

Na-Diffusion Enhanced p-type Conductivity in Cu(In,Ga)Se₂: A New Mechanism for Efficient Doping in Semiconductors

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Incorporation of sodium (Na) or potassium (K) has been found to be crucial for manufacturing high-efficiency Cu(In,Ga)Se₂ (CIGS) thin film solar cells.^[1,2] In standard coevaporation process of CIGS using soda-lime glass (SLG) substrates, Na is introduced during CIGS growth by diffusion from the heated SLG substrate (>600 °C) through the Mo back contact.^[3,4] On Na-free substrates, a thin NaF layer is deposited on the CIGS layer and then the substrate is heated to about 400 °C to let Na diffuse into the CIGS layer.^[5,6]

Although it is widely believed that the beneficial effect of Na (K) results partially from the enhanced p-type conductivity inside the absorber layer which can contribute to higher open-circuit voltage (V_{oc}),^[7–11] why the Na or K^[12–14] incorporation enhances the p-type conductivity is not well understood.^[15–17] Two different mechanisms have been proposed, assuming that the Na (K) dopants stay at the grain boundary and in the CIGS grains, respectively.

In the mechanism that assumes Na (K) at the grain boundary, it was proposed that the Na passivates the donor-like defects at grain boundaries, such as In_{Cu} ^[5,18,19] or Se vacancies (in conjunction with O_2),^[20,21] thus increasing the net hole concentration.^[22,23] This grain-boundary mechanism

prevails recently because high concentration of Na segregation at grain boundaries was observed in CIGS films.^[18,21,24–27] This mechanism considered only the effect near grain boundaries. Experiments, however, observed that the hole concentration throughout the CIGS layers is also increased after Na doping.^[8,23,28,29] Both Schroeder and Rockett^[30] and Timmo et al.^[31] show that even in a single crystal CIGS or CuInSe₂ (CIS) layer, Na doping increases the hole concentration. Moreover, recent atom probe tomography studies provide clear evidence for the presence of Na inside the CIGS grains. Laemmle et al.^[32] reported a high diffusivity of Na in CIGS and showed that Na diffuses into the CIGS grain interiors even at a low temperature of 157 °C. Choi et al.,^[18] Couzinie-Devy et al.,^[25,33] Laemmle et al.,^[32] and Cojocaru-Mirédin et al.^[34] found that the concentration of Na in the CIGS grain interiors is around 13–150 ppm (around 10^{17} – 10^{18} cm⁻³), which is high enough to alter the electrical properties significantly. However, the role of Na in the CIGS grain interior is completely neglected in the grain-boundary mechanism.

In the mechanism that assumes Na (K) in the grains, it was proposed that Na dopants create new acceptors through forming Na_{In} (Na_{Ga}) antisites, or eliminate the donor defects In_{Cu} (Ga_{Cu}),^[12,30,35–37] thus increasing the net hole concentration. However, this mechanism is challenged by the recent theoretical and experimental studies. Oikkonen et al.^[38] and Ghorbani et al.^[39] showed by first-principles calculations that the creation of Na_{In} antisite is energetically unfavorable. The electrical characterization by Schroeder and Rockett^[30] and Schuler et al.^[40] confirmed that there is no acceptor defect like Na_{In} . Schroeder and Rockett reported that Na eliminates the donor defect In_{Cu} , leading to the reduction in the compensating electrons, but Schuler et al. showed the contrary is the case: the degree of compensation increases with the increased net acceptor density due to Na. The latter is supported by the first-principles calculations which shows that Na would not eliminate In_{Cu} due to the unfavorable kinetics.^[41] If Na_{In} (Na_{Ga}) antisites are not formed and the donor defects In_{Cu} (Ga_{Cu}) are not eliminated by Na, it is still an open question how Na doping increases the hole concentration in the CIGS grains.

In this communication, we found through first-principles calculations that the Na-doping induced increase of hole concentration in CIGS grains cannot be understood according to the traditional equilibrium doping theory, and proposed a new mechanism to explain this increase based on the Na (K) out-diffusion during cooling and water rinsing. This dopant-diffusion mechanism also explains the smaller hole concentration increase

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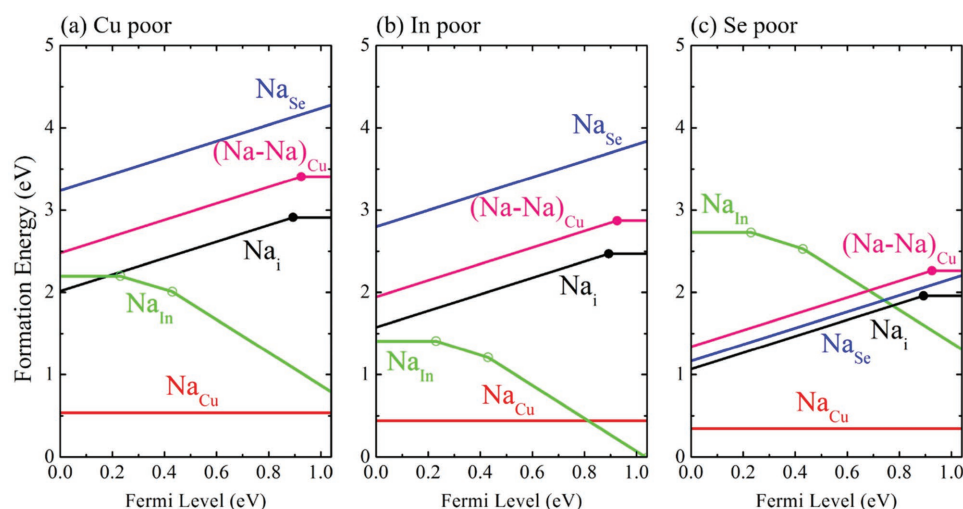


Figure 1. The calculated formation energy of Na dopants at different sites in CIS as a function of Fermi level, in Cu-poor, In-poor, and Se-poor conditions (as defined in the Section 2 of the Supporting Information). Na is assumed to be as rich as possible in each condition but with no Na-related secondary phases such as Na_2Se or NaInSe_2 forming (more details are given in Table S1 of the Supporting Information). The Fermi level is referenced to the valence band maximum (VBM) level.

induced by K doping, and provides new strategies for efficient p-type or n-type doping in semiconductors.

According to traditional doping theory, the equilibrium concentration (solubility) of dopants in crystalline semiconductors depends on their formation energies and the temperature, following

$$c(\text{Na}) = N_{\text{sites}} e^{-\frac{\Delta H}{kT}} \quad (1)$$

where N_{sites} is the number of possible doping sites in the crystal, ΔH is the formation energy at different doping sites, k is the Boltzmann constant, and T is the temperature. The formation energies of dopants at different sites can be calculated using the supercell model.^[42–44] Figure 1 shows the calculated formation energies of Na dopant at four different doping sites in CIS, as a function of Fermi level under the Cu poor, In poor and Se poor growth conditions, respectively (Details about the calculation procedure and the growth conditions are given in the Sections 1 and 2 of the Supporting Information).

Two obvious characters can be seen from Figure 1: (i) among all the dopant sites, Na_{Cu} doping site (Na substitution for Cu) has the lowest formation energy in the p-type CIS samples (thus the Fermi level is located near 0, i.e., the valence band maximum (VBM) level), regardless of the growth conditions, (ii) Na_{In} doping site (Na substitution for In) has higher formation energy, always higher than 1.4 eV, so it is energetically unfavorable in p-type CIGS films, consistent with the results of Oikkonen et al.^[38] and Ghorbani et al.^[39] Our calculated formation energies of $(\text{Na-Na})_{\text{Cu}}$ dumbbell (two Na substitution for one Cu, it is a donor defect) are much higher than that of Na_{Cu} , and always higher than 1.3 eV (Ghorbani et al.^[39] and Oikkonen et al.^[38] neglected the thermodynamic limiting conditions to the elemental chemical potentials of Na, as discussed in the Supporting Information. Hence, their calculated values for the formation energy of $(\text{Na-Na})_{\text{Cu}}$ dumbbells, Na_{Cu} , and

Na_{In} are negative). Therefore, Na dopants in p-type CIS prefer occupying the Cu sites (forming Na_{Cu}), which is general under equilibrium conditions and cannot be changed by varying the richness of Cu, In or Se during the growth.

Since the formation energy of Na_{Cu} is in the range of 0.35–0.55 eV, its equilibrium concentration (solubility) in CIGS at room temperature should be around 10^{13} – 10^{17} cm^{-3} . One may expect that these antisite dopants could generate free carriers with a concentration on the same order of magnitude, if they can be ionized. However, because Na_{Cu} is an isovalent substitution, it is charge-neutral and cannot be ionized to generate free electron or hole carriers, i.e., it is electrically inactive. This is supported by the calculated ionized energy levels (see Figure 2). There is no ionization level of Na_{Cu} in the band gap, consistent with previous electronic calculations.^[37]

In contrast to Na_{Cu} , Na_{In} substitution is heterovalent and is an active acceptor, so it can generate hole carriers. However, the ionization levels of Na_{In} are relatively deep in the band gap, i.e., 0.24 eV (–/0) and 0.43 eV (2–/–) levels above the VBM level, as illustrated in Figure 2, which are much deeper than the 30 meV (0/–) level of the dominant defect V_{Cu} in CIS.^[42] Furthermore, the equilibrium concentration of Na_{In} is negligibly low, i.e., an 1.4 eV formation energy corresponds to an equilibrium concentration on the order of 10^0 cm^{-3} at room temperature, much lower than that of Na_{Cu} . Such a low Na_{In} concentration explains why Schroeder and Rockett^[30] and Schuler et al.^[40] did not observe the Na_{In} acceptor in their electrical characterization, but cannot explain the observed increase in the hole concentration (especially considering that the Na_{In} acceptor levels are relatively deep).

Considering all the possible Na doping sites, we can see that Na dopants in the CIGS grains mainly take place of Cu, but Na_{Cu} is electrically inactive, and though Na_{In} could act as active acceptor, the formation of Na_{In} is energetically unfavorable. Therefore, the Na doping in CIGS lattice should not increase the hole concentration and enhance p-type conductivity in the

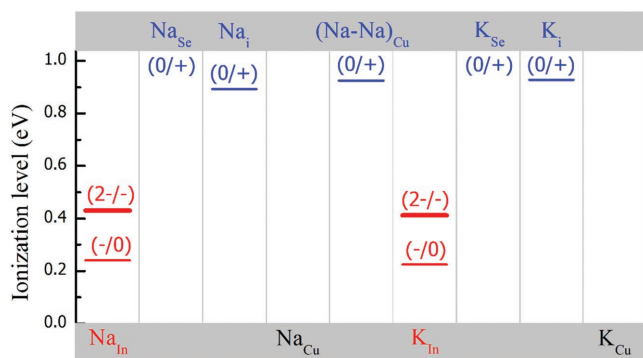


Figure 2. The calculated ionization levels of Na and K dopants at different sites in the band gap of CIS. The red bars denote the acceptor levels and the blue bars denote the donor levels, with the deep levels displayed as thick bars. Both the Na_{Se} (0/+) and K_{Se} (0/+) levels are resonant donor states in the conduction band.

CIGS grains under a thermodynamic equilibrium condition. Furthermore, some of Na dopants may fill the Cu vacancies (V_{Cu}) in the lattice and decrease the concentration of V_{Cu} which is an effective acceptor defect, so the hole concentration would even be decreased if a high concentration of Na is doped in the CIGS lattice. Therefore, the observed p-type conductivity enhancement in CIGS grains cannot be explained according to the traditional doping theory.

Since the traditional doping theory cannot explain the p-type conductivity enhancement, we investigated the Na doping process in more detail. Na is doped into CIGS layer in a Na-rich environment at high temperature ($>600^\circ\text{C}$ by SLG or $\approx 400^\circ\text{C}$ via post-deposition treatment, PDT), and then the thin film is cooled down and rinsed in water for subsequent low-temperature ($\approx 60^\circ\text{C}$) deposition of CdS buffer layer.

At the high-temperature and Na-rich environment, the equilibrium concentration (solubility) of Na dopants in CIGS increases as the temperature increases, as determined by

Equation (1). Therefore, a high concentration of Na can be doped into the CIGS lattice at this environment. If we use the formation energy (0.55 eV, see Figure 1a) of Na_{Cu} at the Cu-poor condition and the PDT temperature 400°C , we can estimate that the concentration of Na_{Cu} can be as high as 10^{18} cm^{-3} . During this high-temperature Na-doping process, Na diffuses into the CIGS grains and occupies the Cu sites (forming Na_{Cu} antisites), whereas Cu diffuses out of the grains to the surfaces or grain boundaries of the CIGS thin films.

However, during cooling, the equilibrium concentration (solubility) of Na in the bulk of CIGS becomes lower and lower according to Equation (1). Na_{Cu} is not thermodynamically stable any more in the CIGS grains at low temperature and Na tends to diffuse out of the CIGS grains. Since Na is a fast diffusor in bulk CIGS with a small migration energy (0.36 eV as measured by Laemmle et al., and 0.31 eV as calculated by Maeda et al. assuming that Na_{Cu} diffuses through Cu vacancies in CuInSe_2),^[32,38,45] Na can diffuse out of the CIGS grains and leaves the Cu sites unoccupied, then a high concentration of Cu vacancies (V_{Cu}) are formed within the grains. The subsequent rinsing in water can further facilitate the formation of V_{Cu} . Because the water rinsing can significantly dissolve Na at the CIGS surface^[19,46] and decrease the chemical potential of Na (the environment becomes more and more Na-poor, so the formation energy of Na dopants in CIGS lattice increases), the out-diffusion of Na from the CIGS grain interiors is enhanced, which leads to a higher concentration of V_{Cu} within the CIGS grains. Since the surfaces and grain boundaries of CIGS films are usually Cu-depleted (more Cu poor than in the grains),^[2,8,47] so less Cu can diffuse back from the surfaces or grain boundaries into the CIGS grains, then a higher concentration of Cu vacancies (V_{Cu}) are formed within the grains. This Na-diffusion induced formation of V_{Cu} is schematically plotted in Figure 3a–c.

It is well known that V_{Cu} is a shallow acceptor defect in CIGS with an ionization level about 30 meV above the VBM

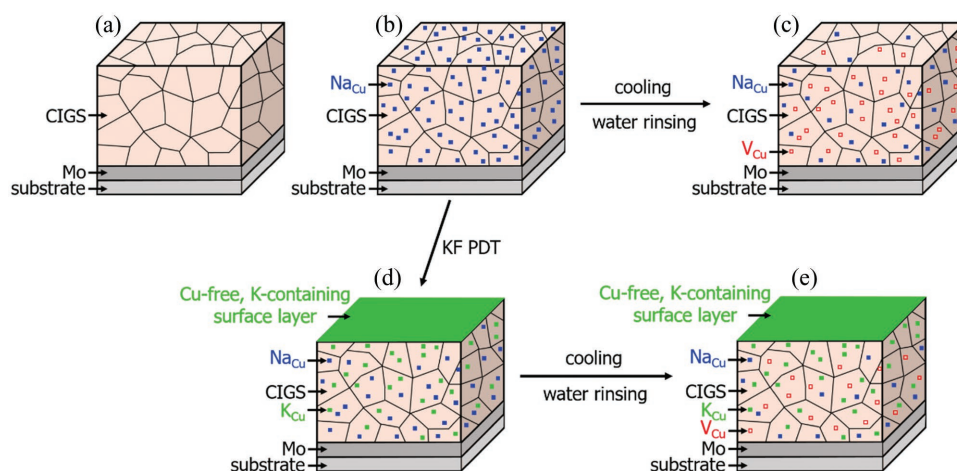


Figure 3. Schematic illustration of how Na (K) doping increases the concentration of V_{Cu} within the CIGS grains. a) CIGS grains free of Na (K). b) Na is introduced into the CIGS grain interiors either from a SLG substrate ($>600^\circ\text{C}$) or via NaF PDT ($\approx 400^\circ\text{C}$), and exists as Na_{Cu} antisite. c) After cooling and water rinsing, Na diffusion-out promotes the formation of V_{Cu} within the CIGS grains. d) K is introduced by KF PDT following Na doping, and exists as K_{Cu} antisite in the CIGS grains or forms a K-enriched layer on the CIGS surface. e) After cooling and water rinsing, both Na and K diffusion-out promotes the formation of V_{Cu} within the CIGS grains, however, the K-enriched surface layer is water-insoluble and thus hinders the out-diffusion of K, so less V_{Cu} are formed after K doping.

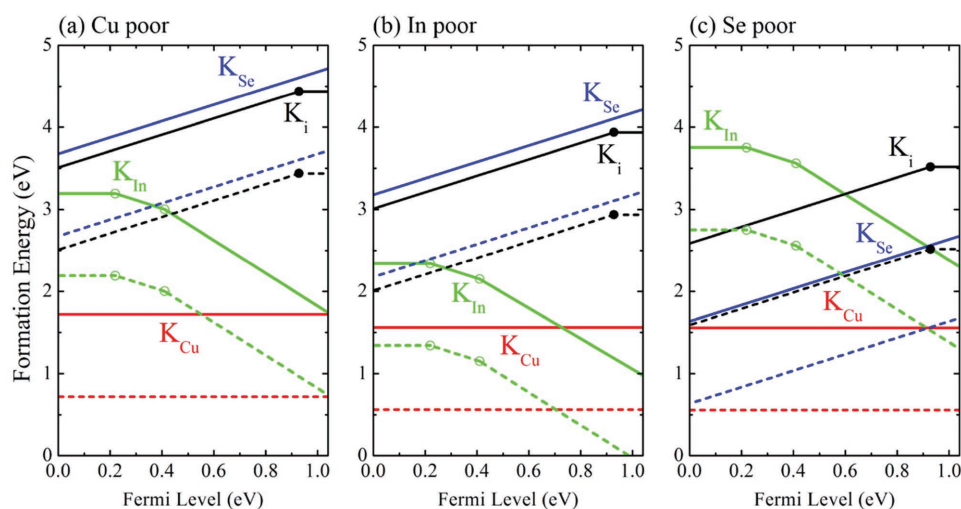


Figure 4. The calculated formation energy of K dopants at different sites in CIS as a function of Fermi level, in Cu-poor, In-poor, and Se-poor conditions. The solid lines show that K is as rich as possible in the condition but with no K-related secondary phases such as K_2Se and $KInSe_2$ forming, while the dashed lines show that K is so rich in the condition that K_2Se or $KInSe_2$ can form and coexist (more details are given in Section 3 of the Supporting Information).

level,^[42,48] which determines the intrinsic p-type conductivity of CIGS. The higher concentration of V_{Cu} after the Na diffusion-out increases the hole concentration, thus explaining the observed p-type conductivity enhancement.^[5,8,12]

According to Equation (1), we can estimate that the equilibrium concentration of Na_{Cu} decreases to only 10^{13} cm^{-3} at room temperature (the formation energy of Na_{Cu} is 0.55 eV), i.e., most of the Na atoms that enter into the CIGS lattice at 400 °C will diffuse out at room temperature, so in principle a high concentration (10^{18} – $10^{13} \approx 10^{18} \text{ cm}^{-3}$) of V_{Cu} and hole carriers will be formed. Considering that the diffusion barrier of Na in CIGS was measured and calculated to be around 0.31–0.51 eV,^[32,38,45,49] only part of the Na can diffuse out and some of Cu can also diffuse back from the surfaces and grain boundaries into the grains, so the resultant increase of the V_{Cu} and hole concentration should be much lower than 10^{18} cm^{-3} . With this Na-diffusion mechanism, we can explain quantitatively the experimental observations that the hole concentration increases from 10^{14} cm^{-3} before Na doping to 10^{16} cm^{-3} after Na doping.^[8,23] Since the resultant increase of the V_{Cu} and hole concentration is only 10^{16} cm^{-3} , much lower than the ideal value ($10^{18} - 10^{13} \approx 10^{18} \text{ cm}^{-3}$), there should be a high concentration of Cu diffusing back or leftover of Na_{Cu} in the grains with a concentration on the order of 10^{18} – $10^{16} \approx 10^{18} \text{ cm}^{-3}$. Choi et al.,^[18] Couzinie-Devy et al.,^[25,33] Laemmle et al.,^[32] and Cojocar-Mirédin et al.^[34] found that the concentration of Na in the CIGS grain interiors is around 13–150 ppm (around 10^{17} – 10^{18} cm^{-3}), which can be explained according to the leftover of Na_{Cu} .

This new mechanism is completely different from the two traditional mechanisms described in the introduction, and agrees with a series of experimental observations. First, Contreras et al.^[12] found that the increase in electrical conductivity due to Na (or K) doping is independent of the Ga/(Ga+In) ratio in CIS films, but dependent on the Cu content. Second, Kronik et al.^[20] observed more dramatic Na-doping induced

improvement in the solar cell performance when the CIGS film is more Cu-poor. In more Cu-poor CIGS film, the concentration of V_{Cu} and free hole carriers can be higher and the Fermi level is lower, which decreases the formation energies of the compensating donor defects such as In_{Cu} , causing the formation of the $2V_{Cu}+In_{Cu}$ defect complexes and the related ordered vacancy compounds (OVCs) such as $CuIn_5Se_8$ ^[42] during the high-temperature synthesis of CIGS films. When Na is doped into the CIGS films at high temperature, more V_{Cu} sites will be filled by Na and thus the concentration of Na_{Cu} antisites can be even higher in a more Cu-poor CIGS film. Meanwhile, the concentration of V_{Cu} and free hole carriers is decreased and the Fermi level is shifted upward, which increases the formation energy of In_{Cu} and suppresses the formation of $2V_{Cu}+In_{Cu}$ and OVCs. After cooling and water rinsing, the diffusion-out of Na should produce more V_{Cu} , a larger increase in the hole concentration and a larger downward shift of the Fermi level. Since the CIGS film is cooled down, the formation of $2V_{Cu}+In_{Cu}$ and OVCs in the CIGS grains becomes difficult because it requires the diffusion of In from the surface into the CIGS grains at low temperature and the diffusion barrier of In is high^[50] (different from the condition during the high-temperature synthesis of CIGS films). Because the hole concentration is increased and the formation of $2V_{Cu}+In_{Cu}$ and OVCs is still suppressed in the CIGS grains, we can explain the observed more dramatic Na-doping induced improvement in more Cu-poor CIGS film. Third, by temperature-dependent conductivity measurements, Holz et al.^[51] reported a decrease in the electrical activation energy from ≈ 350 to ≈ 30 –50 meV after Na doping. All these observations correlate well with the increase of the shallow V_{Cu} concentration in CIGS layer after Na doping.

Recently, K doping is also found to enhance the performance of CIGS solar cells.^[2,13] Figure 4 shows the calculated formation energies of K dopants at different lattice sites. By comparing Figure 1 and Figure 4 (the solid lines, corresponding to no coexistence or appearance of K-related secondary phases), we find

that the formation energies of K dopants are generally higher than that of Na dopants at the same lattice site. This can be attributed to the larger strain energy cost caused by the larger size difference between K and Cu. Therefore, K is difficult to be incorporated into the bulk of CIGS and has a lower solubility in the single-phase CIGS thin films compared to Na. According to the traditional doping theory, the high formation energies of K dopants indicate that the equilibrium concentration of K in the CIGS grains should be very low and its influence on the hole concentration should be negligible.

However, it should be noted that K-enriched surface layers are always formed after K doping (may be Cu free, K-In-Se compounds such as KIn_3Se_5 or KInSe_2 , though it is difficult to determine the exact composition),^[14,46,52,53] i.e., the CIGS grains are actually in a very K-rich condition, so the chemical potential of K can be higher. According to Equation (S1) in the Supporting Information, if μ_K is increased by 1 eV, the formation energies of K_{In} and K_{Cu} can be decreased to the same level as those of Na_{In} and Na_{Cu} , respectively (dashed lines of Figure 4). Then under the very K-rich condition, a high concentration of K can still be doped into CIGS grains at high temperature, as observed by the experiments.^[2,8,13,14] Most often, K is doped by KF PDT following Na doping.^[2,13] Assuming the ion exchange mechanism,^[2] Na is replaced by K and may diffuse toward the surface of the film or the Mo back contact layer. Considering the higher formation energy of K dopants than that of Na dopants in the CIGS bulk, a certain amount of Na_{Cu} still remains inside the CIGS grains after K doping. During cooling and water rinsing, both Na and K diffuse out, which increases the concentration of V_{Cu} within the CIGS grains. Therefore, the enhanced p-type conductivity after K doping can also be explained according to our alkaline-diffusion based mechanism, as shown schematically in Figure 3d–e.

Compared to Na, the K doping induces smaller increase in the concentration of V_{Cu} and hole carriers. First, less K_{Cu} antisites can be formed in the CIGS grains at high temperature because of the higher formation energy of K_{Cu} . Second, unlike Na doping, K doping leads to the formation of a K-enriched layer on the CIGS surface,^[14,46,52,53] which is water-insoluble and hinders the out-diffusion of K from the CIGS grain interiors. Both effects lead to a smaller increase of the final V_{Cu} concentration after cooling and water rinsing. We then conclude that K is not as efficient as Na in increasing the p-type conductivity of CIGS films, in good agreement with the experimental observations that K is not as efficient as Na in increasing the hole concentration in CIGS films.^[8,12–14]

Using the new dopant-diffusion mechanism, we can also explain the p-type conductivity enhancement after Na doping in $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe), which is also an important thin film photovoltaic absorber material.^[54] In kesterite CZTSSe solar cells, the p-type conductivity enhancement was also observed after Na doping.^[55–57] Since Na is a fast diffusor in CZTSSe^[58,59] and prefers replacing Cu when incorporated into the CZTSSe grains,^[60,61] Na can also promote the formation of V_{Cu} and thus increase the hole concentration in the CZTSSe grains, similar to the case in CIGS.

Bipolar doping (to both p-type and n-type) is critical for the device application of semiconductors,^[62–65] however, it is still very challenging for many semiconductors, especially for those

with wide band gaps.^[44] According to the traditional doping theory, a semiconductor is difficult to be doped p-type (n-type) if its VBM (CBM) level is low (high), because the compensating donor (acceptor) defects will form spontaneously as the desired dopant shifts the Fermi level downward to VBM level (upward to CBM level).^[65] This thermodynamic mechanism explains the p-type doping difficulty in ZnO ,^[66,67] GaN ,^[68,69] and many other wide-gap semiconductors.^[62,66,70,71]

Using the new mechanism based on the dopant diffusion, we propose that the bipolar doping difficulty in the wide-gap semiconductors may be overcome, and efficient bipolar doping may be achieved if one can find proper dopant elements that satisfy three requirements: (i) the dopant has reasonably high solubility in these semiconductors at high temperature while low solubility at room temperature, (ii) it is a fast diffusor in the crystal (small diffusion barrier), and (iii) it can be eliminated easily in the postprocessing.

When doped into the bulk of CIGS, Na is most likely to form electrically inactive Na_{Cu} antisite, irrespective of the growth condition, and the formation of the Na_{In} acceptor is energetically unfavorable, so we cannot explain the p-type conductivity enhancement in CIGS grains according to the traditional doping theory. To explain the observed p-type enhancement in the CIGS films after Na doping, we propose a new mechanism based on the fast diffusion of Na: a high concentration of Na_{Cu} is incorporated into the CIGS grains at high temperature and Na-rich conditions, but the Na diffusion out of the Na_{Cu} sites leads to a high concentration of V_{Cu} formed in the CIGS grains during cooling and water rinsing, thus increasing the hole concentration and enhancing the p-type conductivity. Compared to Na doping, K doping has a lower solubility in CIGS and the formed K-enriched surface layers hinder the K diffusion out of the grain interior, so the hole concentration increase is not as significant as that of Na doping, in good agreement with the available experiments. Based on this dopant-diffusion mechanism, we can also understand the p-type conductivity enhancement in Na-doped CZTSSe, and may design new strategies for achieving efficient bipolar doping in wide-gap semiconductors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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