

Stability Issues of Cu(In,Ga)Se₂-Based Solar Cells

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Stability aspects of the Mo/Cu(In,Ga)Se₂/CdS/ZnO solar cell are reviewed and assessed. These include (i) the chemical stability of the various interfaces present in the device, (ii) the long-term behavior of metastable defects found in the Cu(In,Ga)Se₂ (CIGS) compound, and (iii) the impact of Cu migration on device performance and lifetime. We find that (i) all interfaces within the structure are chemically stable, (ii) metastable defects have a beneficial effect on performance, and (iii) Cu migration effects are reversible and their possible detrimental effects are eclipsed by the beneficial effect of the metastable states. Moreover, Cu out-diffusion from the CIGS layer is absent in photovoltaic-quality CIGS. Finally, we propose a model that explains the exceptional radiation hardness and impurity tolerance of CIGS-based devices, based on the synergetic effect of copper migration and point defect reactions.

1. Introduction

Over the past few years, the performance of Cu(In,Ga)Se₂ (CIGS)-based solar cells has made significant strides forward. Laboratory devices with conversion efficiencies exceeding 17% have been demonstrated by several groups^{1–4} and a record efficiency of 18.8% has been recently reported.⁵ Simultaneously, much progress has been made in the industrialization of the technology and it now appears mature enough to head for large scale production,^{6–9} with a *module* efficiency above 12% announced recently.¹⁰ Both the single cell and the module record efficiencies are the best obtained yet for *any* kind of single junction thin film solar cell. However, for achieving true commercial viability, the long-term *stability* of cell performance is just as critical an issue. This is because the lifetime of a solar module contributes at least as much as the efficiency in determining the final ratio of solar energy produced to cost invested.

Stability issues merit particular scrutiny because they have already proven to be a source of constant worry in other thin film solar cell material systems. In Cu₂S/CdS solar cells, the significant mobility of Cu was shown to result in Cu⁰ plating upon placing the cell under forward bias. To some extent, this degradation was reversible and acceptable module lifetimes could be obtained with proper processing. However, the cost of these processes was (at least at that time) prohibitive and as a result the technology was by and large abandoned.^{11,12} In a-Si:H solar cells, illumination-induced production of metastable defects acting as recombination centers was found to degrade cell performance.^{11,13} This degradation was also essentially reversible and the original performance could be recovered via annealing treatments in the dark, but this was impractical on a

system level. The problem was finally reduced substantially by using stacked cells with a thinner absorber layer, where the increased electric field made the cells less sensitive to the detrimental effects of the metastable states (see, e.g., ref 14). Nevertheless, technology development was delayed by at least one decade.

We also recall that the formation of a stable Ohmic back-contact to a p-type absorber, which is almost taken for granted in CIGS-based solar cells, can be the Achilles heel of cells with other materials. For example, this issue is at the heart of much delay in the development of CdTe-based solar cells.^{15–18}

In light of the above discussion, the implications of CIGS and CuInSe₂ (CIS) material properties to solar cell stability appear to be doubly problematic. This is because *both* Cu migration^{19,20} and metastable defect reactions^{21,22} have been observed in CI(G)S. Indeed, the electrical properties of CI(G)S solar cells were found to change significantly after illumination, electrical bias, or extended storage in the dark.^{23,24} Moreover, the solid state chemistry of the ZnO/CdS/CIGS/Mo/glass structure, invariably used in all top-performing CIGS-based solar cells, is undoubtedly more complex than that of any other single junction thin film solar cell material system. This fact further raises serious concerns about undesired chemical reactions in the long term.

Despite this seemingly unfavorable situation, CIGS-based solar cells appear to be remarkably durable. Empirically, they have proven their stability in long-term outdoor tests^{8,9,25} as well as under accelerated lifetime test conditions.^{9,26} If anything, their performance is actually found to *improve*, after some use under their normal operating conditions.²⁵ A particularly surprising feature of this type of solar cells is their excellent radiation hardness, confirmed under proton and electron irradiation, as well as under space conditions.^{27–30} The only detrimental effect

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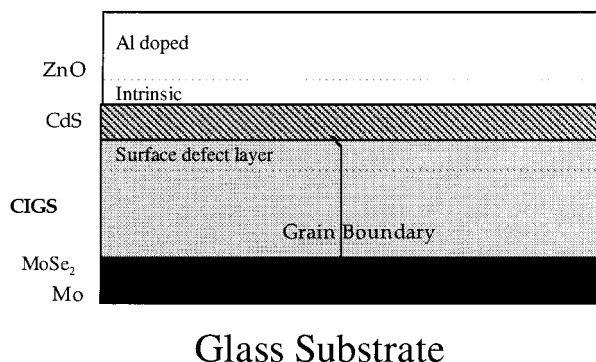


Figure 1. Typical structure of a high-performance, CIGS-based solar cell.

recorded to date was the adverse effect of humidity on unprotected ZnO^{26,31} and CIGS^{32,33} layers. In the former case, degradation was shown to come from a resistivity increase of the window layer³¹ but this drawback was overcome with proper encapsulation.^{9,26} This will not be addressed further here as such issues would occur in virtually any optoelectronic device, if it were not properly encapsulated.

In this article, we attempt to resolve the apparent contradiction between the microscopic and macroscopic stability aspects of CIGS-based solar cells. This is achieved by considering all three major aspects of cell stability related to CI(G)S and stressing the chemical point of view. First, we consider possible long-term damages due to either interfacial chemical reactions or Cu out-diffusion from the CIGS layer. Next, we examine the electrical effects of metastable defect reactions and Cu migration and explain why both are at worst harmless and at best beneficial to solar cell performance. Finally, we present a detailed chemical and electrical model for the extraordinary radiation hardness. We find that in all cases the microscopic instabilities do not translate into macroscopic ones. Moreover, the above-mentioned problematic CIGS material properties may in fact be a *pre-requisite* for the radiation hardness. This is because they allow the material a degree of *flexibility* that is essential for accommodating externally imposed changes by self-annealing of radiation-induced defects.

Throughout this paper, we review the stability-related experimental data found in the literature in light of our theoretical concepts. We survey results obtained on both thin films and single crystals from as far back as the late 1970s to the present day. This allows us to examine general trends that are independent of specific growth or fabrication details. In some cases, these trends are additionally highlighted by experiments performed for this study.

2. Interface Stability Issues

A typical device structure of a CIGS-based solar cell is shown in Figure 1. The structure shown consists of as many as seven layers, with some being just tens of nanometers thick. The layers contain nine different constituent elements (Mo, Cu, In, Ga, Se, Cd, S, Zn, and O) and actually 11 different deliberately introduced atoms, if one includes the Na contents of the CIGS layer and the Al doping of the second ZnO layer. Thus, the global chemical system is undoubtedly very complex and the chemical aspects of cell stability are expected to be much more important than in, e.g., Si solar cells. In this section, we present an overview of such issues. First, we consider detrimental interfacial reactions in general. We then concentrate on the specific chemical stability problems, which the relatively fast diffusion of Cu in CIGS may cause.

TABLE 1: Standard Free Energies, G° , of Some Compounds Relevant to the Mo/CIGS/CdS/ZnO System^a

compound	G° (298 K), kJ/mol	ref
CdO	-274.7	153
CdS	-176.8	153
CdSe	-170.7	153
CdIn ₂ Se ₄	<-557.1	
CdIn ₆ Se ₁₀	<-1329.9	
Cu ₂ O	-198.2	153
Cu ₂ S	-115.6	153
Cu ₂ Se	-103.9	153
CuInSe ₂	<-245	
CuInS ₂	<-260	
CuGaSe ₂	<-283	
CuO	-168.8	153
CuS	-73.6	153
CuSe	-65.2	153
Cu ⁰	-10.0	153
Ga ₂ O ₃	-1114.4	153
Ga ₂ S ₃	-558.7	153
Ga ₂ Se ₃	-462.4	153
Ga ⁰	-12.2	153
In ₂ O ₃	-957.0	153
In ₂ S ₃	-404.4	153
In ₂ Se ₃	-360	154
In ⁰	-17.2	153
MoSe ₂	-180.2	153
Mo ⁰	-8.5	153
ZnO	-363.6	153
ZnS	-222.2	153
ZnSe	-193.5	153

^a The standard enthalpies of formation of the elements are taken at 25 °C, 1 bar, and their entropies at 0 K are set to zero.

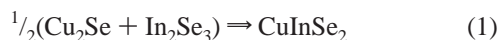
TABLE 2: Free Energies of Reaction of Selected Possible Chemical Reactions at Mo/CIGS/CdS/ZnO Cell Interfaces

#	reactions	ΔG (298 K), kJ/mol	possible
Back Contact			
1	Mo + 2Cu ₂ Se \Rightarrow MoSe ₂ + 4Cu ⁰	-3.5	yes
2	3Mo + 2In ₂ Se ₃ \Rightarrow 3MoSe ₂ + 4In ⁰	+188	no
3	3Mo + 2Ga ₂ Se ₃ \Rightarrow 3MoSe ₂ + 4Ga ⁰	+361	no
Buffer			
4	Cu ₂ Se + CdS \rightarrow Cu ₂ S + CdSe	-5.6	yes
5	In ₂ Se ₃ + 3CdS \rightarrow 3CdSe + In ₂ S ₃	0.3	no
6	Ga ₂ Se ₃ + 3CdS \rightarrow 3CdSe + Ga ₂ S ₃	-78	yes
7	In ₂ Se ₃ + CdSe \rightarrow CdIn ₂ Se ₄	<0	yes
8	In ₂ Se ₃ + CdS \rightarrow CdIn ₂ Se ₃	<-11.9	yes
Window			
9	CdS + ZnO \rightarrow CdO + ZnS	43.5	no
10	Cu ₂ Se + ZnO \rightarrow Cu ₂ O + ZnSe	75.8	no
11	In ₂ Se ₃ + 3ZnO \rightarrow In ₂ O ₃ + 3ZnSe	-60.3	yes
12	Ga ₂ Se ₃ + 3ZnO \rightarrow Ga ₂ O ₃ + 3ZnSe	-141.7	yes

2.1. Interface Reactivity. In light of the above-mentioned chemical instability of the Cu₂S/CdS interface, the CdS/CIGS interface appears to be the one most suspect of possible instabilities. Indeed, of all interfaces in the cell it is the one whose chemistry was investigated most. We shall therefore begin our analysis by considering this interface in detail and discuss other interfaces subsequently. To facilitate our discussion, the free energies of formation ΔG of different pertinent compounds are compiled in Table 1. On the basis of these values, the thermodynamic possibilities of specific, potentially troublesome interface reactions are evaluated in Table 2 and discussed below, as appropriate.

We note that for assessing the possible interface reactions involving CIGS we need the free energy of formation of that compound. Unfortunately, ΔG of CIGS from binary compounds

(Cu₂Se, In₂Se₃, and Ga₂Se₃) is not precisely known. For example, according to Mooney and Lamoreaux³⁴ CIS is only 9 kJ/mol more stable than the stoichiometric mixture of Cu₂Se and In₂Se₃ at 298 K, whereas the *ab initio* calculations of Zhang et al. with hexagonal In₂Se₃³⁵ enable us to compute a value of 26 kJ/mol for the same reaction at 0 K. Clearly, the span of values is quite large. Other values are available from an earlier compilation.³⁶ Nevertheless, the problem is complicated by the consistency of the data originating from different sources, an issue treated in ref 37. Therefore, in the following we shall sometimes rely on a different argument. Because the thermodynamic stability of CIS is an experimental fact, the ΔG of the reaction

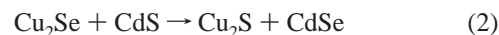


must be negative. Its absolute value is at least in the 10–30 kJ/mol range and, according to a careful examination of the full ternary phase diagram,³⁷ is probably around 50 kJ/mol. The situation is less well documented for CuGaSe₂, but according to the values reported,³⁶ the corresponding stabilization energy for this compound should be about 25 kJ/mol. Consequently, a reaction that is not thermodynamically allowed with *any* of the three constituent binaries (Cu₂Se, In₂Se₃ and Ga₂Se₃) cannot be allowed with CIGS either.

We first consider the Mo/CIGS interface. This interface has been studied by a number of authors^{38,39} and was invariably found to be very stable with no evidence of Mo diffusion into the CIGS film. It was found that during growth, an interfacial MoSe₂ layer of a ~10 nm thickness can be formed *with the help of the excess Se* used in all methods, leading to a photovoltaic-quality film.^{40–42} This layer is possibly beneficial in buffering elastic constraints during growth/cool down and in producing an adequate ohmic back contact at room temperature.⁴³

From the thermodynamic point of view, the formation of MoSe₂ provides more than a *kinetic* barrier to further CIGS–Mo reactions at room temperature. From Table 2 we see that the MoSe₂-forming reaction with each of the three binary compounds is thermodynamically forbidden. Thus, in the absence of excess Se, which is found during growth only, there is no driving force for further reaction with CIGS. We now turn our attention to the active interface, i.e., the CdS/CIGS one, in most cases. In high-efficiency cells, CdS is prepared by precipitation from an aqueous solution at 60 °C.⁴⁴ The solution removes secondary oxide phases on the surface of CIGS⁴⁵ and creates an electrically inverted surface that reduces the interface recombination.⁴⁶ The deposited CdS layer is typically several tens of nanometers thick. It provides very good coverage and protects the CIGS surface from interaction with the ambient in general and from damage produced during the sputter deposition of ZnO in particular. Thus, CdS-capped CIGS was found to be insensitive to humidity in the ambient air, whereas the opposite was true for unprotected CIGS.³²

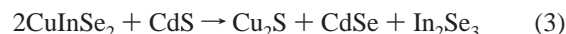
The first cause for concern as to the interface stability is the potential of new binary compound formation at the interface. The dependence of such reactions on the stoichiometry of the CIGS film was studied by Niemi and Stolt,⁴⁷ who compared CdS grown on Cu-rich, stoichiometric, and In-rich CIS samples. They found a formation of Cu₂S on Cu-rich and to some extent also on stoichiometric material, but not on In-rich material. These results are explained by considering that the surface of Cu-rich CIS films is well-known to contain some Cu₂Se.^{48,49} Because the reaction



is thermodynamically allowed (see Table 2), the observation of Cu₂S is logical. According to the most recent phase diagram data available,⁵⁰ stoichiometric films may contain some Cu_{2–x}Se binaries as well, so the same explanation applies. Indeed, the growth of Cu₂S on stoichiometric films was found to occur only on Cu-rich islands, further substantiating the above thermodynamic analysis.

Similarly, a recent transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) microprobe analysis of the CdS/CuGaSe₂ (CGS) interface has detected the formation of some Cu_{2–x}S at the interface.⁵¹ However, the authors pointed out that because Cu_{2–x}Se inclusions were present in the analyzed CGS film, the mechanism described by eq 2 may well apply here too. They also noted that the ion milling process used to prepare the samples for the TEM measurement may have also promoted a reaction between the CGS and CdS layers.

If the Cu₂Se phase is absent from the CIS film, no reaction forming interface binaries is expected. This is because Table 2 shows that even if the low value of $\Delta G = -9$ kJ/mol is assumed for the formation of CIS from Cu₂Se and In₂Se₃, the reaction



which would have provided Cu₂S, is not thermodynamically allowed. This agrees well with the above-mentioned experimental findings of Niemi and Stolt.⁴⁷ It is worthwhile to note, however, that the situation for CGS may be different due to the possibility of a reaction between Ga₂Se₃ and CdS (see Table 2). If the free energy difference of CGS with respect to its constituent binaries (Cu₂Se and Ga₂Se₃) is less than -40 kJ/mol, then CGS may spontaneously react with CdS. We therefore conclude that the CdS/CIGS is thermodynamically immune to the formation of Cu₂S as long as photovoltaic quality CIGS is used. The only possible exception is that of alloys containing a high Ga fraction. However, these are not currently in use in high-performance CIGS-based cells.

Such stability is not achieved with, e.g., ZnO. Interestingly, Table 2 indicates that the interface reaction of ZnO and In₂Se₃ to yield In₂O₃ and ZnSe has a strong thermodynamic driving force, strong enough to cause some decomposition of CIGS and the formation of a mixed interfacial layer. This could be another reason (in addition to the damage-protecting nature and electrical significance^{52–54} of the CdS film) why the performance of buffer-less ZnO/CIS cells is still slightly inferior to that of buffer-containing cells. The thermodynamic free energies also point to an increased instability of the ZnO/CIGS interface when the Ga content is increased. The next potential cause for concern is S/Se exchange. However, because both S and Se possess large ionic radii (as compared to the cations) and correspondingly low diffusion coefficients in CIGS and CdS at the relevant temperature range (<300 °C), such exchange is strongly limited kinetically. Furthermore, S/Se exchange requires some diffusion of Se in the CIGS layer as well, but tracer diffusion studies of Se diffusion in CIS⁵⁵ found a diffusion coefficient on the order of 10–12 cm²/s at a temperature as high as 700 °C, indicating a negligibly slow diffusion around room temperature, assuming a reasonable activation energy (>1 eV). Indeed, an absence of exchange was reported for both CdS evaporated at 200 °C⁴⁷ and chemical bath-deposited CdS.^{56,57} Some small-scale (5–10 nm) S/Se intermixing is suggested by recent experiments that combined X-ray photoelectron spectroscopy (XPS) with X-ray emission spectroscopy (XES)⁵⁸ and transmission electron microscopy with energy-dispersive X-ray spectroscopy.⁵⁹ Large

scale (>100 nm) exchange was found to take place only near the growth temperature of CIS.^{60,61}

The above studies are in general agreement with a detailed study of the temperature dependence of the CdS/CIS interface stability, performed by Kazmerski et al.⁶² In that study, an interfacial region containing Cu₂S and Cu₂Se binaries was found, which suggests, in light of the previous discussion, that stoichiometric or slightly Cu-rich films were used. Nevertheless, no interdiffusion was found at the CdS/CIS interface up to temperatures as high as 150 °C. Possible signs of S and Se interdiffusion were found between 200 and 300 °C,⁶² but even if so, on a limited scale. Significant diffusion was only found above 350 °C and was due to a rapid diffusion of Cd in CIS (which is discussed below). Usually, 200 °C is assumed to be the maximal temperature that the cells can withstand without suffering a deterioration in their photovoltaic performance. Thus, this is usually the temperature of choice for air anneal treatments, which have a positive effect on the electrical properties of the grain boundaries.^{52,63,64}

Inspection of recent investigations done on CuInSe₂/CdS as well as on CuGaSe₂/CdS interfaces do not substantiate any extensive S/Se exchange.⁶⁵ Therefore, a detrimental long-term evolution of the interface due to S/Se exchange in the completed device, should that exchange result indeed in a device degradation, is not expected on theoretical grounds, nor is it supported by existing experimental evidence.

A third cause for concern is Cu/Cd exchange at the interface. Wada et al. have reported some interdiffusion, on the scale of 10 nm, based on SIMS profiles of CdS/CIGS junctions, where the CdS was CBD grown in a temperature range of 60–80 °C.⁶⁶ Similar results were obtained by Ramanathan et al. on surfaces treated in Cd-containing ammonia baths.⁵³ One should note that the roughness of the substrates makes an unequivocal conclusion difficult. However, these findings were corroborated by the more recent TEM and EDX microprobe analysis of Nakada and Kunioka.⁵⁹ Indeed, some uptake of Cd from the chemical bath by the CIS was shown by XPS as early as 1992.^{44,45} Therefore, Cu/Cd exchange in the CBD solution was suggested. This view is further supported by the recent data of Heske et al., who reported In_xSe_y/CdS intermixing by using a combination of XPS and XES.⁵⁸

The driving force for Cu/Cd exchange may result from the energy of formation of defined compounds, such as CdIn₆Se₁₀ and CdIn₂Se₄, whereas no known ternary compounds exist in the (Cu,Cd,Se) system.^{44,45,67} Thus, both experimental evidence and theoretical considerations indicate that Cd/Cu exchange is *not* thermodynamically forbidden. We must therefore consider its kinetics. We explore Cd in-diffusion here and Cu out-diffusion in section 2.2.

Cd diffusion in CIS has been studied in crystals^{68–70} and in thin films.⁷¹ Interdiffusion with CdS was also observed with thin CIGS films,⁷² from which an estimate of the rate of Cd diffusion can be obtained. A summary of these studies is given in Figure 2. Surprisingly, the obtained diffusion coefficients are smaller by orders of magnitude in thin films than in single crystals. This may be due to a bias of the method used for thin films (Rutherford backscattering) for the detection of the slower diffusion component in one case⁷¹ and to the formation of a defined compound (CuCd₂InSe₄) at the interface in the other.⁷² Extrapolation of the single-crystal data to room-temperature yields diffusion coefficients that are at most in the 10^{−19} cm²/s range. Such values are consistent with a diffusion of several nanometers at a CBD temperature up to 80 °C. This modest interdiffusion has in fact been suggested to be *beneficial* to the

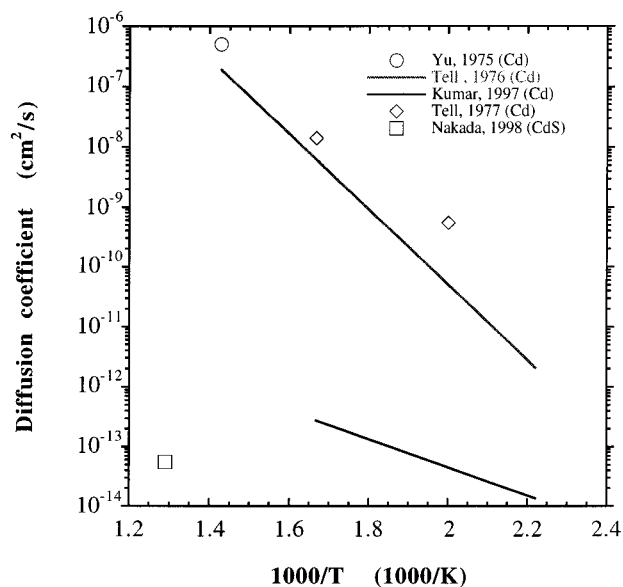


Figure 2. Diffusion coefficients of Cd in CIS thin films and crystals as a function of temperature. Data were collected from refs 68–72. The first three were obtained with single crystals and the last two with thin films. In all cases except the last reference (which relates to CdS/CIGS interdiffusion), Cd metal was used.

photovoltaic performance of the cell, by assisting in inverting the CIGS interface region⁵³ and by reducing the possible “spike” in the CdS/CIGS conduction band offset.⁵⁸ At the same time, these diffusion coefficient values imply that tens of years would be required for Cd diffusion on the scale of 100 nm at room temperature. Thus, Cd in-diffusion is *kinetically limited* and poses no threat to the interface stability.

2.2. Cu Diffusion and Out-Diffusion. Evidence for the mobility of Cu in CIS crystals was provided by a variety of experimental methods, including nuclear magnetic resonance,²⁰ galvanostatic decay,⁷³ p/n junction migration,⁷⁴ tracer diffusion,¹⁹ point-probe measurements,⁷⁵ transient ion drift,⁷⁶ and potentiostatic step measurements.^{77,78} From these measurements, the room-temperature Cu diffusion coefficient in CIS was found to be in the range of 10^{−13} to 10^{−10} cm²/s. The significant scatter in values was attributed to different sample preparation conditions and to systematic errors pertaining to some of these indirect measurement methods.⁷⁹ Recently, a 100 °C value of 10^{−11} cm²/s was obtained on coevaporated photovoltaic-quality CIGS by means of electrochemical methods.⁸⁰ Regardless of the exact values, such diffusion is quite fast because it implies that Cu can diffuse across the space charge region (SCR) of the CIGS absorber in a few minutes to several days at most.⁸¹ Such a rapidly migrating species potentially raises serious concerns as to the long-term stability of CIGS-based devices.

Three possible major consequences of Cu migration on the stable performance of CIGS-based solar cells have been identified: (i) Cu may out-diffuse into the CdS overlayer. (ii) Because Cu moves as a positive ion,¹⁹ its distribution is affected by the electric field in the absorber SCR and by any modification of it.^{23,24,46,52,82} (iii) Cu migration appears to be involved in some of the observed electrical metastabilities of CIGS-based devices.^{23,24,83,84} In this section, we focus on the first effect, which is pertinent to the interface stability. Discussion of the other two effects is deferred to section 3.3.

As noted in the Introduction, Cu out-diffusion from the absorber is a well-known phenomenon in the Cu₂S/CdS heterojunction,^{11,85} but was never observed in the CIGS/CdS heterojunction, even though the absorbers of both types of solar cells

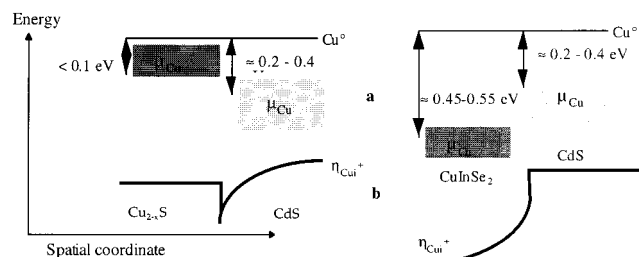


Figure 3. Ion potential diagrams for Cu^+ in $\text{Cu}_2\text{S}/\text{CdS}$ (left) and $\text{CuInSe}_2/\text{CdS}$ (right) heterojunctions. (a) Reference and true chemical potentials of Cu (μ_{Cu}) in the neutral regions of the heterojunction. The reference chemical potential of Cu is that of Cu in its metallic state, Cu° . (b) Electrochemical potential of Cu_i^+ (η_{Cu^+}), obtained by adding the electric potential. After ref 87.

are Cu chalcogenides. Because Cu migrates as an *ionic* species, we must rely on the construction of ion potential diagrams^{86,87} for explaining this unexpected difference. Briefly, an ion potential diagram is the ion-based transport analogue of the well-known electron band diagrams used for the analysis of electron-based transport. In chemical terms, a diagram of the conduction band provides the spatial dependence of the electron chemical potential. Likewise, an ion diagram provides the spatial dependence of the chemical potential of a given ionic species. By definition, both diagrams include the contribution of macroscopic electric fields (e.g., those due to p–n junctions) and chemical environment to the chemical potential, μ . Both can also be used for assessing the system evolution, if driven out of equilibrium: for electronic charge carriers, this is dictated by the quasi-Fermi levels, for ionic ones, by the electrochemical potential, η . The reference potential for an ion diagram is given by the chemical potential that corresponds to the saturation concentration of the ion in one of the materials of interest (this potential must be the same in *all* materials of interest, for otherwise ion flow between saturated solid solutions would ensue).

Ion potential diagrams for the Cu_i^+ ion in both the $\text{Cu}_2\text{S}/\text{CdS}$ and the CIS/CdS heterojunctions are given in Figure 3.⁸⁷ These diagrams were built according to the following principles: First, the reference and true chemical potentials in the neutral regions of the junctions were estimated from known Cu concentrations and/or electrochemical measurements (Figure 3a). Next, the contribution of the junction built-in potential was added, based on values obtained in electrical measurements. The potential was assumed to drop mostly across the CdS layer in the case of the $\text{Cu}_2\text{S}/\text{CdS}$ due to its lower doping with respect to the Cu_2S . The opposite was assumed in the case of the CIS/CdS heterojunction (Figure 3b).

The ion diagrams of Figure 3 immediately show why Cu out-diffusion is very likely in $\text{Cu}_2\text{S}/\text{CdS}$ cells but highly unlikely in CIGS/CdS cells. The chemical potential of Cu in Cu_2S is higher than in CdS. Moreover, the electric potential drop across the Cu_2S layer is small, so that under forward bias the generation of an overpotential that results in a driving force for Cu out-diffusion is relatively easy. However, the chemical potential of Cu in CIS is lower than that of Cu in Cu_2S by at least 500 mV in photovoltaically relevant material and is subsequently much lower than that of Cu in CdS (and gets lower still the more In-rich the film is). Cu out-diffusion from the CIGS layer is further inhibited by the significant built-in potential drop (over 600 mV at the very least) across the SCR of the CIGS layer, so that a driving force for Cu out-diffusion is absent even under a sizable forward bias. An additional factor in favor of CIS is that the Cu-poor surface composition of it (not explicitly shown

in Figure 3) can act as a sink for Cu ions, which prevents their out-diffusion.^{87,88} Thus, CIGS-based solar cells will not deteriorate due to Cu out-diffusion into CdS.

3. Electrical Stability of CIGS

While the above-established chemical stability of CIGS-based solar cells is a necessary condition for long-term stability, it is by no means a sufficient one, because the end user is ultimately interested in the stability of the *electrical* performance of the device. Herberholz et al.^{23,24} have distinguished between two basic mechanisms for electrical instability in CIGS layers: (i) a *short range*, illumination-induced metastability due to defect-state reactions and (ii) a *long range*, bias-induced metastability due to Cu-migration in the absorber material. Here, we expand on these findings by considering the impact of these two processes on cell stability, discussed separately in sections 3.2 and 3.3 below. As both effects are universally found in CIGS (see below), both are related to intrinsic defects in the material. We therefore begin our discussion with a brief overview of the pertinent facts about these defects.

3.1. Intrinsic Defects in CIGS. In many nonstoichiometric binary compounds (e.g., WO_{3-x} , Cu_{2-x}Se , $\text{In}_2\text{O}_{3-x}$, etc.), the deviation from stoichiometry generates ionized point defects that are compensated by electrons or holes. Therefore, relatively small deviations from stoichiometry (in the 10^{18} cm^{-3} range) already result in a degenerate doping concentration of the material.⁸⁹ In chalcopyrites, the doping level is found to remain nondegenerate (i.e., a maximum electron or hole doping concentration below 10^{18} cm^{-3}) for composition changes which are larger by as much as 3 orders of magnitude. (i.e., in the 10^{21} cm^{-3} range). This indicates that chalcopyrite compounds are strongly self-compensated, a fact supported by many independent experimental results (for a review see, e.g., ref 90).

For self-compensation in a material to be favored, the formation energy of the compensating ionic defect(s) must be small enough so as to be energetically favorable with respect to the formation of an electronic defect (i.e., the compensating defect is then the free carrier).⁹¹ When this is the case, the Fermi level position is self-stabilized between a lower and an upper value, as has indeed been found in many compound semiconductors.⁹² A good example is GaAs, where a large electronic contribution to the free energy of formation of point defects results in a Fermi-level dependent stability of these defects: V_{Ga} is stable in n-type GaAs but transforms into an $(\text{As}_{\text{Ga}}, V_{\text{As}})$ donor complex in p-type material.⁹³

The relatively wide single-phase domain of CIGS suggests that such self-compensation must take place in this case too.⁹⁴ Moreover, because photovoltaic-quality CIGS, which exhibits very good electronic properties, deviates significantly from stoichiometry, most of the defects or defect complexes present must be electronically inactive with respect to carrier recombination. Thus, their corresponding energy levels must either be very shallow or altogether outside the band gap.

Unfortunately, no direct measurements of defect formation energies are currently available. However, an estimate of cation and cation site related defects was recently provided by Zhang et al. on the basis of first principles, self-consistent calculations.³⁵ (Similar results were obtained for Frenkel pairs and antisite defects using a different computation method.⁹⁵) Zhang et al. considered the contributions of the Fermi level position and the chemical potential of the constituents to the free energy of defect formation. Indeed, they found formation energies much lower than those previously estimated from cohesive energies or from analogies with II–VI or III–V compounds. The actual formation

energies could be even lower, because Zhang et al. did not incorporate the Jahn–Teller effect, necessary for establishing the true minimum energy of the lattice relaxation, into their calculation.

In the following, we try to get estimates of the concentrations of various defects and defect complexes in CIGS. As the calculations of Zhang et al. assumed a 0 K temperature, we must estimate the entropy of defect formation for obtaining a 300 K value. In metals and ionic compounds, this entropy is about $1-3k$,⁹⁶ where k is the Boltzmann constant. In semiconducting materials, the entropy of defect formation is larger due to larger lattice distortions, up to $16k$ in silicon.⁹⁶ A value of $3k$ per defect was assumed in a previous study.⁹⁷ Using the latter, rather conservative value, the free energy of formation per defect at room temperature would therefore be lower by only some 75 meV than that at 0 K, which does not alter the following analysis drastically. We can therefore consider the 0 K calculations as relevant and proceed with considering their implications, keeping in mind that entropies of formation can reduce the free energies of formation of point defects by up to a few hundred millielectronvolts, i.e., result in an underestimation of the concentration of the related point defects by up to 4 orders of magnitude when the 0 K values are used. In the discussion below, we assume that these calculations, performed for CIS, are (as a first-order approximation) also valid for CIGS, because defect energy calculation are not available for the alloy.

Zhang et al. found that the most energetically favorable isolated point defect is the Cu vacancy, V_{Cu} , with a formation energy that is 0.6 eV at most (on the Cu-rich side of the composition range) and that would be negative if the existence range of the compound includes values of the chemical potential of Cu lower than -0.6 eV.³⁵ This value is much smaller than the formation energy of the In vacancy, V_{In} , which is larger than 3 eV. The same calculations indicated that *defect complexes* are highly probable. In light of the above discussion, the most important property of these complexes is that they may be *neutral* (depending on the Fermi level position) and therefore electrically inactive. The most energetically favorable defect complex found was the $(2V_{Cu}, In_{Cu})$ complex. The formation energy of this defect was calculated to decrease as the In-content increases along the $Cu_2Se-In_2Se_3$ tie line, finally assuming negative values³⁵ if those were compatible with the existence range of the compound.^{37,98} Interestingly, ordered arrays of $(2V_{Cu}, In_{Cu})$ complexes were proposed by Zhang et al. to account for the formation of the well-known CIS ordered defect compounds, e.g., $CuIn_3Se_5$, $CuIn_5Se_8$, etc. The stoichiometry of these compounds can be predicted by subtracting an integer number of the defect complexes at regular intervals along the crystal lattice.³⁵

Those calculations also explain why the phase boundary of CIGS extends on the In_2Se_3 -rich side of the tie line, but not on the Cu_2Se -rich one. Theoretically, this could have been due to the lower formation energy of V_{Cu} with respect to V_{In} , but as both these defects are charged, this does not explain the nondegenerate doping. A more sophisticated explanation invokes the existence of stable, neutral $(2V_{Cu}, In_{Cu})$ on the In-rich side, while neutral defect complexes appropriate for the Cu-poor side, e.g., $(2Cu_i, Cu_{In})$, have a large energy of formation.⁹⁹ Assuming that the $(2V_{Cu}, In_{Cu})$ defect complex plays the dominant role in preventing a degenerate doping in Cu-poor layers, its concentration can be easily estimated. As the Cu concentration in typical photovoltaic quality CIGS layers is about 22 at. %, the defect complex concentration should be at least 2 at. %, i.e., above the 10^{20} cm^{-3} range.

Other complexes with a reasonably low (and composition independent) formation energy were also found. (In_{Cu}, Cu_{In}) complexes were calculated to have a formation energy of 0.65 eV for a *single* defect complex. We recall that if the material has a degree of disorder, the distinction between In and Cu sites (and hence between associated vacancies or complexes) should become less significant. In the ideal lattice, the difference is due to the second nearest neighbor shell, which consists of 12 cations, four of which are the same as the central ion. For an In atom that is next to an In_{Cu} defect (which is assumed to be ubiquitous in In-rich material) the second neighbor environment consists of 7 Cu and 5 In atoms. The asymmetry of this environment is even lower if the In atom is next to a $(2V_{Cu}, In_{Cu})$, etc. A degree of disorder is expected to decrease the free energy of formation of (In_{Cu}, Cu_{In}) defects (as well as other ones) and indeed a value as low as 0.2 eV was calculated¹⁰⁰ if many such complexes are present. The latter value is also in agreement with a simple quasi-chemical estimate, according to which the 0 K formation energy of the randomized (In_{Cu}, Cu_{In}) pair, H° , depends on the sphalerite–chalcopyrite transition temperature T_c (1083 K) according to $kT_c = \lambda H^\circ$, where λ is a coefficient not much larger than 1.¹⁰¹

An upper bound for the concentration of the (In_{Cu}, Cu_{In}) pair can be estimated from the mass action law by using the equation

$$(In_{Cu}, Cu_{In}) = (Cu_{Cu}, In_{In})_0 \exp(-\Delta G/kT) \quad (4)$$

where $(Cu_{Cu}, In_{In})_0$ is the equilibrium concentration of cation site concentration. Assuming the latter to be 10^{22} cm^{-3} and a 0.2 eV formation energy appropriate for a disordered material,¹⁰⁰ the defect pair concentration can be as high as $\sim 4.5 \times 10^{18} \text{ cm}^{-3}$. Using the formation energy values given by Zhang et al. for other complexes (most notably that of (V_{Cu}, Cu_i) complexes, with a formation energy of 1.5 eV), a similar calculation predicts a concentration smaller than the observed doping level. Nevertheless, we do not exclude the possibility that other neutral defect complexes not considered by Zhang et al. (e.g., those involving Se) may have a low formation energy and therefore a significantly high concentration. Additionally, the temperature to be used in the mass action law (4) may not be the room-temperature one. This is because photovoltaic-grade samples are prepared at 800–900 K and then *rapidly* cooled to room temperature. An increase in the temperature used would, of course, increase the defect concentrations involved. Therefore, other complexes or single point defects such as V_{In} or Cu_i , whose (computed) energy of formation is relatively high, could still be present in electrically significant quantities.

3.2. Short-Range Effects. It is commonly observed that the performance of CIGS-based solar cells does not degrade upon illumination. On the contrary, the open-circuit voltage is usually found to increase somewhat.^{102–107} Moreover, light soaking treatments are sometimes used systematically for reestablishing fill factor losses that have occurred during thermal cycling of CIGS-based solar cells.^{26,108} As discussed below, both effects can be interpreted by a metastable capture of charge carriers in defect states.¹⁰⁹ This effect takes place both at the CIGS absorber and at the CdS buffer layer. The capture site can be distinguished by testing the response to different wavelengths.^{110,111} We therefore discuss the absorber and buffer effect separately.

3.2.1. Absorber Metastabilities. The above-mentioned illumination-induced increase in the open-circuit voltage is clearly related to the CIGS absorber layer, as it is observed even when using photon energies below the band gap of the CdS buffer layer, for which the latter is transparent.^{104,105} Such light is often called “red light”, as opposed to “blue light”, which is

absorbed in the CdS layer. Exposure to “red light” has been observed to result in a significant persistent photoconductivity (PPC) in the absorber,^{104,105} as well as in a consistent increase in the capacitance of the absorber SCR.^{104–106,110} All three phenomena can be reconciled within a simple model, in which the “red light” causes a metastable increase in the net hole density of the absorber.^{104–106,110} Such an increase would result in an increased conductivity and would contribute to the enhancement of the open-circuit voltage. Additionally, it would result in a decrease of the absorber SCR width. This would explain the increased SCR capacitance and the decreased SCR recombination.^{46,106} It therefore contributes further to the increase in the open-circuit voltage and may also improve the fill factor.

A significant hint for the microscopic origin of the hole density increase was provided by DLTS studies of CIS thin films, performed by Igalson and Schock.²¹ They found that electron capture, induced by strong injection of minority carriers (electrons), results in an inversion of the sign of the DLTS signal that decreases with time or disappears upon annealing at room temperature. This indicates the formation of metastable defect centers, interpreted as hole traps, the activation energy of which was found to be ~ 260 meV above the valence band edge. These states have been observed in CIGS in many independent studies on both thin film and single-crystal samples of various origins,¹¹² implying that the defect level involved in the metastable reaction is of an *intrinsic* nature. The inverse DLTS signal is due to hole emission from these states. Recent studies confirmed that the metastable states were situated within the CIGS film.²² Theoretically, one could argue that these metastable states are located at grain boundaries. However, the excellent passivation of CIGS thin films and the occurrence of similar metastabilities in CIGS single crystals^{113,114} seem to rule this option out. Thus, the metastable states are most likely true bulk states.

Importantly, the persistent increase of the *net* acceptor density was found to be twice as large as the increase in the metastable defect density, indicating that the formation of a metastable defect “consumes” *two* electrons;²¹ i.e., the defect has a negative effective correlation energy (“negative U ”).¹⁰⁹ In other words, due to the large energy contribution of the lattice relaxation associated with charge capture, it is energetically more favorable for the defect to accept two electrons than to have one. Moreover, this metastable defect formation was later found to occur after both optical and electrical minority carrier injection.^{22,115} This suggests that it is indeed the capture of charge that controls the PPC, rather than some direct photon interaction.

The other important findings of the studies on this defect relate to the time constant of the phenomena. The conversion of the stable defect into the metastable one is slow under low illumination levels¹¹⁶ but can occur in the millisecond time scale under high injection levels.^{110,117} Once created, this defect is able to capture a second electron (respectively, emit a hole). It is then the reverse of this second process that is observed by DLTS with a time constant having an activation energy of about 260 meV, and within the detection window of the setup (22 s^{-1} at 170 K). The reconversion of the metastable state into the stable one has a much longer time constant (hours at room temperature) and is seen in the photoconductivity experiments (but not by DLTS). Such large time constants are not consistent with a purely electronic process and probably imply that a local atomic displacement is involved in the *first* electron capture.

Metastable defect conversion is often interpreted by means of a large lattice relaxation, associated with charge capture in a defect.¹⁰⁹ This relaxation modifies the microscopic potential

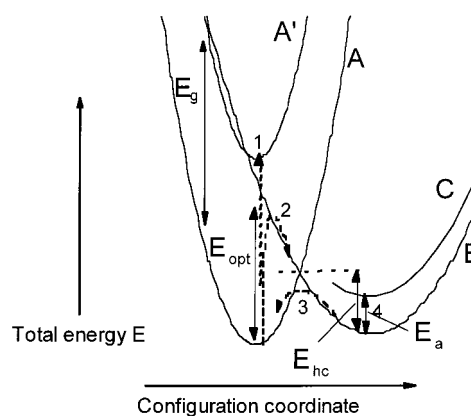


Figure 4. Schematic configuration coordinate diagram (energy versus configuration coordinate), explaining metastable defect formation, which involves large lattice relaxation. The represented states are (A) electron in the valence band and trap in the stable state, (A') electron in the conduction band and trap in the stable state, (B) electron in the trap band and trap relaxed in the metastable state, and (C) a second electron captured by the trap. Represented transitions are (1) band to band transition and relaxation of an electron in the CB into the metastable state, (2) direct optical filling of the trap at an energy lower than the band to band transition, (3) thermal relaxation into the stable state that is responsible for the long time constants of PPC, and (4) second electron capture (or equivalently hole emission) by the trap that yields the transition observed by DLTS.

distribution in the vicinity of the defect and may consequently alter its properties. If the new lattice position is also at a potential minimum, it is metastable, so that the new configuration may persist for an extended time before the equilibrium position is restored. This mechanism is widely agreed to be the source of the PPC associated with the “DX center” in AlGaAs.^{118–120} It has also been invoked to explain PPC in a host of other semiconductors, notably including binary chalcogenides.¹⁰⁹ Large lattice relaxation effects are best understood by means of a schematic “coordinate-configuration diagram”,¹²¹ shown in Figure 4. In this diagram, the overall (electronic and lattice) energy of any defect configuration is plotted as a function of a “generalized configuration coordinate”, which is a symbolic representation in one dimension of the entire set of real coordinates that specify the position of the defect itself and all nearby atoms that interact with it.¹⁰⁹ In Figure 4, the lowest curve corresponds to the total energy of the system in its ground state, the upper curve is the threshold energy of an electron–hole pair plus an empty defect, and the shifted central curve is for a free hole plus an occupied defect. The figure shows that the defect can be found not only in its *stable*, absolute minimum energy position but also in a *metastable*, local minimum energy position. The two positions are separated by an energy barrier. The second transition seen by DLTS is also represented. This view is also supported by recent results,¹²² which show that direct optical conversion (electron capture) of the metastable center only occurs at excitation energies above ~ 0.6 – 0.7 eV.¹¹⁶ Such a difference between the activation energies deduced by thermal and optical processes is typical of a lattice reorganization.^{118,119,123,124}

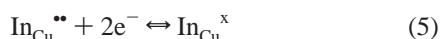
We propose that the conclusions of Igalson and Schock should be interpreted so as to apply to two different possible scenarios: In the first scenario, the metastable defect pertains to a different charge state of the same donor defect. Then, Figure 4 implies that the DLTS sign inversion should be attributed to an electron capture process into the doubly unoccupied donor (by path 1 or 2 in Figure 4). The ~ 260 meV energy (and thus the DLTS signal itself) would then be related to the energy barrier posed to hole emission from, or equivalently electron emission

into, the valence band of the second free carrier. The increase in net acceptor density is then due to the annihilation of a part of the compensating donors in the material. The initial donor energy position is probably relatively shallow, i.e., close to the conduction band, as it is not directly observed in DLTS measurements.

In the second scenario, a true donor to acceptor conversion occurs, for which one must assume a more general defect–defect reaction.^{83,84} This reaction first consumes one electron, but as the formed acceptor state is created with a transition energy below the Fermi level in the space charge region, it captures another electron from the valence band (which is equivalent to hole emission). The activation energy can then be identified with its true energy position.

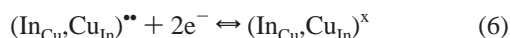
Before proceeding to discuss the possible microscopic origins of the metastable states, we comment on their effects on cell performance. CIGS is seen to exhibit metastable reactions associated with intrinsic defects. At a first glance, such reactions are reminiscent of the infamous Staebler–Wronski effect in a-Si: H¹³ and appear to be a cause for concern. However, there are two critical differences between the two cases, which suggest that the concern is unnecessary. First, here the defect reactions actually *improve* the cell performance, rather than degrade it. Second, *all* metastable effects surveyed above were found to be *completely reversible at room temperature*, with a time constant of several hours at most. Therefore, the defect reactions that improve the cell performance at its operating point should be self-annealed each night, which explains the absence of cumulative, long-term damage.

3.2.2. Candidates for the Metastable Absorber Reaction. As discussed above, the electron–lattice coupling that results in the metastable defect reaction can be due to either a rearrangement of an isolated point defect or a defect–defect interaction. Originally, a specific isolated point defect, namely the substitutional In_{Cu} defect, was hypothesized to account for the observed metastability, according to the reaction²¹



where from here on the superscripts “•”, “x”, and “••”, respectively, denote a positive, neutral, and negative relative *formal* charge of the defect with respect to its site in the ideal lattice, which is given by the subscript. This defect was selected because it is supposed to be present in large quantities in the photovoltaic quality, In-rich material, and because its charge states differ by two electrons, as expected from the DLTS data.

Reaction 5 corresponds to the first scenario discussed above, i.e., a metastable conversion of the charge state of a donor defect. As defect complexes are highly likely in CIGS (see section 3.1), a natural extension of reaction 1 would involve a defect *pair*, rather than a true point defect. Such an extension is obtained by considering the (In_{Cu}, Cu_{In}) complex discussed above, where the metastable defect reaction could be



The advantage of reaction 6 over reaction 5 is that the large interaction energy of the (In_{Cu}, Cu_{In}) complex³⁵ could account more easily for the large lattice relaxation necessary for obtaining a sizable decrease in the donor energy position.

The second scenario discussed above, i.e., defect–defect reactions that convert donors to acceptors, can be facilitated most easily by reactions involving Cu-related defects. In section 2.2 we noted that the Cu interstitial, Cu_i[•], as well as the Cu vacancy, V_{Cu}[•], are mobile defects found in sizable quantities.

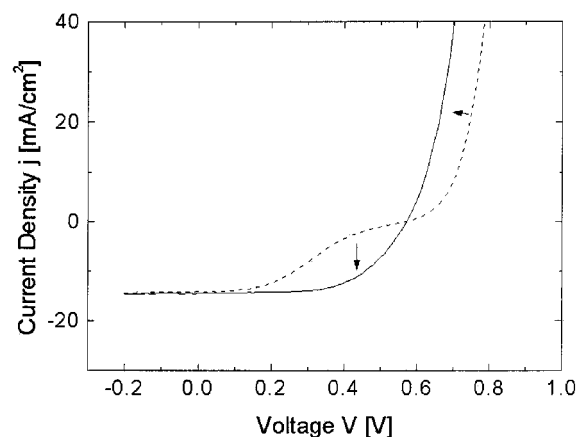
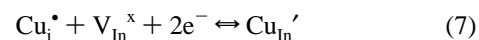


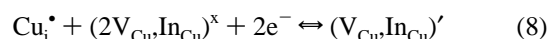
Figure 5. Current–voltage characteristics of a ZnO/CdS/Cu(In,Ga)-Se₂ solar cell under illumination with filtered light of wavelength $\lambda > 630$ nm and an intensity of approximately 50 mW/cm². Dashed line: curve measured after storing the cell in the dark for 8 h at room temperature. Solid line: curve obtained after illuminating the sample for 1 h with filtered “blue” light (wavelength $\lambda < 500$ nm).

The metastable reaction could be facilitated by the participation of mobile defects, as these could more easily “find” the suitable partner for the interaction. One candidate reaction could then be^{83,84}



as it seems likely that the Cu_{In} defect can exist in a singly ionized state rather than just in the chemically more plausible doubly ionized state. While at first sight the indium vacancy may not seem likely in photovoltaic-grade In-rich material, one should bear in mind that the concentrations needed here are orders of magnitude below the stoichiometric ones and should therefore be available, especially given the abundance of defect complexes that disrupt the ideal lattice.

A different possible reaction, in which the Cu interstitial donor is converted into an acceptor complex by direct interaction with an *abundant* complex is



This process could possibly involve a change in the redox state of the neighboring Se as well, a change not explicitly expressed in the reaction. Reaction 8 is appealing because it is in agreement with recent theoretical calculations,³⁵ which suggest that at 0 K Cu_i is indeed a shallow donor and that the Cu_{In} energy level is indeed 0.3 eV above the valence band edge, in agreement with the DLTS observation. At this point, it is clearly too early to conclude which defect reaction actually dominates the observed electrical effects because of lack of direct evidence. It is also conceivable that more than one of the options considered here plays an active role. However, all defect reactions to be considered within the framework of this model must comply with the rules of one of the two scenarios given above. The reactions given here should be considered as plausible mechanisms only in view of the available experimental findings.

3.2.3. Buffer Metastabilities. In many cases, the I–V curves of ZnO/CdS/CIGS solar cells display a significantly reduced fill factor that is due to a “kink” in the I–V curve.^{110,111,125} This kink is observed to disappear upon exposure to “blue light”, i.e., photons with energy greater than the CdS band gap and reappear after storage in the dark. An example of this behavior is given in Figure 5, which features two I–V curves measured

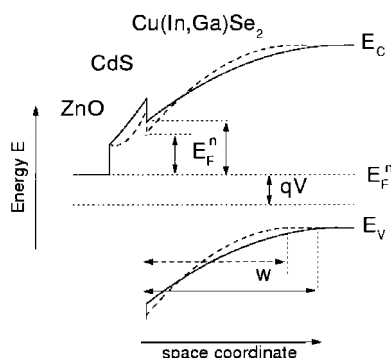


Figure 6. Schematic band diagram of a ZnO/CdS/Cu(In,Ga)Se₂ solar cell under bias voltage V , illustrating the effect of “blue illumination”. Solid lines: after extended storage in the dark. Dashed lines: After extended “blue” illumination. E_c and E_v are the energy positions of the conduction and valence bands, respectively, E_{fn} is the electron quasi Fermi level, ΔE_{fn} is $E_c - E_{fn}$. A spike was drawn at the CdS/CIGS interface for illustration purposes (this does not take interdiffusion into account).

under “red light” illumination: one taken after storage in the dark and one taken after exposure to “blue light”.

Hou et al. proposed that the characteristic kink is due to an effective barrier for electron transport across the buffer layer, brought about by an insufficient electron density in the CdS film, which results in an excessive potential drop over it.¹²⁵ Ostensibly, similar conclusions were obtained in subsequent studies.^{110,111,126} It is generally agreed that “blue light” reduces this effective barrier to harmless values. This is because the photogenerated holes are persistently captured in acceptor states in the CdS film, thus passivating these states. This increases the *net* donor (and hence electron) density in the CdS film and reduces the potential drop across it, as illustrated in Figure 6.

From the microscopic point of view, it is yet unclear whether the persistent capture of holes is due to a large lattice relaxation, as in the absorber, or is a pure electronic effect associated with trapping in a deep state with a very small emission coefficient. In either case, it turns out that in the buffer, as in the absorber, we are again met with a very fortunate case, where unsatisfactory properties found in the dark are automatically improved upon as soon as the cell is brought to proper working conditions (in this case, exposure to the *full* solar spectrum).

3.3. Long-Range Effects. As discussed above in the context of copper out-diffusion and of Cu-involving defect reactions, Cu is highly mobile in CIGS. Because Cu transport involves ionized species (Cu_i^+ or V_{Cu}'), its distribution must be sensitive to electric fields. Any variations in the latter may therefore result in significant effects that involve a *long range* rearrangement of Cu-related defects. The electrical consequences of such effects and their possible implications for solar cell stability are addressed in this section.

Cu mobility is not only a cause for concern. For example, thermally assisted Cu electromigration has been employed in a beneficial manner for the low-temperature preparation of diodes and transistors,⁷⁴ where type conversion was obtained by a significant manipulation of the Cu content. Using this technique, CIS-based transistors with a cross-section as small 50 nm were demonstrated recently.¹²⁷ In these devices, the electric field necessary for their formation was applied by means of an atomic force microscope tip.

Cu migration has also been suggested to be the origin of the significantly Cu-poor surface composition found on Cu-poor films even if their overall composition is close to stoichiometry.^{23,24,86} According to this explanation, the electric field of

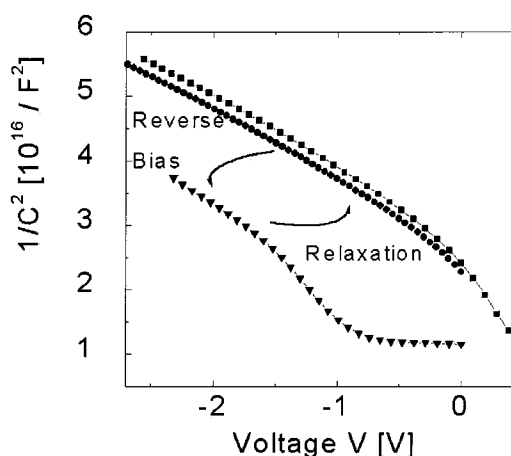


Figure 7. Mott-Schottky plots of a ZnO/CdS/CuInSe₂ solar cell, determined at 80 K and a test frequency of 100 kHz at equilibrium (circles), after application of reverse bias of -2 V for 2 min at 340 K (triangles), and after relaxation of the sample for 60 min at 340 K (squares).

the surface SCR raises the position of the Fermi level, which increases the formation of Cu vacancies. The resulting Cu_i^+ ions are repelled from the CIGS surface (or, equivalently, the V_{Cu}' defects are attracted to it) under the influence of the electric field of the surface SCR, thereby reducing the surface concentration of Cu significantly. Notable evidence supporting this model has been provided recently by Klein and Jaegermann.⁸² Using photoelectron spectroscopy measurements, they demonstrated that both CdS and Na deposition on single-crystalline CIS, which increases the band bending at the CIS surface, results in a significant removal of Cu from the near-surface area.

The electric field related large-scale changes in Cu concentration suggest that even under the relatively mild bias, temperature, and illumination conditions used in an operating solar cell, Cu migration effects could be significant. At the very least, shifts in the effective doping profile of the layer can be expected. Such an influence has indeed been observed by several authors.^{23,24,83,84}

The influence of bias on the effective doping of CI(G)S layers is demonstrated by the Mott-Schottky plots obtained from capacitance-voltage ($C-V$) measurements of a photovoltaic grade, CIS-based solar cell under equilibrium, after the application of a -2 V reverse bias for 2 min, and after subsequent annealing at 340 K for 60 min, shown in Figure 7. All measurements were taken at a temperature of 80 K, where the capacitance corresponds to that of the space charge only, because the time constants of deep trap levels involved are too long to allow a trap contribution to the observed capacitance.^{23,24,83} Further details concerning cell preparation and the experimental setup, both of which are standard, have been given elsewhere^{23,24,83} and are omitted here for brevity.

The application of reverse bias has clearly led to considerable changes in the $C^{-2}-V$ curve. However, after the annealing step, a curve very close to the original one is obtained. Restoration of the original curve was also observed after an overnight relaxation at room temperature. This is a direct consequence of the recovery of the equilibrium Cu distribution once the “normal” conditions have been resumed. Thus, long-range effects associated with Cu migration are *not* expected to result in irreversible effects and no long-term impacts on cell stability are expected.

More insight into the nature of the changes induced by the bias and annealing treatments is provided by considering that

the capacitance decreases upon application of reverse bias; i.e., the interface is negatively charged. This can be interpreted as follows. Equilibrium doping profiles indicating an increase of the acceptor density toward the CdS/CIS interface were consistently found in several recent studies of thin films,^{21,23,24,83} in older studies of thin films produced with a “previous generation” of technology,^{128,129} and even in studies of single crystals.⁸⁴ This strongly points out that an *intrinsic* property of the material is involved. Both the increase in the acceptor concentration toward the CdS/CIS interface and its intrinsic nature are consistent with the above-mentioned model, whereby the built-in field of the absorber SCR attracts acceptors (V_{Cu}^-) and repels donors (Cu_i^+). After application of reverse bias, the increase of the electric field attracts acceptors and repels donors further, resulting in capacitance reduction. This interpretation is also consistent with a recent observation of a significant concentration of (what are most likely Cu) interstitials in CIS crystals using synchrotron-based X-ray diffraction experiments,¹³⁰ especially in light of the observation of electric field effects on these interstitials and on the occupancy of Cu lattice sites. While this explanation is self-consistent, one should also check if short-range effects, i.e., local bias-induced changes in acceptor or donor charge, cannot explain the observed phenomena, too. This is especially so in light of the previous section, where they have been found to be of much importance in CIGS layers. Several factors argue decisively against such an interpretation. First, the change in doping profile is *more pronounced* the higher the temperature.^{23,24,74} However, the degree to which metastable defects would self-anneal should increase with temperature, resulting in a *less pronounced* effect. Second, the change is more pronounced the longer the bias time.^{23,24} However, a “short range” metastable reaction, initiated by minority carrier injection, is instantaneous on the scale of the many minutes found here. Third, had metastable states alone been involved, the effect of electrical forward bias and of illumination-induced photobias on the doping profile should have been similar, at least qualitatively. However, previous studies have shown that whereas illumination induces an *overall* increase in the hole density, forward bias causes a *shift* of the dopant profile.^{23,24,83}

We conclude this section by discussing the electrical consequences of Cu migration for the cell. Exposure to reverse bias may occur for single cells within a series-connected module by the partial shading of the module. Thus, the cell structure should be stable against reverse bias within the possible range of operating temperatures. It should also be stable against forward bias, found under normal operation. From the discussion above, we see that the effects are reversible, at least under the mild (temperature, bias) conditions relevant for the solar cell. Moreover, application of a forward bias leads to a decrease of the acceptor concentration in the SCR, due to Cu migration. This in itself would *decrease* the performance of the cell because of an increased SCR recombination. Fortunately, this is more than compensated for by the illumination-induced formation of metastable states.

4. Radiation Hardness and Impurity Tolerance

4.1. Empirical Findings. A particularly intriguing phenomenon in CIGS-based solar cells is their outstanding radiation hardness, found in several independent studies.^{27,28, 131} In fact, the radiation hardness of CIGS-based solar cells was found to be superior to that of solar cells based on Si, InP, and InGaP,^{28,131} for both proton and electron irradiation. For a detailed presentation, see refs 132 and 133. For example,

irradiation doses of several 10^{12} (10 MeV) protons/cm² or 10^{17} (1 MeV) electrons/cm² only caused a relative reduction of less than 5% in cell efficiency, whereas doses smaller by 1 order of magnitude caused a degradation of at least several tens of percent in other types of solar cells.¹³¹ Furthermore, in a different study (10 keV) proton doses smaller than 10^{15} cm⁻² actually resulted in a small *improvement* of the lattice structure (as determined by Rutherford backscattering and Raman spectroscopies).^{134,135} Interestingly, the improvement of chalcopyrite material under radiation by megaelectronvolt electrons is a more general finding. It is used, for instance, to reduce substantially sub-bandgap absorption in nonlinear optical materials.¹³⁶

Polity et al. have explicitly studied the impact of ionizing radiation on the defect structure in CIS.¹³⁷ They reported a formation of divacancies upon irradiation with a dose of 10^{17} (2 MeV) electrons/cm² at 4 K. To put these numbers in perspective, we note that the average number of Cu atoms displaced by one 1.5 MeV electron or one 10 MeV deuteron is 1 or 5, respectively.¹³⁸ Most interestingly, Polity et al. discovered that these defects are at least partially annealed already at 270 K, i.e., *below room temperature*. This strongly suggests that the radiation hardness of CI(G)S is not entirely due to a *resistance* of the material to damage formation, but at least some of it is due to *self-repair* of irradiation-induced damages, as suggested by us in a recent communication.⁸¹ Here, we build on our previous work to present a detailed discussion of the mechanisms of defect self-passivation.

A different aspect of the capability of CIGS for defect accommodation is the unusual tolerance of CIGS to impurities. For instance, implanted doses of Cd as large as 10^{19} cm⁻³ did not appear to damage the optoelectronic properties of the material once it was annealed under a Se flux at the growth temperature.¹³⁹ Low (98%) purity starting materials (evaporation sources) have been successfully used for making efficient solar cells based on coevaporated CIGS layers.¹²²

4.2. Model for Defect Passivation. For understanding how self-repair of irradiation-induced defects takes place, we must first examine the microscopic consequences of such irradiation. Clearly, damage is brought about if one of the constituent atoms is knocked out of its lattice position. The three possibilities are therefore the formation of a $\text{Cu}_i\text{--}V_{\text{Cu}}$, an $\text{In}_i\text{--}V_{\text{In}}$, or a $\text{Se}_i\text{--}V_{\text{Se}}$ defect pair. (To first order, we ignore irradiation-induced movements of substitutional or interstitial atoms. This is because such a process does not create new defects, but rather converts a given defect into a different one.) Of the three defect pairs, the first is generally the one estimated to have the lowest formation energy.¹⁴⁰ Cu is also much lighter than In and has a smaller ionic radius than Se, so that the Cu atom is the most likely one to be knocked out of its site. Finally, we recall that most of the energy deposited by radiation results in heat dissipation and that much of the damage does not remain for long in the solid; i.e., the Frenkel pairs formed recombine if the vacancy–interstitial separation is not large.¹³⁸ We therefore begin with discussing how the Cu interstitial and the Cu vacancy defect can be passivated.

As discussed in section 2.2 above, the Cu interstitial is highly mobile in CIGS. This makes the Cu vacancy effectively mobile as well, in a manner analogous to the transport of holes. Given a Cu diffusion coefficient of 10^{-13} to 10^{-10} cm²/s, a straightforward calculation⁸¹ shows that Cu may traverse the entire SCR of the absorber within several days at most even under the most pessimistic assumptions. This means that the Cu concentration in the CIGS layer is essentially at equilibrium. The concentration of Cu defects will therefore also be at equilibrium and will be

governed by a mass-action law. Consequently, any disruption of the equilibrium distribution will result in a driving force for reequilibration, in agreement with the Le Chatelier principle. Thus, Cu defects will be self-annealed. An instructive special case of the above principle is the transformation of a Cu_{Cu} atom, residing within the SCR, into a Cu_i⁺–V_{Cu}[−] pair. Upon formation, the Cu_i⁺ defect will be repelled from the CdS/CIGS interface and the V_{Cu}[−] defect will be attracted to it. This will serve to set up an electric field that opposes the original one (much like the photovoltaic effect is due to electron–hole separation that sets up an electric field opposing the original one). This opposing electric field would provide the driving force for reequilibration.

A different mechanism that exploits Cu mobility for defect annealing relies on defect reactions. If new charged defects are introduced into or removed from some region of the sample (via irradiation or diffusion), the local defect equilibrium is disrupted. Defect reactions such as reactions 7 and 8 above would therefore proceed in a direction that opposes the original change, again according to the Le Chatelier principle, so that the net effect of the damage on the defect distribution would be much smaller, and potentially negligible in the presence of a significant defect pool. In other words, the defect complex pool acts as a reservoir, capable of receiving or delivering electronic and ionic charge carriers so that their net amount remains fixed. Such defect reactions therefore act as both *electronic* and *chemical* buffers, by controlling both the electron concentration and the Cu concentration, respectively.

The proposed buffering action also explains why Cu in-diffusion, up to a certain point, does not disrupt the p-type conductivity of the film. This is especially important given that Na and O treatments, generally deemed to be beneficial for the photovoltaic properties of the CIGS absorber, may result in Cu in-diffusion as well.^{52,64}

The buffering action of the defect pool is essentially similar to the role of a buffer solution in aqueous electrolytes, where complexes in large concentrations (e.g., acids with a concentration such that the pH is close to their pK_A) are used to fix the ionic concentration, e.g., the pH. In semiconductor science, the corresponding concept is that of Fermi level pinning by a large concentration of defect states. Such an analogy between defects in solids and solutes in electrolytes has been proposed and developed previously,^{91,141} but mainly for binary compounds and for low defect concentrations. Such autocompensation of donor or acceptor species is frequently invoked to explain doping limits in various semiconductors,⁹² including CIGS.¹⁴² However, the striking difference here is that the defect formation energies are small enough to allow such processes to take place *at room temperature*—a prerequisite to effective elimination of radiation damages in the course of normal solar cell operation. Moreover, *self-passivation*, rather than simply *self-compensation*, is at work, because the defect complexes are effectively inactive with respect to either carrier recombination or mobility.¹⁴³ We also note that in many materials, self-stabilization of the doping level is actually *detrimental*, as it makes the attainment of a doping level (or even type) desired for optimal device operation very difficult. Fortunately, the doping level that can be obtained with CIGS is appropriate for photovoltaic applications.

Two conditions must be satisfied if the buffer effect is to function well. First, the defect complex must be amenable to Cu exchange, as only Cu is sufficiently mobile so as to reach a defect complex site with high probability. Second, the reaction must involve free carriers as well. For example, if only Cu_i⁺ were trapped, the additional electron would cause the Fermi

level to increase and eventually type conversion could take place. Reactions 7 and 8 meet both conditions.

We now turn to assessing the possibility of self-healing of In-related defects, which are the second most probable consequence of particle irradiation. At first sight, such healing appears to be very difficult: as In-related defects are much less mobile at room temperature, they are much less likely to be healed merely by reestablishing their equilibrium distribution or to migrate to a site where In-exchanging buffer reactions can (theoretically) take place. However, In-related defects can be annealed by *Cu-exchanging* reactions as well. For example, reaction 7 (proceeding from left to right), passivates an In vacancy and reaction 8 (proceeding from right to left) passivates an In_{Cu} substitutional defect. Thus, Cu may act as a mobile “healing agent” for In defects as well.¹⁴⁴ We also note that the defect complexes calculated by Zhang et al.³⁵ result in electronic states that are far from midgap (and farther from it relative to the isolated point defects), thus making them rather ineffective as recombination centers. This further aids in the “healing” of the electronic properties.

We tentatively propose that, while experimental and theoretical data of Se-related defect complexes is currently lacking, other Cu-involving “healing” reactions may account for repair of the (much less likely due to the expected high formation energy of Se_i) Se-related irradiation damage. By extrapolation, one may also assume that the remarkable capability of the material to form neutral or shallow defect complexes may also account for its tolerance to extrinsic defects. The existence of metastable centers in CIGS is, in this respect, another manifestation of this capability. Finally, we note that materials that are easy to fabricate possess a stable energetic minimum to which many different paths lead. They may therefore *a priori* be expected to be more robust because more opportunities for returning to the equilibrium state from a perturbed state are present. Indeed, it has been noted by several groups that CI(G)S can be fabricated with a large variety of methods and under a wide range of conditions,^{145–150} further supporting our model.

This brings us to an interesting parallel. Hitherto “autorepair” features have been observed only in living systems. Their absence in man-made devices limited the choice of materials that could be used. Another parallel with living systems is the so-called principle of robustness, one of the three plausibility arguments used to construct biogenesis (origin of life) models.¹⁵¹ Essentially, it tells us that we need to look for materials that can form in many different ways (from the prebiotic soup ingredients) as the starting point for biogenesis models. These last two points are not mere curiosities. Mostly, if there is a choice, we find that in nature stability wins over efficiency. Here, we seem to be enjoying both. Thus, the CIS-based solar cells appear to be an example that may well contain a lesson for future material and device designers.

5. Conclusions

In this article, we have considered the apparent contradiction between the empirically observed long-term stability of CI(G)S-based solar cells and the fundamental instabilities of the material system, namely, interface reactions, defect metastability, and constituent element (Cu) mobility.

Specifically, we have shown that: (1) All reasonably anticipated detrimental interface reactions at either the back-contact/absorber, absorber/buffer or buffer/window interfaces are either thermodynamically or kinetically limited. In particular, unlike in Cu₂S/CdS cells, Cu mobility does not contradict long-term stability. (2) Unlike in a-Si:H cells, defect metastabilities

are self-annealed at room temperature and are actually beneficial to cell performance because they increase the effective doping level in the absorber. The origin of the metastable center(s) was also discussed.

We have then shown that two important features of CI(G)S, namely the presence of a large defect pool and the ionic migration, though seemingly problematic, are actually an asset and not a liability. Their synergetic action is the key to explaining the remarkable radiation hardness and impurity tolerance of CI(G)S-based solar cells. The former point arises because the mobility of Cu provides a means of undoing defect-related gradients in the chemical potential of the material. Specifically, Cu-related defect complex pools are used to buffer electronic and chemical changes, where Cu migration enables the passivation of a defect appearing anywhere within the absorber and reaction energies are low enough to permit this passivation to occur even at room temperature.

We thus conclude that the electrical stability of CI(G)S is not static but is rather *dynamic*. In other words, stability is not obtained because the material is "strong", but because it is *flexible*. In a sense, CI(G)S may therefore be considered to be a "smart material", which has been defined as one "that is capable of sensing changes in its environment and responding to them".¹⁵²

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