the implications of the selected model, which leads to some insights into the thermodynamic origins of the instability in CZTS, which are elaborated with reference to literature data. Application of the same reasoning to $CuInS_2$ shows that CZTS is significantly less stable than its indium-containing relative. Finally, we make some conclusions about the stability of CZTS during single-stage and multistage processing.

Derivation of Kinetic Models of CZTS Decomposition. The first model, model I, is for a single step decomposition reaction as reported previously,[6] in which S_2 and SnS are evolved directly (and reversibly) into the gas phase

$$Cu_2ZnSnS_4(s) \rightleftharpoons Cu_2S(s) + ZnS(s) + SnS(g) + \frac{1}{2}S_2(g) \qquad \text{(reaction 1)}$$

The choice of S_2 as the standard state for sulfur vapor is valid under most conditions of CZTS synthesis. Although saturated sulfur vapor is a mixture of oligomers $S_n(g)$, where $n = 1, 2, 3, ..., 8$, the proportions of the different species depend on the temperature and total sulfur pressure. A detailed discussion of the physical properties of sulfur vapor can be found elsewhere,[7] but in short, when we are dealing with unsaturated sulfur

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atmospheres at sulfur pressures lower than around 100 mbar and temperatures above 300 °C, S_2 is by far the dominant component of the vapor. We can then consider the partial pressure of S_2 to be the same as the total pressure of sulfur vapor.

Considering first a perfect CZTS surface, random fluctuations leading to decomposition events will occur at a constant rate, expressed as the rate constant k_d, with units of mol cm^{-2} s^{-1}. These fluctuations can be for example lattice vibrations, which depend on the thermal energy. k_d is therefore an exponential function of temperature, according to the Boltzmann model. If S_2 and SnS are not present in the gas phase, the CZTS surface will decompose at a maximum rate, k_d. If S_2 and SnS are present in the gas phase, then decomposition can be reversed to some extent, and the Cu_2S and ZnS units left on the decomposed surface can be reconverted to CZTS. The rate of this depends on the pressure of SnS and the square-root of the pressure of S_2 (because only half an S_2 unit is generated in each decomposition event). The overall decomposition rate is

$$R_I = k_d - k_c p_{SnS}(p_{S_2})^{1/2} \qquad \text{(eq2)}$$

where k_c is a rate constant for CZTS crystallization from solid Cu_2S, ZnS and gaseous SnS and S_2. We have made the usual approximation that the chemical activity of all solid phases is unity, and that the activity of the gaseous species is equal to their partial pressure (valid at pressures below around one atmosphere). We are also making the assumption that blocking of the surface by the decomposition products Cu_2S and ZnS can be neglected. Furthermore, throughout this analysis we are neglecting reactions involving the less stable Cu−Sn−S phases, i.e., we are assuming that sufficient Zn is present that the quaternary compound is always favored.

If heated in a sealed system, a sample of CZTS would, according to reaction 1, generate a pressure of vapor with a 2:1 molar ratio of SnS and S_2. The net decomposition rate R_I will become zero when the pressures of SnS and S_2 reach their equilibrium values, $p^c_{S_2}$ and p^c_{SnS}, i.e., when the rate of decomposition and regeneration exactly oppose each other. $p^c_{S_2}$ and p^c_{SnS} are the equilibrium vapor pressures of S_2 and SnS above CZTS, and are functions of temperature. In this situation we have the equality

$$p^c_{SnS}(p^c_{S_2})^{1/2} = \frac{k_d}{k_c} \qquad \text{(eq3)}$$

eq 2 can be rewritten with reference to the equilibrium situation, as follows

$$R_I = k_d\left\{1 - \frac{p_{SnS}}{p^c_{SnS}}\left(\frac{p_{S_2}}{p^c_{S_2}}\right)^{1/2}\right\} \qquad \text{(eq4)}$$

This tells us that the minimum requirement to avoid decomposition (to make R_I zero) is that the product p_{SnS} $(p_{S_2})^{1/2}$ exceeds the product p^c_{SnS} $(p^c_{S_2})^{1/2}$ at the given process temperature. If either or both of S_2 and SnS are absent from the gas phase, then the decomposition rate R_I is equal to k_d, and the CZTS surface will continually decompose. Stability of CZTS in this scheme cannot be achieved unless both SnS and S_2 are present in the vapor phase.

One problem with model I is the assumption that the SnS generated goes directly to the gas phase as decomposition occurs. If instead the SnS molecules reside on the CZTS surface for a certain time before evaporating, they may participate in further solid state reactions, for example the regeneration of CZTS (the reverse of reaction 1). The separation of chemical reactions into elementary steps is a prerequisite for developing good kinetic models for them. Therefore, we propose a second model (model II) for the decomposition, based on the two stages shown below

$$Cu_2ZnSnS_4(s) \rightleftharpoons Cu_2S(s) + ZnS(s) + SnS(s) + \frac{1}{2}S_2(g) \qquad \text{(reaction2)}$$

$$SnS(s) \rightleftharpoons SnS(g) \qquad \text{(reaction3)}$$

The first step here corresponds to decomposition of CZTS, when it goes in the forward direction. All decomposition products remain on the surface except S_2. The second step is the reversible desorption of SnS from the surface into the gas phase.

Beginning from a perfect CZTS surface, we consider reaction 2. As before, fluctuations leading to the decomposition of a CZTS unit occur with rate constant k_d. If the sample is in a vacuum, the evolved S_2 molecules are removed, and the decomposition is irreversible. Under such conditions, decomposition of CZTS occurs at its maximum rate, k_d. If S_2 is provided in the vapor phase, as is nearly always the case, then decomposition may be reversed. In the presence of the solid phases Cu_2S, ZnS, and SnS, the rate of the reversal depends only on the partial pressure of S_2, raised to the power 1/2. The rate of reversal is equal to $k_c p_{S_2}{}^{1/2}$, where k_c is a rate constant for crystallization of CZTS from the binary sulfides and S_2 vapor. In the presence of all phases shown in reaction 2, the net rate of decomposition is

$$R_d = k_d - k_c(p_{S_2})^{1/2} \qquad \text{(eq5)}$$

To attain equilibrium, where R_d is zero, we find that there is a unique value of sulfur pressure required, equal to k_d/k_c, or to the equilibrium constant for CZTS decomposition, K_{CZTS}. This pressure we define as the equilibrium partial pressure of sulfur above a CZTS surface, and it is only a function of temperature

$$(p^c_{S_2})^{1/2} = \frac{k_d}{k_c} = K_{CZTS} \qquad \text{(eq6)}$$

Using this definition, we can rewrite the net rate of decomposition as:

$$R_d = k_d\left\{1 - \left(\frac{p_{S_2}}{p^c_{S_2}}\right)^{1/2}\right\} \qquad \text{(eq7)}$$

This simply shows that R_d is positive when the sulfur pressure is below the equilibrium value, and decomposition occurs, and negative when the sulfur pressure is above the equilibrium value, meaning that Cu_2ZnSnS_4 will crystallize from the binary sulfides and gaseous S_2.

Consider now the equilibrium situation. A key point is that, as with all chemical equilibria, the forward and back reactions still proceed continually at equilibrium, even though their effects cancel each other out: the equilibrium is "dynamic". Decomposition events are always occurring at a rate of k_d, even if they are reversed very rapidly in the following instants, so that the overall decomposition rate is zero.

As a consequence of this dynamic equilibrium, SnS molecules adsorbed to the CZTS surface are constantly being created and consumed again. This is where reaction 3 comes into effect. Because the lifetime of an SnS molecule at the surface is nonzero, it may also evaporate into the gas phase instead of being reconverted to CZTS. If the evaporated SnS molecules are not replaced, then decomposition can never be completely reversed. Therefore the overall decomposition rate can be positive even when R_d is negative. This could be termed "decomposition due to irreversible conditions", as opposed to decomposition due to an instability of CZTS (as when R_d is positive).

Our approach to analyzing this second decomposition mechanism begins by considering a perfect CZTS surface, in conditions where R_d is negative (i.e., $p_{S_2} > p^c_{S_2}$). During one second of heating, k_d moles of SnS will be produced at the CZTS surface due to decomposition events. In the presence of SnS vapor, we may also have some adsorption of SnS from the gas phase, at a rate $k_a p_{SnS}$, where k_a is a rate constant for SnS adsorption. The total number of SnS molecules at the surface is now $k_d + k_a p_{SnS}$. These SnS molecules may now either back-react to regenerate CZTS, at a rate $k_c\ (p_{S_2})^{1/2}$ *or* they may evaporate, at a rate k_e (a rate constant for SnS evaporation). When these two reactions compete, the fraction of SnS molecules that follows each of them depends on the relative sizes of $k_c\ (p_{S_2})^{1/2}$ and k_e. The fraction of SnS molecules returning to the CZTS phase is given by $k_c\ (p_{S_2})^{1/2}/k_e + k_c\ (p_{S_2})^{1/2}$. The rate of SnS molecules returning to the CZTS phase is given by eq 8

$$R_c = \frac{k_c(p_{S_2})^{1/2}}{k_e + k_c(p_{S_2})^{1/2}}(k_d + k_a p_{SnS}) \tag{eq8}$$

up to a maximum value of $k_c(p_{S_2})^{1/2}$. We can now write the net rate of CZTS decomposition as

$$R_{II} = k_d - R_c = k_d - \frac{k_c(p_{S_2})^{1/2}}{k_e + k_c(p_{S_2})^{1/2}}(k_d + k_a p_{SnS}) \tag{eq9}$$

We can make some substitutions to help analyze this expression. First, we define an equilibrium pressure of SnS, p^0_{SnS}, as being equal to k_e/k_a. Note that this is no longer the pressure of SnS generated above CZTS, it is the pressure generated above SnS molecules adsorbed at a CZTS surface. Second, we use the definition of the equilibrium sulfur pressure above the CZTS surface, eq 6, to rearrange the expression and write

$$R_{II} = \frac{k_d k_e}{k_e + k_d\left(\frac{p_{S_2}}{p^c_{S_2}}\right)^{1/2}}\left\{1 - \frac{p_{SnS}}{p^0_{SnS}}\left(\frac{p_{S_2}}{p^c_{S_2}}\right)^{1/2}\right\} \tag{eq10}$$

This expression is valid when the rate of appearance of SnS molecules at the surface (by CZTS decomposition or adsorption from the gas phase) is less than the rate of their removal (by re-crystallisation of CZTS or evaporation), that is, when $k_d + k_a p_{SnS} < k_c(p_{S_2})^{1/2} + k_e$. In addition, for an initially stoichiometric film, the decomposition rate cannot physically be less than zero, since Cu_2S and ZnS will be consumed completely. However, a negative numeric value of R_{d2} indicates an excess of stability with respect to the equilibrium situation. Note the similarity with R_I, the decomposition rate for model I (eq 4). The term in curly brackets has the same form as eq 4, but is multiplied by a sulfur pressure-dependent factor. As in Model I, the decomposition rate here can only be negative, indicating stability, when both SnS and S are present. Otherwise, it is always positive.

For the rate of decomposition to be zero or negative, we need to meet the condition

$$p_{SnS}(p_{S_2})^{1/2} > p^0_{SnS}(p^c_{S_2})^{1/2} \tag{eq11}$$

In model II, there is also a threshold value of p_{S_2} below which decomposition cannot be avoided. We must ensure that

$$p_{S_2} \geq p^c_{S_2} \tag{eq12}$$

The rate of decomposition also has more complex behavior in model II. If we examine how eq 10 behaves in the absence of SnS, we find the following

$$R_{II} = \frac{k_d k_e}{k_e + k_d\left(\frac{p_{S_2}}{p^c_{S_2}}\right)^{1/2}} \tag{eq13}$$

This shows that in the absence of SnS, although the rate of decomposition is always positive, it is slowed by the presence of S_2. This is because reaction 2 may still be partially reversed. This may provide a means of effectively stabilizing the surface by using high pressures of sulfur; however, that will depend on the relative sizes of the rate constants, which are as yet unknown. On the other hand, model II predicts that in the absence of S_2, reaction 2 cannot be reversed at all, and CZTS decomposition will proceed at the rate k_d; the same as predicted by the model I.

When we compare the two models for CZTS decomposition with one another, we see that both models predict that both sulfur vapor and SnS vapor are prerequisites for stability of CZTS surfaces. This is a very important point, since nearly all examples of CZTS annealing operate without deliberate addition of SnS, and therefore under conditions where the CZTS film surface is unstable. Model II goes further by predicting a minimum pressure of sulfur, $p^c_{S_2}$, below which the decomposition of CZTS is unavoidable even in the presence of an excess of SnS. In the absence of sulfur, both models predict decomposition at the maximum rate, regardless of the pressure of SnS. This rate, k_d, is dependent only upon temperature.

Both models predict that if the product of the sulfur and SnS pressures exceeds a certain value, the CZTS surface will be completely stabilized. It is therefore important to determine this critical value, in order to produce CZTS with the good surface quality that is vital for solar cell performance. To do this, the extent of decomposition of CZTS films is studied as a function of the SnS and S_2 pressures during annealing. The results are compared against the two models described above, which allows us to select the most realistic model. Then, the ranges of stability and instability of CZTS surfaces can be predicted. After that, we look further into the origins of the instability leading to SnS loss.

■ EXPERIMENTAL SECTION

Precursor films were deposited by cosputtering from two targets, Cu:Sn (60:40) alloy and ZnS. The depositions were carried out using a high vacuum system (Von Ardenne CS 600) with a background pressure below 1×10^{-6} mbar, at a constant Ar pressure of 4.4×10^{-3} mbar. DC sputtering was used for metallic targets and RF sputtering for the insulating ZnS target. Films were deposited on Mo coated SLG substrates. These precursors were then annealed at 550 °C in sulfur vapor to form CZTS films. The annealing system used in this study was a tube furnace which operates under a flow of argon. Separate argon flows pass at a controlled rate over elemental sulfur (99.999%, Alfa Aesar), and tin sulfide (see below) sources, before being mixed and introduced into the center of the furnace. The sources are separately heated to control their partial pressures. The total pressure is measured by a capacitance manometer, and the total argon flow rate controlled to maintain constant pressure. Samples were placed on a titanium plate with an embedded thermocouple. The sample plate was held in a cold chamber adjoining the furnace until the atmosphere in the furnace was prepared. The samples were then transferred directly into the heated reaction zone, giving a heating rate from room temperature to 550 °C of around 3 °Cs^{1-}. After annealing, the samples were withdrawn to the cold zone, cooling to below 200 °C within four minutes. The total pressure in the system was 30 mbar. The steady state S_2 and SnS partial pressures were calculated from the mass changes in the source materials occurring during long steady-state annealing periods, with knowledge of the gas flow rate and total pressure. The flowing system ensures that gaseous decomposition products from the samples are continuously removed, and therefore do not affect the controlled partial pressures in the annealing system. The tin sulfide source was tin(II) sulfide, SnS (99.999%, Alfa Aesar). Powder XRD (Siemens D5000) showed the as-purchased material to contain a considerable fraction of Sn_2S_3 and a small amount of SnS_2 in addition to SnS. As a consequence of these impurities, the SnS source could also act as a source of sulfur, because these other phases decompose thermally to release SnS and S_2.[8]

Therefore, before use, the material was pretreated at 500 °C in flowing argon for ten hours, after which XRD showed only SnS and very minor quantities of Sn_2S_3.

For the CZTS decomposition experiments, 5 h anneals were used to exaggerate the extent of decomposition and make it easily measurable. Between each run, the annealing system was cleaned by flowing argon at 200 sccm at a pressure of one millibar for 12−14 h at 350 °C. This cleaning removes any residual sulfur from the process zone of the system.

The film compositions were measured using XRF (Panalytical Epsilon 5), which was calibrated by RBS measurements on Cu/Sn and Zn films of various thicknesses. It was ensured that the CZTS samples used for further experiments had a Cu/Sn ratio very close to 2.0, so that any losses of SnS could be attributed to loss from CZTS and not from secondary phases. The tin loss percentage was measured from the absolute change in the calibrated XRF signal intensity. In order to study SnS loss from CZTS films, we need to ensure that the films do not contain Sn-rich secondary phases. The films were prepared slightly Zn-rich (Zn/Sn ≈ 1.3) to avoid the formation of the ternary phases Cu_2SnS_3 and Cu_4SnS_4.[9] ZnS secondary phases will not play a significant role in the decomposition of the film. Raman spectroscopy showed the peaks expected for CZTS,[10] and Cu−Sn−S phases were not observed. As well as the compositional changes that occurred as a result of decomposition, the presence of Cu_2S decomposition products could be observed by Raman and XRD measurements (not shown). These techniques were also used to confirm the addition of SnS to Sn-poor films (i.e., the reversibility of reaction 1) by annealing in the presence of excess SnS vapor.

■ RESULTS AND DISCUSSION

Part A: Comparison of Observed Decomposition Behavior with Models I and II. Two kinetic models for CZTS decomposition were proposed in the introduction. A prediction from both models is that the decomposition rate should be constant with time. Figure 1 shows the Sn/Cu ratio measured by EDS as a function of annealing time at 550 °C, in the absence of sulfur or SnS vapor. It can be seen that decomposition does indeed proceed roughly linearly for several hours, but that the rate then slows down. This slowing can be attributed to gradual blocking of the surface by the decomposition products, causing a reduction of the reaction surface area. From this, we conclude that as long as decomposition does not proceed too far, we can treat the decomposition rate as constant, and that the approximation of a constant reaction surface area is valid. This means that the extent of the reaction after a certain time is simply proportional to, and therefore a measure of, its rate.

The key distinguishing feature of the two kinetic models was their prediction of the decomposition rate in the absence of SnS vapor. model I predicted that in this case the presence of sulfur vapor would have no effect on the decomposition rate, whereas model II predicted a strong effect of the sulfur pressure. Table 1 compares some annealing experiments with different combinations of sulfur and SnS pressures, carried out at 550 °C for five hours each.

From Table 1 we can conclude the following:

(a) Comparing 1 and 2: The decomposition rate was strongly affected by the presence of sulfur, even when SnS was absent.

(b) Comparing 1 and 3: In the absence of S_2 the decomposition rate was essentially unaffected by the presence of SnS, even when SnS was present as a reasonable fraction of its saturation pressure (which is about 2.5×10^{-3} mbar at 550 °C[8]).

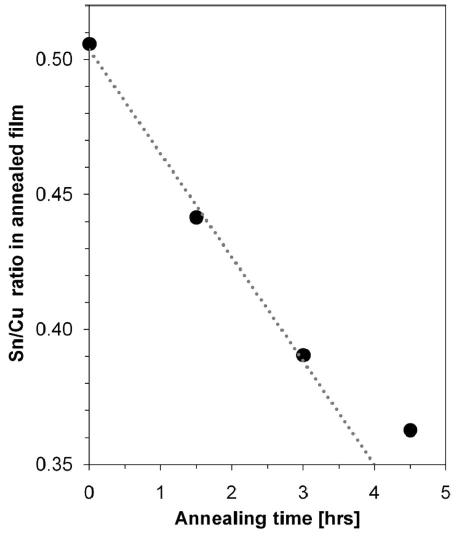

Figure 1. Composition of CZTS films as a function of annealing time at 550 °C in the absence of added sulfur or SnS vapor.

Table 1. Summary of Compositional Changes of CZTS Films Annealed for 5 h at 550°C in Different Combinations and Pressures of S_2 and SnS Vapor

experiment	p_{S_2} (mbar)	p_{SnS} (mbar)	$(Cu/Sn)_{initial}$	$(Cu/Sn)_{final}$	tin loss %
1. no SnS or S_2			1.98	11.3	81
2. S_2, no SnS	0.08		1.98	2.06	3.4
3. SnS, no S_2		1×10^{-4}	1.97	9.30	77
4. SnS and S_2	0.09	1×10^{-4}	2.01	2.00	0.3
5. SnS and S_2					
stoichiometric sample	0.08	2.5×10^{-4}	2.01	1.98	−0.3
Sn-poor sample	0.08	2.5×10^{-4}	2.29	1.97	−13

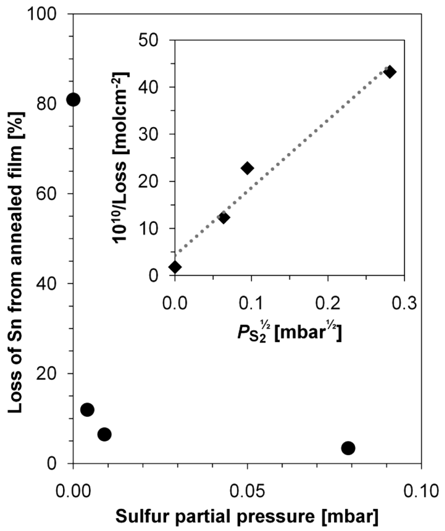

Figure 2. Influence of S_2 partial pressure on the extent of Sn loss from CZTS films annealed for 5 h at 550 °C in the absence of SnS vapor. Inset: Data replotted to show agreement with eq eq 13.

(c) Comparing 2, 3, and 4: The addition of the same pressure of SnS reduced the decomposition rate by a factor of 10, but only when S_2 was present.

(d) Comparing 4 and 5: A higher pressure of SnS not only prevented Sn loss, but actually caused the Sn content of the film to increase, in accordance with Redinger.[6] This is especially clear in samples that were initially Sn-poor (i.e., with excess Cu_2S and ZnS).

Figure 2 shows how the pressure of sulfur vapor affects the decomposition extent, in the absence of SnS. Just as predicted by model II, the decomposition rate drops rapidly as the sulfur pressure rises, but remains positive and does not reach zero; eq 13 predicted that the reciprocal of the decomposition extent (which is roughly proportional to the decomposition rate, as shown in figure 1) is a linear function of the square root of the sulfur pressure. This plot is shown in the inset to Figure 2, and the predicted linearity is confirmed to a reasonable degree.

Because the sulfur vapor is able to influence the rate of decomposition in the absence of SnS, this is clear evidence that the reaction step causing decomposition depends on sulfur alone. It would be impossible for sulfur alone to slow the decomposition rate in the scheme of model I, where both gases occur in the same reaction step. We therefore conclude that model II, which uncouples CZTS decomposition and SnS evaporation, is more realistic. Reasons for this stemming from the chemistry of the system will be explored in the next section.

Having established that a combination of SnS and S_2 vapor is required to stabilize CZTS surfaces, and that the two-step kinetic model proposed in the introduction has the necessary characteristics to describe the decomposition reaction, the next step is to determine the critical pressures that are required to avoid decomposition, according to model II. This requires determination of the product $p^0_{\mathrm{SnS}}\,(p^{\mathrm{c}}_{\mathrm{S_2}})^{1/2}$ (see eq 10 and eq 11).

Our approach to determining the value of $p^0_{\mathrm{SnS}}\,(p^{\mathrm{c}}_{\mathrm{S_2}})^{1/2}$ was to perform a series of annealing experiments with a fixed sulfur pressure while varying the SnS pressure independently. The change in Sn content of CZTS films during annealing was measured as an indicator of the decomposition progress. According to model II, at a certain pressure of SnS the decomposition rate will reach zero and no Sn loss will be observed. At that point, we have reached an equilibrium where $p_{\mathrm{SnS}}\,(p_{\mathrm{S_2}})^{1/2} = p^0_{SnS}\,(p^{\mathrm{c}}_{\mathrm{S_2}})^{1/2}$. Figure 3 shows the change in Sn content as a function of SnS pressure with a fixed sulfur pressure. The linear fit predicted by the two-step mode is indeed observed, and the *x*-axis crossing point was determined as $(1.3 \pm 0.4) \times 10^{-4}$ mbar.

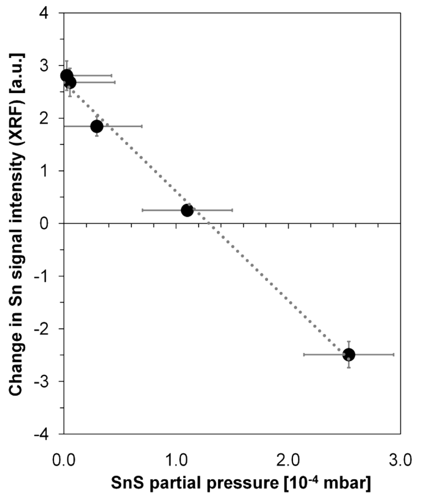

Figure 3. Influence of SnS partial pressure on the extent of Sn loss from CZTS films annealed for 5 h at 550 °C at a constant S_2 pressure of 0.09 mbar.

From this analysis, the critical product $p^0_{\mathrm{SnS}}\,(p^{\mathrm{c}}_{\mathrm{S_2}})^{1/2}$ was found to be $(3.8 \pm 1.2) \times 10^{-5}$ $\mathrm{mbar}^{3/2}$ at a sample temperature of 550 °C. Making the approximation that p^0_{SnS} is equal to the value for pure tin sulfide, i.e., 2.5×10^{-3} mbar at 550 °C,[8] we can calculate $p^{\mathrm{c}}_{\mathrm{S_2}}$, the equilibrium vapor pressure of S_2 above CZTS at 550 °C, as $(2.3 \pm 0.7) \times 10^{-4}$ mbar (This approximation would mean that k_{e} and k_{a}, the rate constants for adsorption and evaporation of SnS from CZTS surfaces are the same as the rate constants at SnS surfaces, i.e., the assumption is that the interaction of SnS gas molecules with SnS surfaces is similar to their interaction with CZTS surfaces. If this is not accurate, the calculated value of $p^{\mathrm{c}}_{\mathrm{S_2}}$ will change, but the value of the product $p^0_{\mathrm{SnS}}\,(p^{\mathrm{c}}_{\mathrm{S_2}})^{1/2}$ will remain correct.). On the basis of these critical values, Table 2 summarizes some key conditions for stability of CZTS surfaces at 550 °C.

The top row of Table 2 shows the situation where the atmosphere is saturated with SnS, such that SnS is condensing at the CZTS surface. In this case, the rate of decomposition is not affected by SnS evaporation, and we only have to provide sufficient sulfur to balance the first step in the decomposition reaction (reaction 2). This value of sulfur pressure corresponds to $p^{\mathrm{c}}_{\mathrm{S_2}}$. If ever any sulfur pressure below this value is used, then decomposition of CZTS is always faster than its regeneration, and CZTS surfaces are intrinsically unstable. The second row shows the situation where the total pressure $p_{\mathrm{T}} = p_{\mathrm{SnS}} + p_{\mathrm{S2}}$ is minimized. If any process is operated at a total pressure less than this value, 2.1×10^{-3} mbar, the CZTS surface must be unstable. We can see immediately that any vacuum-based processing of CZTS at temperatures around 550 °C will risk decomposition of the film surface. The final row of Table 2 shows the situation where a very high sulfur pressure is provided, such that the atmosphere is saturated with S_2. This kind of situation occurs when CZTS films are annealed in small-volume reaction chambers loaded with solid sulfur (e.g., ref 6). The pressure of S_2 in a

Table 2. Predicted Minimum SnS and S_2 Pressures Needed for Stability of CZTS Surfaces at 550°C under Different Conditions (see text for explanation)

condition	p_{S_2} (mbar)	minimum p_{SnS} (mbar)	total pressure (mbar)
saturated SnS atmosphere	2.3×10^{-4} (= $p^{c}_{S_2}$)	2.5×10^{-3} (= p^{0}_{SnS})	2.7×10^{-3}
minimum total pressure	7×10^{-4}	1.4×10^{-3}	2.1×10^{-3}
saturated S atmosphere	300	2×10^{-6}	300

saturated sulfur atmosphere was taken from Rau et al. as: $\log(p_{S_2}, \text{atm}) = 6.8052 - 6.0323/T \times 10^{-3}$.[11] In this case, the high sulfur pressure means that SnS molecules arising from decomposition have very little time to evaporate from the film surface before they are reconverted to CZTS. Nevertheless, an SnS pressure of at least 2×10^{-6} mbar is required in order to make the film surface completely stable against decomposition.

In Table 2, we have taken an experimentally determined equilibrium point and used model II to make predictions about other equilibrium points at different SnS and S_2 pressures. Of course, it is possible that deviations from the model occur outside the range of our experimental conditions. However, it would be very difficult for a single annealing system to probe the full range of S_2 and SnS pressure required to determine experimental equilibrium points under all reported annealing situations for CZTS. Therefore, the values of equilibrium pressures given here should be treated as a rough guide to researchers in the field, and the importance of choosing annealing conditions correctly is highlighted.

Part B: The Driving Force for CZTS Decomposition. We now turn our attention to the source of instability in CZTS, to determine whether instability is intrinsic or whether it can be avoided. Previously,[5,6] it was implied that CZTS decomposes because of the high vapor pressure of SnS. This argument seems plausible but it is incorrect. Although the vapor pressure of SnS is relatively high − 2.5×10^{-3} mbar at 550 °C − it is nevertheless 6 orders of magnitude lower than the vapor pressure of sulfur at the same temperature. If high vapor pressures were really the driving force for decomposition, then very few sulfide compounds would be stable. The claim of model II given in the introduction − and validated to some extent in Part A − is that SnS vapor is not even involved in the reaction step that causes CZTS dissociation. In that scheme, the relative volatility of SnS only exaggerated decomposition that had already occurred, by making it irreversible.

A more plausible driving force is evident from looking at the decomposition reaction from a chemical viewpoint. CZTS contains Sn in its (IV) oxidation state, as shown by Mössbauer spectroscopy,[12,13] whereas the decomposition product SnS contains Sn in its (II) oxidation state. Therefore, the generation of SnS from CZTS is in fact a reduction−oxidation process, as shown below

$$Cu_2ZnSn(IV)S(\text{-}II)_4 \rightleftharpoons Cu_2S + ZnS + Sn(II)S + \frac{1}{2}S(0)_2 \qquad \text{(reaction4)}$$

At the same time, the S atoms go from their (-II) state in CZTS to their (0) state in S_2. Therefore it seems that the chemical driving force for decomposition may be the reduction of Sn(IV) to Sn(II), alongside a loss of S_2. This reduction may be tolerable to some extent within the CZTS lattice, although the defect chemistry of Sn(II) and S vacancies would then become relevant.[14] At some point however, dissociation of the structure into simpler units is inevitable, since the electrons left behind after S_2 evaporation will occupy antibonding orbitals. After dissociation, SnS evaporation can follow. In this light, we can see that the commonly observed losses of Sn from CZTS, instead of being the driving force for decomposition, occur only as a consequence of a more fundamental process. We can also see that the instability of CZTS at high temperatures stems from the ability of Sn to adopt multiple oxidation states.

Elements that can adopt multiple oxidation states, such as Sn, but also Cu, for example, always have the potential to undergo reduction−oxidation reactions. The factor that favors one oxidation state over another is the oxidizing or reducing power of the environment. S_2, like O_2, is an oxidizing agent, capable of withdrawing electrons from a metal atom to form a compound with it, and increasing its oxidation state in the process. Therefore, in sulfide systems like CZTS, the oxidation states of the various metals are simply determined by the partial pressure of S_2 present during processing. At high partial pressures, the environment is oxidizing and Sn(IV) will be favored. At lower partial pressures, Sn(II) will be the more stable state.

We can determine the actual values of sulfur pressure required to stabilize the various oxidation states of the relevant metals. We first consider just the binary sulfides, without formation of higher compounds. The S_2 vapor pressure required to bring about a sulfurization reaction can be derived directly from thermodynamic data, as will be briefly illustrated taking the example of sulfurization of Zn to form ZnS

$$2Zn^0(s) + S_2(g) \rightleftharpoons 2Zn^{II}S(s) \qquad \text{(reaction5)}$$

At a given temperature, there is a single value of S_2 pressure that creates an equilibrium between Zn and ZnS. This value can be calculated from the free energy of formation of the sulfide compound, according to the following expression[15]

$$\log(p^0_{S_2,ZnS}) = \frac{\Delta_S G_{ZnS}}{2.303RT} \qquad \text{(eq14)}$$

where $p^0_{S_2,ZnS}$ is the equilibrium pressure at temperature T, $\Delta_S G_{ZnS}$ is the free energy change during the sulfurization reaction and R is the molar gas constant. The free energy values for many sulfurization reactions have been experimentally determined and tabulated, enabling $p^0_{S_2}(T)$ curves to be calculated. Using literature data,[15] we have calculated $p^0_{S_2}(T)$ curves for some binary sulfurization reactions in the Cu/Zn/Sn/S system. These are shown in Figure 4, and the reactions and thermodynamic parameters are given explicitly in Table 3.

Each curve on the plot defines a boundary between two oxidation states of a particular metal. The regions of stability of the different oxidation states of Sn are delineated by the bold lines. The relative positions of the curves on the plot relate to the relative stabilities of the different oxidation states and their associated sulfide compounds: for example, ZnS can be formed at much lower values of p_{S_2} than the other sulfides because of its large, negative free energy of formation. As p_{S2} is increased, Cu_2S

and SnS will form next. The sulfur pressure has to be increased by several orders of magnitude before SnS is further oxidized to give Sn_2S_3 and SnS_2 in turn. From this data we can already see that, compared to Cu(I) and Zn(II), Sn(IV) is significantly less stable against reduction under typical CZTS processing conditions. The hypothesis that reduction of Sn(IV) is the driving force for CZTS decomposition therefore becomes very plausible.

From Figure 4, we can determine the conditions required to stabilize Sn(IV) in the Sn−S system: at 550 °C, the temperature of the experiments in Part A, a minimum pressure of around 0.5 mbar of S_2 is required. Below that pressure, Sn(IV) in SnS_2 is unstable, and will convert to Sn(II) in Sn_2S_3 or SnS.

Fortunately, Sn(IV) in the environment of CZTS is additionally stabilized by the free energy of compound formation, $\Delta_r G_{CZTS}$, which is released when Cu_2S, ZnS and SnS_2 crystallize to form CZTS. This means that Sn(IV) in CZTS can be stable at lower sulfur pressures than Sn(IV) in SnS_2, because to reduce it would require an additional free energy input to break up the CZTS lattice. Equivalently, Sn(II) can be oxidized at lower pressures of S_2 when in the presence of Cu_2S and ZnS, since CZTS formation and an energy release will follow. To determine the sulfur pressure required to oxidize SnS in the presence of Cu_2S and ZnS, thus forming CZTS, we need to derive a $p^0_{S_2}(T)$ curve for the reaction

$$2Cu_2S(s) + 2ZnS(s) + 2SnS(s) + S_2(g) \rightleftharpoons 2Cu_2ZnSnS_4(s)$$

We approach this problem by considering the reaction to be divided into a series of conceptual steps for which free energy changes are known, and adding up the free energy changes for each step to get the overall free energy change. Starting from SnS, we get the reactions seen in Table 4.

Note that the net reaction here is simply the reversal of the decomposition reaction. The equilibrium value of sulfur pressure calculated from it is therefore the minimum sulfur pressure needed to avoid decomposition. The $p^0_{S_2}(T)$ curve for the oxidation of Sn(II) in SnS to Sn(IV) in Cu_2ZnSnS_4 is given by

$$\log(p^0_{S_2}) = \frac{1}{2.303RT}\left(\frac{1}{2}\Delta_S G_{Sn_2S_3} + \frac{1}{2}\Delta_S G_{SnS} + 2\Delta_r G_{CZTS}\right) \quad \text{(eq15)}$$

where the values of $\Delta_s G_{Sn2S3}$ and $\Delta_s G_{SnS}$ are found from Table 3. $\Delta_r G_{CZTS}$has not been measured as a function of temperature, however in Part A, one point lying on the $p^0_{S_2}(T)$ curve was identified: the equilibrium pressure of S_2 above CZTS at 550 °C was estimated to be $(2.3 \pm 0.7) \times 10^{-4}$ mbar. At that point, the value of $\Delta_r G_{CZTS}$ can be calculated to be -22 ± 6 kJmol^{-1}. This is sufficient to lower the threshold sulfur pressure for oxidation of Sn(II) from 0.5 mbar to 2.3×10^{-4} mbar.

Without further data for lower temperatures, it is impossible to make accurate predictions about the full $p^0_{S_2}(T)$ curve. A tentative estimate of the form of the curve below the temperature for which data was obtained can be made by assuming that$\Delta_r G_{CZTS}$ is purely entropic, and is shown in Figure 5, with the new regions of stability for Sn(IV) and Sn(II).

Despite the extra stability against reduction that Sn(IV) gains in the CZTS environment, it is still relatively unstable when compared to the Cu(I) and Zn(II) also in CZTS. We therefore assert that the driving force for decomposition of CZTS is the relative ease of reduction of Sn(IV) to Sn(II), which is an inherent feature of Sn chemistry. The only way to fully stabilize Sn(IV) and prevent decomposition of CZTS is to provide a sufficiently oxidizing environment during high-temperature processing, which essentially means a significant pressure of sulfur. Otherwise, any exposed surface will be subject to decomposition.

Part C. Implications for Processing of CZTS Films. To summarize the preceding sections, decomposition of CZTS at high temperatures is attributable to two particular aspects of Sn

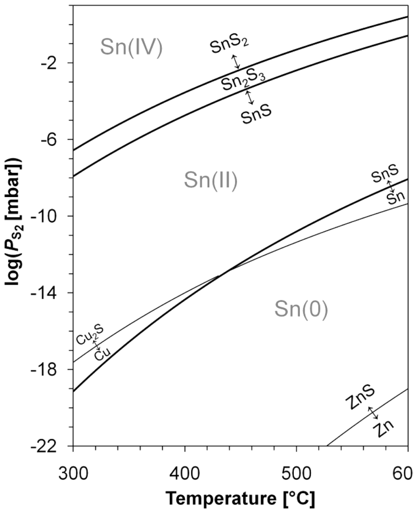

Figure 4. Plot of the domains of stability of different sulfides (different oxidation states) of Cu, Zn and Sn as a function of temperature, where the oxidizing agent is S_2 vapor. Each curve separates the domains of two compounds (or oxidation states), which are indicated alongside it. The bold lines are for reactions involving Sn, and the stable oxidation states of Sn in the presence of S_2 are indicated explicitly. See Table 3 for more details.

Table 3. Reactions and Data[15] Used in Preparation of Figure 4

reaction	oxidation states	$\Delta_s G_i$(J mol^{-1}) (T in units of K)	T range (°C)
$4Cu + S_2 \rightleftharpoons 2Cu_2S$	Cu(0)/Cu(I)	$\Delta_s G_{Cu} = -267\,546 + 72.0T$	103−425
		$-259864 + 61.2T$	435−1067
$2Zn + S_2 \rightleftharpoons ZnS$	Zn(0)/Zn(II)	$\Delta_s G_{Zn} = -537523 + 191.3T$	25−420
		$-548501 + 207.0T$	420 − 1200
$2Sn + S_2 \rightleftharpoons 2SnS$	Sn(0)/Sn(II)	$\Delta_s G_{Sn} = -343866 + 173.1T$	25−232
		$-353845 + 193.4T$	232−600
$4SnS + S_2 \rightleftharpoons 2Sn_2S_3$	Sn(II)/Sn(II) + Sn(IV)	$\Delta_s G_{SnS} = -234304 + 199.9T$	25−600
$2Sn_2S_3 + S_2 \rightleftharpoons 4SnS_2$	Sn(II) + Sn(IV)/Sn(IV)	$\Delta_s G_{Sn2S3} = -222589 + 205.3T$	25−760

Table 4

(1)	$2SnS + 1/2S_2 \rightleftharpoons Sn_2S_3$	$\Delta G_1 = 1/2\Delta_s G_{SnS}$
(2)	$Sn_2S_3 + 1/2S_2 \rightleftharpoons 2SnS_2$	$\Delta G_2 = 1/2\Delta_s G_{Sn_2S_3}$
(3)	$2Cu_2S + 2ZnS + 2SnS_2 \rightleftharpoons 2Cu_2ZnSnS_4$	$\Delta G_3 = 2\Delta_r G_{CZTS}$
(sum)	$2Cu_2S + 2ZnS + 2SnS + S_2 \rightleftharpoons 2Cu_2ZnSnS_4$	$\Delta G_T = 1/2(\Delta_s G_{SnS} + \Delta_I G_{Sn_2S_3}) + 2\Delta_r G_{CZTS}$

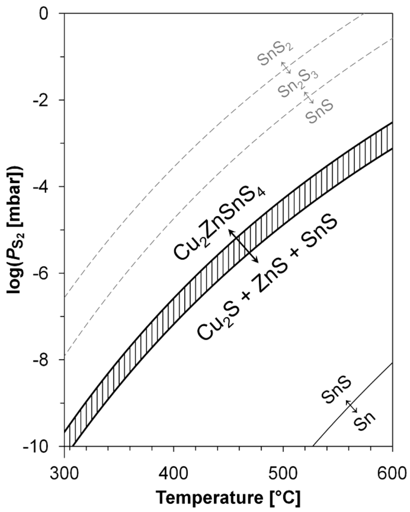

Figure 5. Plot of the minimum S_2 vapor pressure required to stabilize CZTS, as a function of temperature. The shaded area shows an estimate of the uncertainty in the position of the boundary. Below the boundary, CZTS is inherently unstable: it will lose S_2 and decompose into Cu_2S, ZnS, and SnS. Above the boundary, CZTS can be stabilized in the presence of a sufficient partial pressure of SnS (see Table 2). The curves for sulfurization of Sn in the absence of Cu and Zn are also shown for comparison with Figure 4.

chemistry. The first is the instability of Sn(IV) against reduction, which allows decomposition by conversion of Sn(IV) to Sn(II) in the absence of a sufficient, large sulfur pressure. An estimation of the minimum sulfur pressure required at a given temperature can be found in Figure 5. The second aspect is the relatively high vapor pressure of SnS, which reduces the reversibility of the decomposition reaction. To avoid decomposition during high temperature processing therefore requires a partial pressure of SnS to be provided as well. Figure 5 is valid where SnS is near its saturation pressure: a lower pressure of SnS will require a higher pressure of S_2 to compensate. Unfortunately, the indications are that the necessary pressures of S_2 and SnS are incompatible within traditional single-stage vacuum deposition techniques such as coevaporation using high substrate temperatures. So-called "two stage" processing, i.e., low-temperature deposition of a precursor film followed by postdeposition annealing at higher pressure, is implied as the most favorable route to yield good-quality films. This can explain why all of the most efficient CZTS (and, by extension, $Cu_2ZnSn(S,Se)_4$) devices to-date arise from two-stage processes,[1,2,16] in contrast with the great success of single-step vacuum deposition at high temperature for other thin film photovoltaic materials.[17]

It is very interesting to compare the decomposition behavior of CZTS with similar material systems. CZTS is often stated to share similar properties to $CuInS_2$, a more well-studied photovoltaic material. Here, indium also has several possible oxidation states. We can therefore consider the sulfur pressure required to stabilize In(III), according to the following reaction[18]

$$In_2^{III}S_3 \rightleftharpoons In_2^{I}S(g) + S_2(g)$$

The equilibrium vapor pressure of S_2 arising from this reaction is at most 10^{-6} mbar at 550 °C, and the vapor pressure of In_2S is similar:[18,19] compared to Sn(IV), In(III) is substantially more stable, and the decomposition products much less volatile. If the additional stability due to compound formation in $CuInS_2$ is taken into account, then we can expect the S_2 pressure limit to drop several orders of magnitude further. It is clear that the limiting pressures of S_2 and In_2S required to avoid decomposition of $CuInS_2$ surfaces are well within the base pressure range of coevaporation, even at high substrate temperatures. This comparison highlights a fundamental chemical difference between CZTS and its indium-containing relatives, and perhaps provides a straightforward explanation for the relative difficulty of fabrication of efficient CZTS devices using traditional methods. It is to be hoped that understanding of the decomposition process of CZTS surfaces can lead to methods of limiting, negating or avoiding it in future.

CONCLUSIONS

The commonly reported Sn-loss from CZTS films during processing has been analyzed using basic kinetic models. A single step reaction leading to evolution of SnS(g) and S_2(g) could not adequately explain observed decomposition patterns; instead the most appropriate model was one that consisted of two stages: an initial decomposition reaction leading to loss of S_2(g) and the separation of solid binary sulfides including SnS(s). Reversible desorption of SnS was the second step of the decomposition process:

$$(1)\quad Cu_2ZnSn^{IV}S_4(s) \rightleftharpoons Cu_2S(s) + ZnS(s) + Sn^{II}S(s) + \frac{1}{2}S_2(g)$$

$$(2)\quad SnS(s) \rightleftharpoons SnS(g)$$

Using this model, a study of CZTS decomposition progress as a function of S_2 and SnS pressure allowed derivation of the minimum pressures of S_2 and SnS(g) needed for stability at 550 °C. The criteria to achieve stable CZTS surfaces are summarized as follows:

(a) The sulfur partial pressure should be greater than $(2.3 \pm 0.7) \times 10^{-4}$ mbar.
(b) The product of partial pressures $p_{SnS}\,(p_{S_2})^{1/2}$. should be greater than $(3.8 \pm 1.2) \times 10^{-5}$.

The driving force for decomposition was attributed to instability of Sn(IV) in CZTS under conditions of low sulfur pressure. This was explained with reference to available thermodynamic data on metal sulfide compounds. The high vapor pressure of SnS exaggerates the decomposition by making it irreversible. The particular chemistry of multivalent Sn is the source of the decomposition problem for CZTS, a problem that is not shared by related indium-containing materials like $CuInS_2$. This analysis highlights the extreme importance of controlling the annealing conditions for CZTS in order to synthesize good-quality films with intact surfaces, points clearly to the use of two-stage processes for CZTS, and rationalizes their success so far compared to pure vacuum-based syntheses.

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REFERENCES

(1) Todorov, T. K.; Reuter, K. B.; Mitzi, D. B. *Adv. Mater.* **2010**, *22*, 143508–143508-3, DOI: 10.1063/1.3499284.

(2) Wang, K.; Gunawan, O.; Todorov, T.; Shin, B.; Chey, S. J.; Bojarczuk, N. A.; Mitzi, D.; Guha, S. *Appl. Phys. Lett.* **2010**, *97*, DOI: 10.1143/APEX.1.041201.

(3) Katagiri, H.; Jimbo, K.; Yamada, S.; Kamimura, T.; Maw, W. S.; Fukano, T.; Ito, T.; Motohiro, T. *Appl. Phys. Express* **2008**, *1*.

(4) Weber, A.; Krauth, H.; Perlt, S.; Schubert, B.; Kötschau, I.; Schorr, S.; Schock, H. W. *Thin Solid Films* **2009**, *517*, 2524.

(5) Weber, A.; Mainz, R.; Schock, H. W. *J. Appl. Phys.* **2010**, *107*, DOI: 10.1063/1.3273495.

(6) Redinger, A.; Berg, D. M.; Dale, P. J.; Siebentritt, S. *J. Am. Chem. Soc.* **2011**, *133*, 3320.

(7) Rau, H.; Kutty, T. R. N.; Decarval., Jr *J. Chem. Thermodyn.* **1973**, *5*, 833.

(8) Piacente, V.; Foglia, S.; Scardala, P. *J. Alloys Compd.* **1991**, *177*, 17.

(9) Olekseyuk, I. D.; Dudchak, I. V.; Piskach, L. V. *J. Alloys Compd.* **2004**, *368*, 135.

(10) Himmrich, M.; Haeuseler, H. *Spectrochim. Acta, Part A: Mol. Spectrosc.* **1991**, *47*, 933.

(11) Rau, H.; Kutty, T. R. N.; Guedesde., Jr *J. Chem. Thermodyn.* **1973**, *5*, 291.

(12) Di Benedetto, F.; Bernardini, G. P.; Borrini, D.; Lottermoser, W.; Tippelt, G.; Amthauer, G. *Phys. Chem. Miner.* **2005**, *31*, 683.

(13) Rusakov, V. S.; Chistyakova, N. I.; Burkovsky, I. A.; Gapochka, A. M.; Evstigneeva, T. L.; Schorr, S. *J. Phys.: Conf. Ser.* **2010**, *217*, 012038.

(14) Biswas, K.; Lany, S.; Zunger, A. *Appl. Phys. Lett.* **2010**, *96*.

(15) Vaughan, D. J.; Craig, J. R. *Mineral Chemistry of Metal Sulfides*; Cambridge University Press: Cambridge, U.K., 1978.

(16) Guo, Q.; Ford, G. M.; Yang, W.-C.; Walker, B. C.; Stach, E. A.; Hillhouse, H. W.; Agrawal, R. *J. Am. Chem. Soc.* **2010**, *132*, 17384.

(17) Jackson, P.; Hariskos, D.; Lotter, E.; Paetel, S.; Wuerz, R.; Menner, R.; Wischmann, W.; Powalla, M. *Prog. Photovoltaics: Res. Appl.* **2011**, DOI: 10.1002/pip.1078.

(18) Ferro, D.; Piacente, V.; Scardala, P. *J. Mater. Sci. Lett.* **1988**, *7*, 1301.

(19) Miller, A. R.; Searcy, A. W. *J. Phys. Chem.* **1965**, *69*, 3826.

NOTE ADDED AFTER ASAP PUBLICATION

This article was published ASAP on September 22, 2011, with a spelling error in the fifth author's name and errors in the affiliations. The corrected version was published ASAP on September 27, 2011.