Aalto University

Oikkonen, L.E.; Ganchenkova, M.G.; Seitsonen, A.P.; Nieminen, R.M.

Effect of sodium incorporation into CuInSe2 from first principles

Effect of sodium incorporation into CuInSe$_2$ from first principles

L. E. Oikkonen, M. G. Ganchenkova, A. P. Seitsonen, and R. M. Nieminen

Articles you may be interested in

Investigation of the diffusion behavior of sodium in Cu(In,Ga)Se$_2$ layers
Journal of Applied Physics **115**, 154501 (2014); 10.1063/1.4871457

Efficiency enhancement of Cu(In,Ga)Se$_2$ solar cells due to post-deposition Na incorporation
Applied Physics Letters **84**, 1129 (2004); 10.1063/1.1646758

Effects of Na on the electrical and structural properties of CuInSe$_2$
Journal of Applied Physics **85**, 7214 (1999); 10.1063/1.370534

Effects of Ga addition to CuInSe$_2$ on its electronic, structural, and defect properties
Applied Physics Letters **72**, 3199 (1998); 10.1063/1.121548

Defect formation in Cu(In,Ga)Se$_2$ thin films due to the presence of potassium during growth by low temperature co-evaporation process
Journal of Applied Physics **114**, 194508 (2013); 10.1063/1.4832781

Oxygenation and air-annealing effects on the electronic properties of Cu(In,Ga)Se$_2$ films and devices
Journal of Applied Physics **86**, 497 (1999); 10.1063/1.370758

Effect of sodium incorporation into CuInSe$_2$ from first principles

L. E. Oikkonen,[1] M. G. Ganchenkova,[1,2] A. P. Seitsonen,[3] and R. M. Nieminen[1]

[1]*COMP Centre of Excellence, Department of Applied Physics, Aalto University, P.O. Box 11100, FI-00076 Aalto, Espoo, Finland*
[2]*Department of Materials Science, National Research Nuclear University (MEPhI), 31 Kashirskoe Avenue, 115409 Moscow, Russia*
[3]*Physikalisch-Chemisches Institut, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*

The presence of small amounts of sodium has been shown to improve the electronic performance of Cu(In,Ga)Se$_2$ (CIGS) solar cells, but the origins of this effect have not yet been fully resolved. In this work, we have addressed the questions involving the role of sodium in CuInSe$_2$ (CIS) using density-functional-theory-based calculations. We find no direct way how the creation of Na-related point defects in bulk CIS would enhance *p*-type conductivity. Instead, we demonstrate that Na reduces copper mass transport due to the capture of copper vacancies by Na$_{Cu}$ defects. This finding provides an explanation for experimental measurements where the presence of Na has been observed to decrease copper diffusion. The suggested mechanism can also impede V_{Cu}-related cluster formation and lead to measurable effects on defect distribution within the material. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4819105]

I. INTRODUCTION

The incorporation of sodium to a typical concentration of 0.1 at. % has been shown to enhance the conversion efficiencies of CuInSe$_2$ (CIS)-based CuIn$_x$Ga$_{1-x}$Se$_2$ (CIGS) solar cells (see Refs. 1 and 2, and references therein). Na-doped films demonstrate, for instance, higher *p*-type conductivity, better morphology, and modified defect distribution compared to their undoped counterparts. However, the beneficial effect of Na starts to wear off with large amounts of Na and even degrades device performance.[2,3] The impact of sodium was initially realized after it was found to diffuse into the CIGS films from soda-lime substrates during processing. Nowadays, an optimal amount of sodium is incorporated into the films intentionally, either through diffusion from the substrate or from extrinsic sources, yet the mechanisms of how Na affects CIS are still not properly understood.

Na has been mostly studied in polycrystalline CIGS films, where it has been observed to accumulate at grain boundaries: recorded Na concentrations are significantly higher in grain-boundary regions than inside grains.[4,5] Yet no unequivocal proof exists to show that Na effects would arise solely from interactions at the grain boundary[6,7]–even a dilute Na concentration in the bulk may potentially modify the overall electronic properties of the material. Improved *p*-type conductivity has indeed also been reported in single-crystal epitaxial CIGS films.[8]

Several attempts have been made to explain the improvement of electronic properties triggered by the presence of Na starting from bulk effects.[3,8–10] While it cannot be known *a priori* which lattice sites Na atoms would occupy when incorporated into the CIS lattice, they can be assumed to either replace lattice atoms and/or remain in the form of interstitials. In the simplest case, these structural changes would directly alter the electronic properties in a way that promotes the net *p*-type conductivity. For instance, it has

been suggested that Na would reduce the concentration of donor-type In$_{Cu}$ antisites by forming electrically passive Na$_{Cu}$ defects instead, thereby decreasing charge compensation.[3,9] Another possibility is that Na could create acceptor-type Na$_{In}$ defects, which would directly enhance *p*-type conductivity.[10] Going one step further, an indirect mechanism could operate to passivate donors: Na could enhance point defect mobility, promoting the formation of charge-neutral defect complexes.[8] Additionally, it has been suggested that Na would act together with other impurities such as oxygen.[4]

The detrimental effects encountered at exceeding concentrations of Na remain less explored than the beneficial effects at lower concentrations. Still, several speculations on the working mechanism have been presented. For instance, after replacing all In$_{Cu}$ antisites, Na would start to fill acceptor-type copper vacancies, reducing carrier concentrations.[3] Moreover, when available in stoichiometric quantities, Na would lead to the formation of competing phases, transforming the material properties altogether.[3] At this point, carrier concentrations would be overly increased.[2] Device performance may also be degraded by the creation of additional recombination centers.[4]

As the variety of scenarios presented above show, the effect of Na in CIS has raised vivid discussion, yet no consensus on the topic has been reached. It should be noted that the different suggestions do not necessarily cancel each other out—Na probably influences the material in multiple ways instead of only one.[1] Research efforts should be maintained as some working mechanisms might not yet have been identified, while prior suggestions require additional validation. In particular, a clear understanding of how Na behaves in bulk CIS should be established before proceeding with the more complicated grain-boundary region.

In this work, the effect of sodium in CIS has been studied with thorough density-functional-theory-based calculations. Compared to previously reported computational

studies on this topic,[3,11–13] the scope of our work extends beyond defect energetics to diffusion kinetics and complex formation. Our results do not support any direct way how Na-related defects could affect the conductivity in bulk CIS, but instead we discover a novel mechanism how Na changes diffusion kinetics by trapping copper vacancies.

II. COMPUTATIONAL METHOD

The calculations in this work have been carried out in the framework of density-functional theory (DFT) as implemented in the VASP code.[14,15] Exchange-correlation has been described with the semilocal GGA-type (generalized-gradient approximation) PBE (Perdew-Burke-Ernzerhof[16]) and the range-separated hybrid HSE06 (Heyd-Scuseria-Ernzerhof[17]) functionals. The parameter α controlling the amount of Hartree-Fock exchange in the HSE06 functional has been set to 0.25 as derived from perturbation theory[18] and the range-separation parameter ω has been kept at 0.20 1/Å. The projector-augmented-wave (PAW) method[19,20] has been employed with a cutoff energy of 400 eV for the plane-wave basis set.

For defect calculations, supercells have been constructed by adding and/or removing n_i atoms of type i from the bulk supercell. The system has then been allowed to relax until the forces on each atom drop below 0.01 eV/Å. The formation energy of each defect has been calculated as

$$E_f^q = E_{\text{defect}}^q - E_{\text{bulk}} \pm \sum_i n_i \mu_i + q(E_{\text{VBM}} + \mu_e), \quad (1)$$

where E_{bulk} is the total energy of the bulk supercell, E_{defect}^q is the total energy of the supercell containing the defect in charge state q, μ_i is the chemical potential of the atom of type i, and μ_e is the Fermi level position defined relative to the energy at the valence-band maximum, E_{VBM}. The chemical potentials for Cu, In, and Se have been restricted to varying between the chemical potential of the elemental solid and limits imposed by competing compounds of CIS, such as $CuIn_5Se_8$ and Cu_3Se_2 (for further details, see our previous work[21]). The upper limit for the chemical potential for sodium has been taken as that of metallic bcc sodium and the lower limit comes from competing phases, Na_2Se and $NaInSe_2$, following Ref. 3. Errors arising from the finite size of the supercell have been taken into account with finite-size scaling as described in our previous work.[21]

In order to evaluate the stability of Na-related defect complexes, their binding energies have been computed as follows:

$$E_b = E_{\text{tot}}^1 + E_{\text{tot}}^2 - E_{\text{bulk}} - E_{\text{tot}}^{\text{complex}}, \quad (2)$$

where E_{bulk} is the energy of the bulk system, E_{tot}^1 and E_{tot}^2 are total energies of the system containing the isolated constituents of the complex, and $E_{\text{tot}}^{\text{complex}}$ is the total energy corresponding to the system containing the defect complex. For all considered complexes, the values for E_b do not practically depend on the exchange-correlation functional used, but are very sensitive to the supercell size.[22] In this work, the

binding energies have therefore been computed in a 512-atom supercell employing PBE-GGA.

The migrations barriers have been calculated with the climbing-image nudged-elastic-band method (CINEB)[23] as in our previous work, employing HSE06 in a 64-atom supercell.[24]

III. RESULTS

A. Defect energetics

The incorporation of Na into bulk CIS gives rise to Na-related point defects, which can be substitutional or interstitial. The order of preference between possible point defects can be evaluated based on their formation energies. It should be noted that, in this case, the formation energies cannot be used as an absolute measure of defect quantities since the actual Na concentration in CIS films is not determined by thermal concentration but rather by external conditions such as growth.

The point defect formation energies are illustrated in Figure 1. It can be seen that, apart from Na_{Se}, all Na-related defects are stable in only one charge state. The stable charge state corresponds to the slope of the linear function as expressed by Eq. (1). The lack of defect-induced states is reflected in their Kohn-Sham band structures depicted in Figure 2. The defect level induced by Na_{Se} is hybridized with the conduction-band minimum (CBM) in the charge state 1+ and shifts down with the addition of two electrons.

Figure 1 shows that Na prefers to go to vacant copper sites. Among the considered point defects, Na_{Cu} has the lowest formation energy practically irrespective of chemical conditions. Substituting copper with a single sodium atom does not change the valency of the site as both are monovalent cations. In terms of electronic properties, Na_{Cu} is

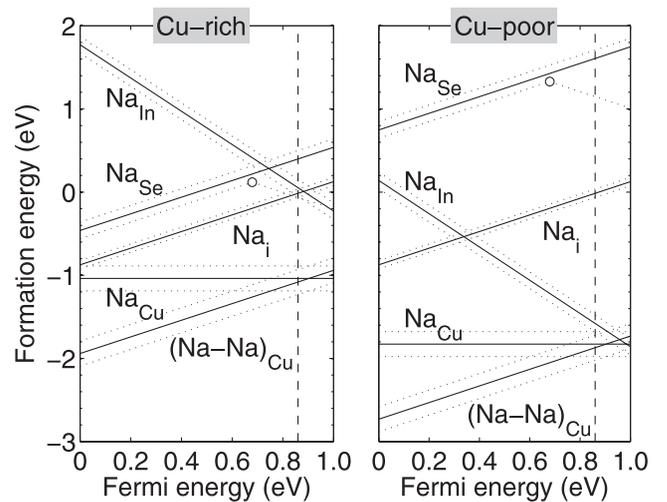FIG. 1. Formation energies of sodium-related point defects and $(Na-Na)_{Cu}$ dumbbell in CIS as a function of Fermi energy. At the Cu-rich limit, the corresponding chemical potentials for In and Se are $\Delta\mu_{In} = 0$ eV and $\Delta\mu_{Se} = -1.21$ eV. At the Cu-poor limit, the chemical potentials are $\Delta\mu_{Cu} = -0.79$ eV, $\Delta\mu_{In} = -1.63$ eV, and $\Delta\mu_{Se} = 0$ eV. The chemical potential for sodium is that of metallic bcc sodium. The dotted lines give error estimates for the formation energies at each Fermi level position. The dashed line marks the band gap obtained with HSE06.
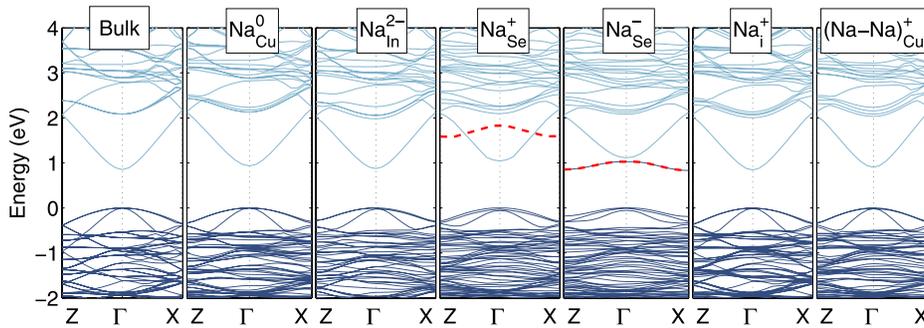
FIG. 2. Kohn-Sham band structures for bulk CIS, Na_{Cu}^0, Na_{In}^{2-}, Na_{Se}^+, Na_{Se}^-, Na_i^+, and $(Na-Na)_{Cu}^+$. The occupied levels are drawn in dark blue and the unoccupied levels in light blue. The dashed lines illustrate the defect-induced levels compared to the bulk band structure for Na_{Se}^+ and Na_{Se}^-.

charge-neutral and electrically passive and therefore cannot bring about any changes to the doping behavior of CIS.

The favorableness of Na_{Cu} has been established also in previous studies,[3,11] but the possibility of it forming part of a defect complex has not been considered until now. For instance, two Na atoms could occupy the same copper site in a dumbbell configuration. Our results show that, provided a supply of Na atoms, the dumbbell configuration would actually be very preferable in terms of formation energy especially under copper-poor conditions. $(Na-Na)_{Cu}$ dumbbells can be oriented in the [110] or [001] directions in the lattice, of which the energetically preferred orientation is [110]–we found that the [001] configuration actually is a saddle-point configuration, which relaxes into [110] with the slightest nudge in its direction. Besides the formation energy, the stability of the complex should be evaluated separately before judging its existence as discussed in Sec. III B. In principle, dumbbells may also exist as a mix of two atomic types, but no combinations such as Na-Cu dumbbells were found to be stable in this study.

Na substituting the other lattice cation, indium, involves a transfer of two electrons and costs more in energy than with copper. Due to its charge state of 2–, the formation energy of Na_{In} decreases fairly rapidly with increasing Fermi level position, and can attain the magnitude of Na_{Cu} under Cu-poor and In-poor conditions in *n*-type material. However, under these conditions, defect formation is strongly limited by Fermi level pinning arising from excess copper vacancies,[21] so the practical concentrations of Na_{In} will probably remain quite negligible. Our results disagree with the previous studies where Na_{In} was competing with the formation of Na_{Cu},[3,11] presumably because of their inadequate finite-size corrections.

Even more improbable is the formation of Na_{Se}—it is the least favorable Na-related point defect, and thus, unlikely to be formed at all. Na_{Se} stands out as the only Na defect introducing a charge transition level within the CIS band gap. Moreover, it also exhibits negative-U behavior, maintaining both 1+ and 1– charge states. Yet its very high formation energy compared to other Na defects indicates that the role of Na_{Se} can be neglected when considering the factors affecting the electronic structure of CIS.

Na can enter the CIS samples as an interstitial Na_i^+. Interstitial atoms may access various types of sites in the chalcopyrite lattice: octahedral, tetrahedral, and trigonal. Out of these options, Na_i is equally likely to occupy tetrahedral and trigonal sites, while octahedral sites are energetically less favorable. However, due to the much lower formation energy of Na_{Cu} compared to Na_i, it is probable that Na_i is transferred to a vacant copper site under copper-poor conditions. In the absence of vacant sites, it is not clear *a priori* whether Na_i would remain as an interstitial or form Na_{Cu}. In this case, the energy of the interstitial should be compared with the sum of formation energies of the outcome: antisite plus interstitial, which is created when the substitutional atom is kicked out of its site. It turns out that the formation energy of Na_i equals within error bars the sum of Na_{Cu} and Cu_i, signifying that both configurations are feasible.

Overall, Na seems to accumulate in the copper sublattice in CIS whenever there are vacant copper lattice sites available. Under copper-rich conditions, Na_i may either stay as an interstitial or replace a lattice copper atom. From the electronic structure point of view, Na-related defects behave very similarly as what we have observed previously about intrinsic defects in CIS:[25] cationic defects induce no deep levels in the gap as opposed to selenium-related defects, in this case Na_{Se}, which may act as electron traps and be detrimental to device operation.

B. Defect migration and interactions

After entering the CIS film, Na atoms may spread via diffusion. Diffusion typically requires assistance from point defects, and in the case of Na, two possible mechanisms can be imagined: Na_i-mediated and V_{Cu}-mediated. Out of these two options, interstitial-mediated diffusion is feasible, whereas Na diffusion in the copper sublattice is hindered by complex formation as will be discussed below. The migration barrier for Na_i is only 0.51 eV, signifying that it is mobile already at relatively low temperatures. The corresponding diffusion path is presented in Figure 3.

Diffusion also shapes the defect distribution in the material by subjecting defects to mutual interactions, which can result in complex formation. Looking at the binding energies of Na-related defect complexes listed in Table I, they do not, however, demonstrate particular stability. Na_{Cu} and V_{Cu} stay basically indifferent to each other with a vanishing binding energy, and the addition of a second copper vacancy or bringing two substitutional impurities together even leads to repulsion. In contrast, two $(Na-Na)_{Cu}$ dumbbells are slightly attracted to each other (E_b of 0.15 eV), which suggests that Na atoms could cluster together–in polycrystalline material, this could occur at grain boundaries, resulting in extended defects consisting of several $(Na-Na)_{Cu}$ dumbbells.
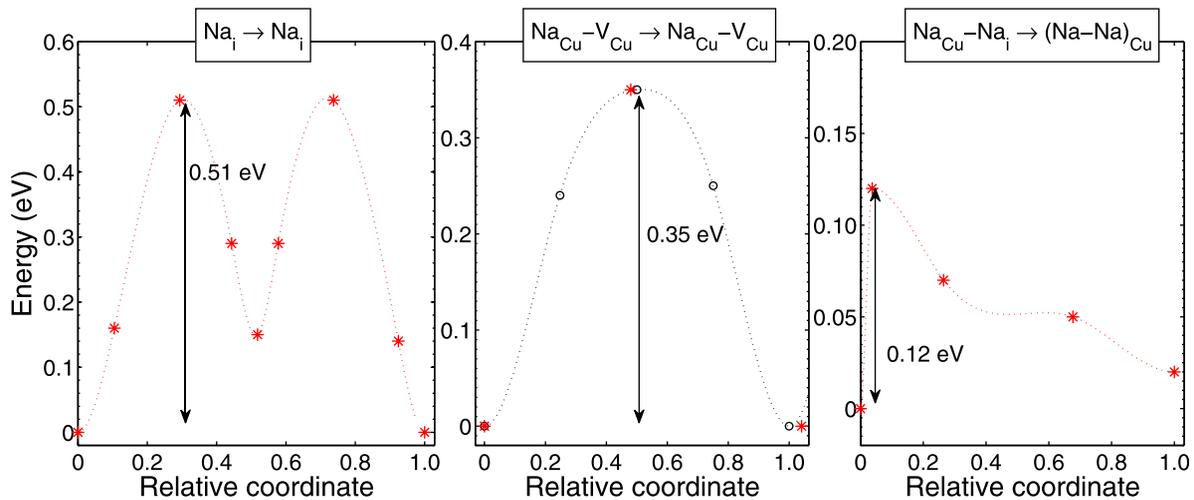
FIG. 3. Diffusion paths of Na-related defects in CIS. The red stars and open circles represent values calculated with HSE06 and PBE-GGA, respectively. The dotted lines are guides to the eye.

Of course, binding energies in the first-nearest-neighbor (1NN) configuration cannot be used as the sole indicator of the stability of defect complexes: interaction strengths change at different separation distances between the defects, affecting the kinetic formation of a complex. However, we found that the binding energy already at the 1NN configuration is practically zero for most considered defect pairs and remains negligible when the two defects are pulled apart. Therefore, the presence of another defect does not alter much the potential energy surface experienced by the other one. This behavior is very different from what has been shown for the most common intrinsic-type defect complexes in CIS, for which the nearest-neighbor configuration is energetically clearly preferred over longer separation distances.[22]

Cluster formation may also be kinetically aided or hindered by the barriers of migration in the vicinity of defects. Such an effect is indeed observed in the case of Na_{Cu} and V_{Cu}. The migration barrier for V_{Cu} in bulk material amounts to $1.09\,eV$.[24] However, exchanging places between V_{Cu} and Na_{Cu} requires remarkably less energy, only $0.35\,eV$. Therefore, if a copper vacancy diffuses in the vicinity of Na_{Cu}, it can be expected to get captured: it is energetically much less costly for the vacancy to jump back and forth with Na_{Cu} than to jump away in the opposite direction, making the complex dynamically stable. We found no indication that the two defects would start diffusing together in a way that promotes long-range diffusion.

TABLE I. Binding energies (E_b) of Na-related defect complexes. The charge states of the isolated defects are 1− for V_{Cu}, 0 for Na_{Cu}, and 1+ for Na_i.

Complex	Charge state	E_b (eV)
$Na_{Cu} - V_{Cu}$	1−	0.00
$Na_{Cu} - 2V_{Cu}$	2−	−0.05
$2Na_{Cu}$	0	−0.03
$Na_{Cu}-Na_i$	1+	0.12
$(Na - Na)_{Cu}$	1+	0.12
$2(Na - Na)_{Cu}$	2+	0.15

Na_i encountering a Na_{Cu} defect can give rise to $Na_{Cu}-Na_i$ or $(Na - Na)_{Cu}$ dumbbell. Both of these complexes are weakly stable, having very similar binding energies according to Table I, and it is not obvious which of them would prevail in CIS. Computing the activation barrier between these two configurations reveals that they are separated only by $0.12\,eV$ as shown in Figure 3. Therefore, already at room temperature, these complexes may switch from one into another rather easily and both can be expected to be encountered in the material.

IV. DISCUSSION

In light of our results, we can evaluate the feasibility of previous suggestions for the improved electronic properties in CIS attributed to Na. According to this work, Na mostly clusters on the copper sublattice and/or stays as an interstitial, neither of which creates deep states in the band gap. It has been suggested earlier[3,9] that Na could populate copper sites not only when they are vacant but also by replacing donor-type In_{Cu} antisites which are considered one of the main point defects in CIS. However, we have previously found In_{Cu} to be very stable[24]–in the unlikely event that Na would be able to invade a copper site and kick out In, In would find its way back to the copper lattice due to favorable kinetics. Thus, Na should not affect the overall concentration of In_{Cu} antisites in the material.

Another suggestion was that Na would create acceptor-type Na_{In} defects in the lattice. Following our formation energy calculations, however, Na_{In} is not among the energetically preferred Na defects in CIS. Its concentration will therefore remain negligible.

It seems more likely, then, that Na influences the dopant concentrations in a more indirect way, such as by modifying point defect mobility, as was speculated in Ref. 8. However, contrary to the suggestion made in Ref. 8 that the defect mobility would be increased, we find exactly the opposite effect: by capturing copper vacancies, Na_{Cu} defects hinder the migration of copper in the material. This finding provides an explanation for experimental measurements in CIGS

samples,[26] where the presence of Na was observed to decrease copper diffusion at low substrate temperatures.[26] Moreover, it agrees with the observation that the sodium effect is stronger the more copper-poor is the material, that is, the more copper vacancies are present.[4]

V_{Cu} capture also affects cluster formation in CIS. The formation of $Na_{Cu} - V_{Cu}$ decreases the amount of available copper vacancies, which in turn disrupts the formation of otherwise common defect complexes such as $In_{Cu} - 2V_{Cu}$ and $V_{Se} - V_{Cu}$, all involving V_{Cu}. Previously, the suppression of $In_{Cu} - 2V_{Cu}$ has also been suggested[3] but based on different grounds: the inhibition of both In_{Cu} and V_{Cu} due to Na. From the experimental side, the presence of Na has been shown to affect the microstructural features in CIS, and evidence for the suppression of ordered-vacancy compounds has been presented in Ref. 27.

V. CONCLUSIONS

In this work, the effect of sodium on bulk CIS has been investigated with first-principles calculations. The calculations show that Na prefers to accumulate in the copper sublattice either as Na_{Cu} or $(Na - Na)_{Cu}$. We find no direct way how the creation of Na-related point defects would enhance *p*-type conductivity in bulk CIS. Instead, we bring forth a mechanism by which Na affects point defect mobility: Na_{Cu} defects can capture copper vacancies, thereby not only hindering the diffusion of copper but also most probably influencing defect cluster formation and defect distribution in CIS. This finding provides an explanation for the experimental observation of Na reducing copper diffusion at low substrate temperatures.

ACKNOWLEDGMENTS

[1] U. Rau and H. W. Schock, Appl. Phys. A: Mater. Sci. Process. **69**, 131–147 (1999).

[2] M. Kemell, M. Ritala, and M. Leskelä, Crit. Rev. Solid State Mater. Sci. **30**, 1–31 (2005).

[3] S.-H. Wei, S. B. Zhang, and A. Zunger, J. Appl. Phys. **85**, 7214–7218 (1999).

[4] L. Kronik, D. Cahen, and H. W. Shock, Adv. Mater. **10**, 31–36 (1998).

[5] O. Cojocaru-Mirédin, P. Choi, R. Wuerz, and D. Raabe, Ultramicroscopy **111**, 552–556 (2011).

[6] D. Rudmann, A. F. da Cunha, M. Kaelin, F. Kurdesau, H. Zogg, and A. N. Tiwari, Appl. Phys. Lett. **84**, 1129–1131 (2004).

[7] S. Ishizuka, A. Yamada, M. M. Islam, H. Shibata, P. Fons, T. Sakurai, K. Akimoto, and S. Niki, J. Appl. Phys. **106**, 034908 (2009).

[8] D. J. Schroeder and A. A. Rockett, J. Appl. Phys. **82**, 4982–4985 (1997).

[9] M. A. Contreras, B. Egaas, P. Dippo, J. Webb, J. Granata, K. Ramanathan, S. Asher, A. Swartzlander, and R. Noufi, *in Proceedings of the 26th IEEE Photovoltaics Specialists Conference* (IEEE, New York, 1997), pp. 359–362.

[10] D. W. Niles, K. Ramanathan, F. Hasoon, R. Noufi, B. J. Tielsch, and J. E. Fulghum, J. Vac. Sci. Technol. A **15**, 3044 (1997).

[11] X. Sun, F. Jiang, and J. Feng, Comput. Mater. Sci. **47**, 31–34 (2009).

[12] Z. B. Li, X. Wang, and K. L. Yao, Solid State Commun. **150**, 1514–1517 (2010).

[13] P. Pluengphon, T. Bovornratanaraks, S. Vannarat, and U. Pinsook, J. Phys. Condens. Matter **24**, 095802 (2012).

[14] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169–11186 (1996).

[15] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15–50 (1996).

[16] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**(18), 3865–3868 (1996).

[17] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).

[18] J. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).

[19] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[20] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[21] L. E. Oikkonen, M. G. Ganchenkova, A. P. Seitsonen, and R. M. Nieminen, J. Phys. Condens. Matter **23**, 422202 (2011).

[22] L. E. Oikkonen, M. G. Ganchenkova, A. P. Seitsonen, and R. M. Nieminen, "Formation, migration, and clustering of point defects in CuInSe$_2$ from first principles," Phys. Rev. B (submitted).

[23] G. Henkelman and H. Jónsson, J. Chem. Phys. **113**, 9978 (2000).

[24] L. E. Oikkonen, M. G. Ganchenkova, A. P. Seitsonen, and R. M. Nieminen, J. Appl. Phys. **113**, 133510 (2013).

[25] L. E. Oikkonen, M. G. Ganchenkova, A. P. Seitsonen, and R. M. Nieminen, Phys. Rev. B **86**, 165115 (2012).

[26] D. Rudmann, Ph.D. dissertation, Swiss Federal Institute of Technology, Zürich, 2004.

[27] S. Seyrling, A. Chirila, D. Güttler, P. Blösch, F. Pianezzi, R. Verma, S. Bücheler, S. Nishiwaki, Y. E. Romanuyk, P. Rossbach, and A. N. Tiwari, Sol. Energy Mater. Sol. Cells **95**, 1477–1481 (2011).