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Ab-initio study of donor-acceptor codoping for n-type CuO

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Ab-initio study of donor-acceptor codoping for n-type CuO

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Single *n*-type dopant in CuO has either a deep donor level or limited solubility, inefficient in generating free electrons. We have performed *ab-initio* study of the donor-acceptor codoping to obtain *n*-type CuO. Our results show that N codoping can slightly improve the donor level of Zr and In by forming shallower *n*-type complexes ($Zr_{Cu}-N_O$ and $2In_{Cu}-N_O$), but their formation energies are too high to be realized in experiments. However, Li codoping with Al and Ga is found to be relatively easy to achieve. $2Al_{Cu}-Li_{Cu}$ and $2Ga_{Cu}-Li_{Cu}$ have shallower donor levels than single Al and Ga by 0.14 eV and 0.08 eV, respectively, and their formation energies are reasonably low to act as efficient codopants. Moreover, Li codoping with both Al and Ga produce an empty impurity band just below the host conduction band minimum, which may reduce the donor ionization energy at high codoping concentrations. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

As a small bandgap semiconductor, cupric oxide (CuO) has received much attention for possible application in photovoltaic devices due to its abundance in earth, non-toxicity, and low production cost as compared to Si.^{1,2} The theoretical Shockley-Queisser photo-energy conversion efficiency of a CuO *p-n* junction solar cell is up to 31%.³ However, the performance achieved so far is limited by the availability of *n*-type material, since most CuO are found to be *p*-type. This is likely related to its intrinsic defects, particularly the Cu vacancies due to high volatility of Cu atoms.⁴ However, oxygen vacancies are calculated to be deep donors, making *n*-type materials difficult to obtain.^{5,6} Although Zr is suggested to be a shallow donor dopant in CuO, its ionization energy of 0.2 eV is too high to be totally ionized at room temperature ($k_B T \sim 0.03$ eV).⁶ Accompanied by the limited thermodynamic solubility of the dopant, it is thus a challenge to produce *n*-type CuO.

In an effort to resolve the above mentioned issue, we notice that there are experimental evidences of shallow defect levels being produced by donor-acceptor (*n-p*) codoping in other systems such as ZnO and GaN.⁷⁻¹⁰ Theoretically, Yamamoto *et al.* first proposed codoping with acceptor and donor (2:1 for *p*-type and 1:2 for *n*-type) to realize low-resistivity *p*-type ZnO¹¹ and GaN.¹² In this case, defect association occurs due to the Columbic attraction between *n*- and *p*-type dopants with opposite charges. The effect of wavefunction interaction between the *n*- and *p*-type dopants on the defect levels has been verified by theoretical calculations.¹³⁻¹⁵ Furthermore, Yan *et al.* explained the experimentally observed shallow acceptor/donor levels with

the change of valence band and/or conduction band edges by the impurity bands formed in the gap upon codoping.¹⁶ It is also noted that *n-p* codoping approach has been intensively utilized in engineering the band structure of wide-gap semiconductors.¹⁷⁻¹⁹ The solubility of dopants may also be enhanced through codoping. Interstitial H or Li donor codoping can increase the concentration of Mn acceptor in GaAs, and can subsequently be removed by thermal annealing.^{20,21} Katayama-Yoshida *et al.* proposed to overcome the low solubility of codopants by the spinodal nano-decomposition method.²² But, there is little literature report on *n-p* codoping in CuO, which we will address in this paper.

In this theoretical study, we examine the effect of *n-p* codoping on reducing the donor ionization energy in CuO using first-principle density functional theory (DFT) calculations, which is very important for fabrication of highly conductive *n*-type CuO and realization of CuO *p-n* junction solar cells. Two kinds of acceptor dopants, which are N on O site and Li on Cu sites, are selected. And two types of donor dopants are selected, which are relatively shallow donors Zr and In and relatively deep donors Al and Ga. We have conducted extensive calculations on different combinations of donor and acceptor, and only presented the important results on N codoping with Zr and In, and Li codoping with Al/Ga. We calculate the binding energies of all defect complexes, and examine the formation energies and transition energy levels for possible *n*-type complexes, which will be compared with the results of single *n*-type dopants.

II. COMPUTATIONAL DETAILS

All calculations are performed using the density functional theory with local density approximation and projector augmented wave (PAW) pseudopotentials, as implemented in the VASP code.^{23,24} The semiempirical LSDA+U method

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where the strong localized Cu 3d electrons are treated by adding a Hubbard-type term (U) to the effective potential is adopted,²⁵ as it has been recognized to accurately describe the crystal and electronic structures of CuO.^{5,6} In this study, a value of $U_{\text{eff}} = 7.5$ eV ($U = 7.5$ eV and $J = 0$ eV) is used following Dudarev's approach,²⁶ which has resulted in lattice parameters and bandgap in good agreement with the experimental values.⁶ An antiferromagnetic spin ordering is assumed for CuO.²⁷ For pseudopotential approximation, Cu 3d, 4s, O 2s, 2p and dopants' outmost s , p , d orbitals are treated as the valence electrons. An energy cutoff of 600 eV for the plane wave expansion is used in all calculations. A 96-atom $2 \times 3 \times 2$ supercell is established to calculate the doping defects, using the optimized theoretical lattice parameters ($a = 4.56$ Å, $b = 3.27$ Å, $c = 4.96$ Å, $\beta = 100.2$, and $u = 0.593$). A gamma centered $3 \times 3 \times 3$ k -point mesh for the Brillouin zone of supercell is employed. A refined $4 \times 4 \times 4$ k -point mesh is used for the density of states plots. The structure optimization is performed for all supercells with all atoms relaxed while the lattice constants are frozen until the Hellmann-Feynman forces are less than 0.02 eV/Å.

The formation energy of a defect complex in CuO is defined as

$$E_f = E_{\text{doped}} - E_{\text{perf}} + \sum_i n_i \mu_i + qE_F, \quad (1)$$

where E_{doped} and E_{perf} are the total energies of the defective and perfect supercells. n_i is the number of atoms being removed from (>0) or added to (<0) the supercell, and μ_i denotes the atomic chemical potential. E_F is the Fermi energy, which is referred to the valence band maximum (VBM) of CuO. In our LSDA+ U calculations, the large U of 7.5 eV gives a bandgap of 1.32 eV, very close to the experimental value.²⁸ The spurious interactions in charged supercells is corrected by using the monopole term in the Makov-Payne (MP) scheme.²⁹ The chemical potentials of Cu and O are restricted to $\mu_{\text{Cu}} + \mu_{\text{O}} = \Delta H_f(\text{CuO})$ and $2\mu_{\text{Cu}} + \mu_{\text{O}} \leq \Delta H_f(\text{Cu}_2\text{O})$. The calculated formation enthalpies (ΔH_f) of CuO and Cu_2O are -2.04 eV and -2.14 eV, respectively, close to experimental values.³⁰ To calculate the formation energies, we use nitrogen gas, ZrO_2 , Li_2O , $\alpha\text{-Al}_2\text{O}_3$, $\beta\text{-Ga}_2\text{O}_3$, and In_2O_3 as the doping sources. The maximum chemical potentials of dopants satisfy the relations: $\mu_{\text{N}} \leq \frac{1}{2}\mu_{\text{N}_2}$, $\mu_{\text{Zr}} + 2\mu_{\text{O}} \leq \Delta H_f(\text{ZrO}_2)$, $2\mu_{\text{Li}} + \mu_{\text{O}} \leq \Delta H_f(\text{Li}_2\text{O})$, $2\mu_{\text{X}} + 3\mu_{\text{O}} \leq \Delta H_f(\text{X}_2\text{O}_3)$ ($\text{X} = \text{Al}$, Ga , and In), and $\mu_{\text{In}} + \mu_{\text{N}} \leq \Delta H_f(\text{InN})$ (for In and N codoping).

III. RESULTS AND DISCUSSION

A. N codoping with Zr and In

In our model, one Zr dopant occupies the nearest Cu sites of N acceptor, forming the $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ n -type defect complex. Similarly, one In dopant occupies the nearest Cu sites of N acceptor, forming the $\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ passive complex, and two In dopants occupy the nearest Cu sites of N acceptor, forming the $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ n -type complex, where the In-In distance is almost twice as long as the In-N distance. To verify if the complex can form in CuO, we calculated the binding

energy between Zr and N using $E_b = E_{\text{tot}}(\text{Zr}_{\text{Cu}} - \text{N}_{\text{O}}) + E_{\text{tot}}(\text{CuO}) - E_{\text{tot}}(\text{Zr}_{\text{Cu}}) - E_{\text{tot}}(\text{N}_{\text{O}})$, where E_{tot} is the total energy of the supercells. The negative binding energy of -0.39 eV indicates that $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ is stable with respect to the isolated defects and is likely to form in CuO. We noticed that, based on the calculated Zr-N binary phase diagram,³¹ it is unlikely to initiate the spinodal nano-decomposition in the $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ codoping as that reported in the Ga-N system.²² However, the binding energy for $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$, which is calculated between $\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ and In_{Cu} is small at -0.1 eV, indicating that $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ is not very stable at high temperature. Similar to the Ga-N system, these $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ complexes may undergo spinodal nano-decomposition into N-rich and N-poor phases and result in high concentration of $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ complexes in CuO.

The formation energies for N codoping with Zr and In are shown in Fig. 1 as a function of Fermi levels. The calculated formation energies for Zr and In single dopants are also shown for comparison. The Fermi level (E_F) varies from 0 eV at the VBM to 1.32 eV at the conduction band minimum (CBM). The Fermi level value at which formation energies of different charge states cross each other is denoted as the transition energy level (solid dots in the figure). For $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ and $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$, there are two possible charge states (0 and +1) in the gap. The slope of the lines indicates the charge state. It is found that the (0/+1) transition energy level for $\text{Zr}_{\text{Cu}}\text{-N}_{\text{O}}$ locates at 0.15 eV below the CBM, slightly shallower than the (0/+1) transition energy level for single Zr dopant, due to the mutual interaction between Zr and N codopants. Also, $2\text{In}_{\text{Cu}}\text{-N}_{\text{O}}$ is found to have a shallower donor level than single In dopant, which is at 0.16 eV below the CBM. All dopants have much lower formation energies under O poor condition than under O rich condition.

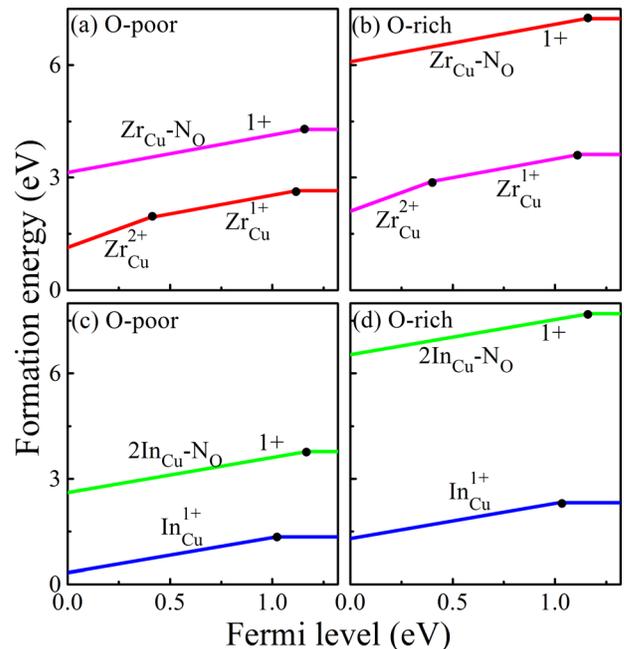


FIG. 1. Formation energies of N codoping with Zr and In as a function of the Fermi level, under the O-poor and O-rich conditions, respectively. The formation energies of Zr and In single dopants are also shown for comparison.

TABLE I. Calculated binding energies E_b of the defect complexes in neutral charge state in CuO. Doping type i means passive doping. All energies are in eV.

Reaction	Type	E_b
$Zr_{Cu} + N_O \rightarrow Zr_{Cu}-N_O$	n	-0.39
$In_{Cu} + N_O \rightarrow In_{Cu}-N_O$	i	-0.85
$In_{Cu} + In_{Cu}-N_O \rightarrow 2In_{Cu}-N_O$	n	-0.10
$Al_{Cu} + Li_{Cu} \rightarrow Al_{Cu}-Li_{Cu}$	i	-1.16
$Ga_{Cu} + Li_{Cu} \rightarrow Ga_{Cu}-Li_{Cu}$	i	-1.37
$In_{Cu} + Li_{Cu} \rightarrow In_{Cu}-Li_{Cu}$	i	-1.45
$Al_{Cu} + Al_{Cu}-Li_{Cu} \rightarrow 2Al_{Cu}-Li_{Cu}$	n	-0.32
$Ga_{Cu} + Ga_{Cu}-Li_{Cu} \rightarrow 2Ga_{Cu}-Li_{Cu}$	n	-0.20
$In_{Cu} + In_{Cu}-Li_{Cu} \rightarrow 2In_{Cu}-Li_{Cu}$	n	0.18

However, the formation energies of the N-related n -type complexes are even higher than those of single donor dopants, which may lead to a low concentration of n -type complexes in CuO under thermal equilibrium condition. However, this issue may be resolved by using non-equilibrium growth methods such as pulsed laser deposition.

B. Li codoping with Al and Ga

In our model, one or two Al/Ga dopants occupy the nearest Cu sites of Li acceptor, forming the $Al_{Cu}/Ga_{Cu}-Li_{Cu}$ passive complexes or the $2Al_{Cu}/2Ga_{Cu}-Li_{Cu}$ n -type complexes, in which two donor dopants are separated from each other. The calculated binding energies for $Al_{Cu}/Ga_{Cu}-Li_{Cu}$ are as large as -1.16 eV and -1.37 eV, respectively, as shown in Table I, which mean that they are very likely to form in CuO. The binding energies for $2Al_{Cu}/2Ga_{Cu}-Li_{Cu}$ are also negative at -0.32 eV and -0.2 eV, respectively, which are calculated between one Al/Ga and one passive complex. Therefore, the n -type complexes are energetically stable and can form if more donors are doped into CuO than Li acceptor. However, the calculated binding energy between one In and one $In_{Cu}-Li_{Cu}$ is positive and the $2In_{Cu}-Li_{Cu}$ n -type complex is not stable in CuO. This is likely due to the large ionic size of In atom as compared with Cu atom. So, we will only discuss the Li and Al/Ga codoping subsequently.

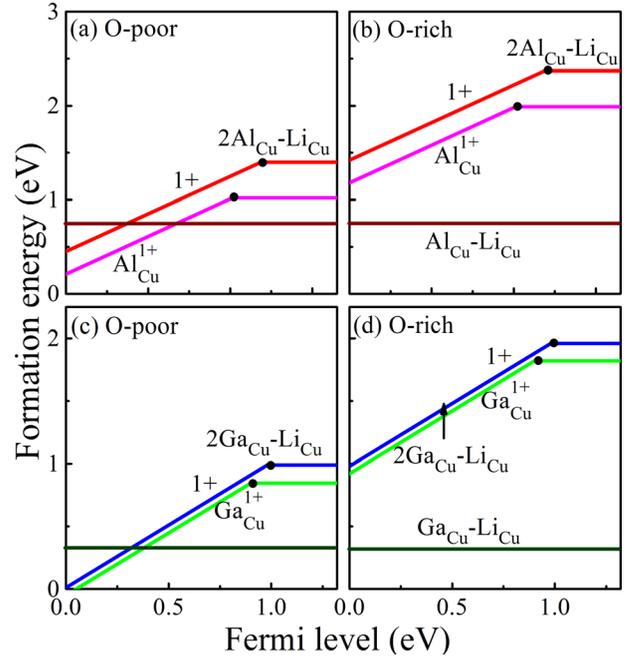


FIG. 2. Formation energies of Li codoping with Al and Ga as functions of the Fermi level, under the O-poor and O-rich conditions, respectively. The formation energies of Al and Ga single dopants are also shown for comparison.

The formation energies for Li codoping with Al and Ga are shown in Fig. 2 as a function of Fermi levels, which are compared with those for Al and Ga single dopants. It is clear that the formation energies of $Al_{Cu}/Ga_{Cu}-Li_{Cu}$ passive complexes are the same under O-poor and O-rich conditions. The low formation energies indicate that the solubility of Al/Ga dopants could be enhanced by Li codoping. However, the passive complexes only have one neutral state in the gap and cannot contribute electrons to the materials. For n -type complexes, their maximum solubility in CuO is achieved under O poor condition. Moreover, each n -type complex has two possible charge states (0 and +1) in the gap, which can donate one electron to the conduction band of CuO. It is found that the donor levels of $2Al_{Cu}/2Ga_{Cu}-Li_{Cu}$ are shallower than those of Al and Ga single dopants by 0.14 eV and

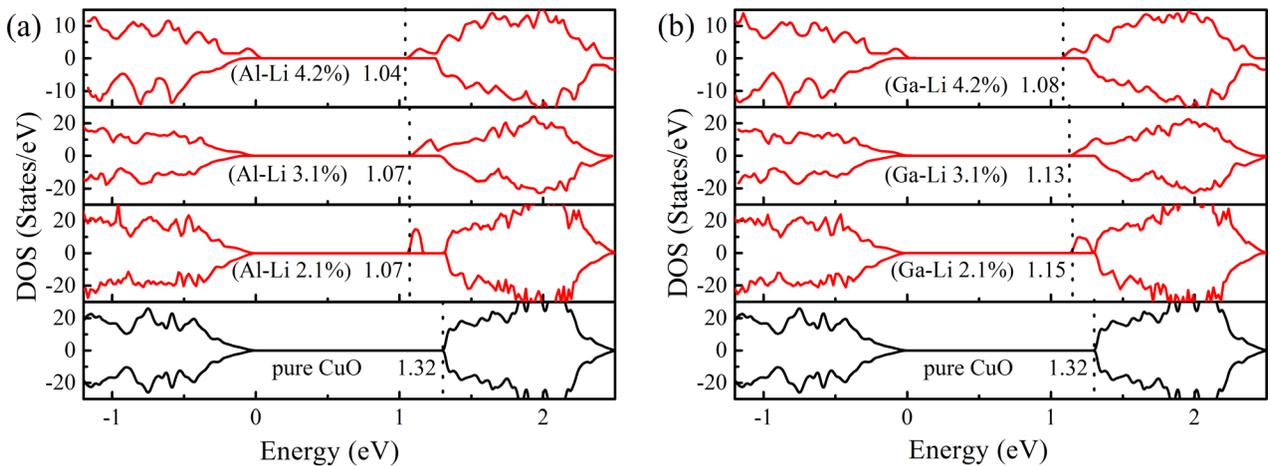


FIG. 3. Total density of states (DOS) for (a) $Al_{Cu}-Li_{Cu}$ and (b) $Ga_{Cu}-Li_{Cu}$ codoped CuO at different concentrations of 2.1%, 3.1%, and 4.2%, respectively. The vertical dotted line indicates the conduction band edge and the number next to it is the bandgap value.

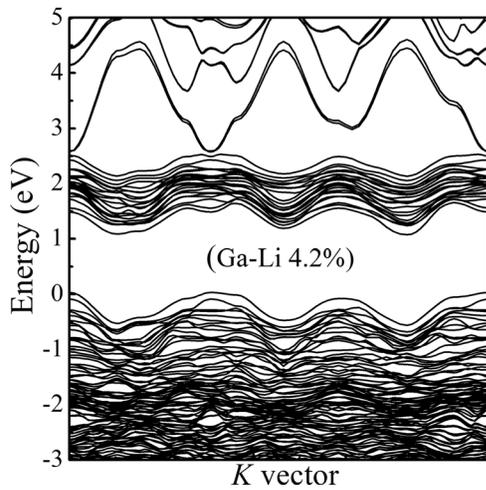


FIG. 4. Calculated band structures (spin up and spin down) for $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ at a high concentration of 4.2% in CuO. The Fermi level of pure CuO is set at zero.

0.08 eV, respectively. Since the formation energy of $2\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is very close to that of single Ga_{Cu} , excess Ga dopants can form either isolated defects (Ga_{Cu}) or n -type complexes with Li. Also, the formation energy of $2\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is not very high to constrain its solubility. Therefore, Li codoping should be able to enhance the n -doping efficiency of Al and Ga dopant in CuO.

We investigate the modified band structure of CuO with passive complexes by calculating the total density of states (DOS), as shown in Figs. 3(a) and 3(b). For these calculations, 96-atom, 64-atom, and 48-atom supercells containing one passive complex are adopted to simulate different codoping concentrations of 2.1%, 3.1%, and 4.2%, respectively. Here, the DOS in the different systems are aligned by referring to the core levels of the atoms far from the impurities. At a low concentration of 2.1%, the basic electronic structure remains the same, while an empty impurity band is created near the CBM of CuO, narrowing the bandgap by -0.25 eV and -0.17 eV for Al/Ga, respectively. Also, it is shown that as the codoping concentration increases, the impurity band broadens and becomes dispersive. The calculated band structure for $\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ at a high concentration of 4.2%

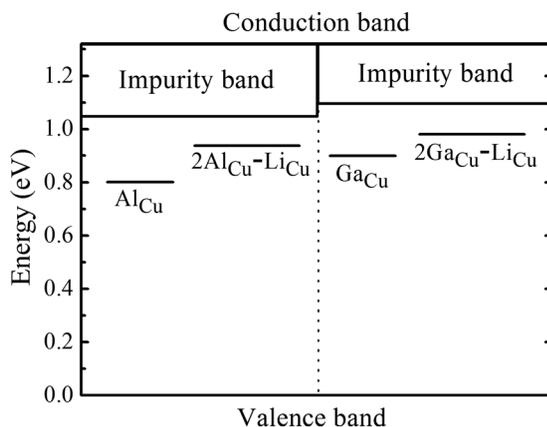


FIG. 5. Schematic band diagrams for Li codoping with Al (left) and Ga (right) in CuO, as well as the calculated donor levels in the gap.

in CuO is shown in Fig. 4. The large curvature at the bottom of the conduction band provides for high carrier mobility, due to the hybridization between Cu $3d$ states and more delocalized sp states of Ga in the impurity states.³² For $\text{Al}_{\text{Cu}}\text{-Li}_{\text{Cu}}$, the calculated band structure at such high concentration (not shown) is very similar to Fig. 4.

In Fig. 5, we show the schematic band diagrams for Li codoping with Al and Ga in CuO at a concentration of 4.2%. Since the impurity band is empty, electron at the deep donor level can be excited to this band. Therefore, the excitation energies of single Al and Ga dopants can be reduced to around 0.2–0.3 eV. If n -type complexes can form, their ionization energies should be even lower ($\sim 0.1\text{--}0.15$ eV), helping to increase the electron concentration. It is noted that to reach reasonable electron mobility, the codoping concentration should go beyond a certain value as it has been demonstrated in Fig. 4.

IV. CONCLUSIONS

In conclusion, we have demonstrated the effect of donor-acceptor (n - p) codoping on reducing donor ionization energies in CuO using first-principles calculations. Our results indicate that N acceptor codoping with both Zr and In can form shallower n -type defect complexes, but their formation energies are high for practical applications. On the other hand, the solubility of Al/Ga can be improved by codoping with Li acceptor, due to the large binding energies between n -type and p -type dopants. Moreover, Li acceptor codoping with Al/Ga can form shallower n -type complexes ($2\text{Al}_{\text{Cu}}/2\text{Ga}_{\text{Cu}}\text{-Li}_{\text{Cu}}$). It is also observed that Li codoping induces an empty impurity band below the CBM, which can narrow the bandgap and reduce donor ionization energies if the codoping concentration is high enough to reach good electron mobility. We have also tested other donor and acceptor combinations. For example, $2\text{In}_{\text{Cu}}\text{-Li}_{\text{Cu}}$ is not a stable complex due to the large atomic size of In. Moreover, N codoping with group III elements (Al, Ga, In) maintains the CBM of CuO but elevates the VBM, which is not beneficial for n -type doping. Our results can be used in the experimental design of suitable n -doping strategy for CuO, which is critical for its application in photovoltaic devices.

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