Difficult of long-standing n-type conductivity in equilibrium and non-equilibrium $\gamma$-CuCl: A first-principles study

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Doping asymmetry is a pervasive issue in wide band gap semiconductors. We demonstrated that $\gamma$-CuCl is one of them with an intrinsic p-type semiconductor by first-principles calculations. The valence band maximum of $\gamma$-CuCl is dominated by the antibonding state of Cu-3d and Cl-3p, resulting in a high energy position. We further find that Cu vacancy has a relatively low diffusion barrier in addition to its low formation energy, implying that the long-standing n-type conductivity is hard to realize in $\gamma$-CuCl even with non-equilibrium approaches.

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1. Introduction

Owing to their promising applications in ultra-violet (UV) optoelectronic devices, such as light-emitting diodes, laser diodes, detectors etc., wide-band-gap (WBG) semiconductor materials, such as zinc oxide (ZnO), gallium nitride (GaN), have been widely studied for many years [1–4]. Although a series of blue and UV devices have been fabricated by using GaN and ZnO, the growth of single crystal GaN layers is still a difficult work because of the shortage of high quality non-polar and low-cost substrates lattice matching GaN [5]. The available lattice-mismatched substrates, typically SiC or $\alpha$-Al$_2$O$_3$ (sapphire), often resulting in the generation of misfit dislocations, are detrimental to the performance of related devices [5]. Furthermore, ZnO is usually grown intrinsically as a n-type semiconductor material [6]. Unfortunately, due to the doping asymmetry problem, it has proven difficult for ZnO to achieve high p-type doping [7] which is essential for the device implementation.

In order to open up new avenues in device applications, it is delightful to obtain n- and p-type films from the same semiconductor materials to form a high-quality homo-junction. However, a severe doping asymmetry problem has been suffered to the most WBG semiconductors experience, i.e., they can be readily doped either n-type or p-type, but not both [8,9], because WBG semiconductors either have a low conduction-band minimum (CBM) or a high valence-band maximum (VBM) with reference to the vacuum level. Like the materials with an O-2p dominated VBM (i.e. ZnO, SnO$_2$ etc.), which is low relative to the vacuum level, excellent n-type conductivity has been achieved on ZnO:Al [6] and SnO$_2$:F [10] etc. However, great efforts have been devoted and long-term p-type stabilities are still hard to realize on them. By investigating the nature of extrinsic and intrinsic p-type defects in SnO$_2$ through a hybrid density functional study, Scanlon and Watson [11] demonstrated that a high-performance p-type SnO$_2$ cannot be achieved.

Recently, $\gamma$-CuCl as an efficient candidate for UV optoelectronics device has drawn much attention [12–23] because it is a zinc-blende direct band gap (3.39 eV) semiconductor and has a large exciton binding energy (190 meV) with its lattice constant closely matched to that of Si (<0.4%). The excitonic binding energy of $\gamma$-CuCl is much higher than that of GaN (20 meV), ZnO (63 meV) [17] and other related direct band gap inorganic materi-
als. The hole conductivity in γ-CuCl has been reported by different groups due to the presence of Cu vacancies [14,15,24,25]. However, the p-type conductance is just at the order of 10⁻ᵀ ᵇ S·cm⁻¹ [14,15]. By using the non-equilibrium process like the pulsed DC magnetron sputtering method [21,22], the n-type conductivity with a large electron concentration at 9.8 × 10¹⁸ cm⁻³ has also been reported [21] in Zn doped CuCl. In light of the experimental results, γ-CuCl seems like it can realize both the n-type and p-type doping and does not suffer the doping asymmetry problem. To above-mentioned situations, it is worthy to analyze the electronic structure and discuss the doping asymmetry in γ-CuCl.

In this letter, using first-principles calculations, we have studied the density of states (DOS), the bonding character, the carrier effective masses m∗, as well as the band edge positions ΔEF and ΔEC of γ-CuCl. Our calculated defect formation energies reveal that the p-type defect Cu vacancy (V_Cu) has low formation energy under all equilibrium growth conditions, especially when the Fermi energy level shifts to CBM. Our results also show V_Cu has a small diffusion barrier and a large diffusion coefficient in γ-CuCl. Therefore, V_Cu can compensate n-type conductivity achieved by non-equilibrium Zn doping in γ-CuCl, and thus the long-standing n-type stability is hard to realize in this compound.

2. Computation details

Our first-principles calculations were performed with the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) [26]. The Perdew–Burke–Ernzerh (PBE) type of generalized gradient approximation (GGA) [27] was used with additional on-site Coulomb corrections (i.e., GGA + U) for the exchange correlation functional. The effective U values (5.2 and 6.5 eV for Cu-3d and Zn-3d states, respectively) were adopted following earlier studies [28,29]. The projector augmented wave method [30] are used to describe the interactions between the core electrons and the valence electrons. A 500 eV was used for the energy cutoff throughout the calculations. The Brillouin zone integrations were sampled with the Γ-centered 6 × 6 × 6 Monkhorst–Pack meshes [31] for the unit cell. For the defect formation energy calculations, the Γ-centered 3 × 3 × 3 mesh was used for the 2 × 2 × 2 supercells (~64 atoms). For the band offset calculations, the Γ-centered 6 × 6 × 1 mesh was used for the A (4 unit cell layers) and B (4 unit cell layers) superlattice changing along (001) direction (64 atoms). The details for the formation energy calculations including the corrections and for the band offset calculations were described in our previous paper [32,33]. The calculations of diffusion paths and corresponding energy barriers are based on the nudged elastic band (NEB) method [34] in a 2 × 2 × 2 supercell (~64 atoms) with GGA + U lattice constants. In order to analyze the chemical bonding characters, the orbital interactions and crystal orbital overlap population (COOP) were obtained by using the Lobster program [35,36].

3. Results and discussions

Our calculated lattice constants are a = b = c = 5.436 Å, which are in agreement with the experimental data [37] a = b = c = 5.42 Å. Fig. 1a shows the partial density of state (PDOS) from the GGA + U calculation. From −5.5 to −4.0 eV with reference to VBM, the lower valence bands are contributed by Cu-3d state and Cl-3p state, and the upper valence bands (i.e. from −2.5 to −0 eV) are dominated by Cu-3d state with a slight contribution from Cl-3p state. In addition, there is an overlap around −5.2 eV between the peak of Cu-4s and Cl-3p. The lower conduction band is mainly made of Cu-4s and Cl-3p. Fig. 1b presents the COOPs of CuCl. The COOPs add the overlap dimension by showing the antibonding (COOP < 0), non-bonding (COOP = 0) or bonding (COOP > 0) character of each electronic state over the system's chemical bonds. Combining with the DOSs and COOPs, we can speculate that the VBM comes from the antibonding state of Cu-3d and Cl-3p and the CBM comes from the antibonding state of Cu-4s and Cl-3p. The bonding state of Cu-3d and Cl-3p locates around −5 to −4 eV and the band state of Cu-4s and Cl-3p coincides with the overlap of Cu-4s and Cl-3p around −5.2 eV. Owing to the VBM from the antibonding state of Cu-3d and Cl-3p and dominated by Cu-3d state, the energy level of VBM with respect to vacuum level would be mainly decided by the cation Cu other than the anion Cl. Our calculated band structure of γ-CuCl indicates it has a direct band gap with 1.69 eV at the Γ point, which is smaller than the reported values 3.39 eV [22], due to the well-known gap underestimation of GGA even with the on-site Coulomb interactions. The carrier effective masses are determined from the energy eigenvalue at a series of defined k-points along the selected symmetry axes. The effective mass tensors m∗(k) of the carriers are obtained by fitting the E − k diagram around the CBM or the VBM with a parabolic expression m∗(k) = ±h²[∂²E(k)/∂k²]⁻¹. As presented in Table 1, the values of the electron effective masses are small and isotropic, which are correlated with the delocalized Cu-4s state and Cl-3p state at CBM. For the hole effective masses, the mass tensor has a bigger value and demonstrates a much more anisotropic characteristics, which should be related to the localized state Cu-3d at the VBM and the bonding direction of the antibonding state between the Cu-3d and Cl-3p. Our calculated hole effective masses of γ-CuCl are heavier than that of γ-CuI [38]. It can be explained by the higher p-orbital energy levels of I than that of Cl, which can contribute more p-state and result in a more delocalized character at VBM.

In order to estimate the type of conductivity of γ-CuCl, we need to find out which kind of defects has low formation energy under certain conditions and is responsible for the conductivity. Fig. 2 shows the formation energies of the intrinsic defects and Zn-related defects in γ-CuCl under Cu-poor and Cu-rich conditions. The Cu-rich condition is corresponding to ΔμCu = 0 and ΔμCl =
Table 1
Calculated carrier effective masses along different axes in $\gamma$-CuCl (unit: $m_e$).
\[
\begin{array}{ccc}
\text{Holes} & m_{001} & m_{011} & m_{111} \\
0.61 & 0.48 & 0.45 \\
1.41 \text{ (twofold)} & 1.41 & 2.80 \text{ (twofold)} \\
\text{Electrons} & 0.30 & 0.31 & 0.31 \\
\end{array}
\]

$\Delta H(\text{CuCl})$, while Cu-poor condition is assumed to $\Delta H_{\text{Cu}} = 0$ and $\Delta H_{\text{Cu}} = \Delta H(\text{CuCl})$. $\Delta H_{\text{Zn}}$ is the maximum Zn chemical potential under the condition of $\Delta H_{\text{Zn}} + 2\Delta H_{\text{Cu}} \leq \Delta H(\text{ZnCl}_2)$. Here, $\Delta H(\text{CuCl})$ and $\Delta H(\text{ZnCl}_2)$ are the calculated formation enthalpies of CuCl and ZnCl$_2$. Our calculated enthalpies of $\gamma$-CuCl and ZnCl$_2$ are $-1.29$ eV and $-3.96$ eV, respectively, which are consistent with the experimental value of $-1.42$ eV and $-4.30$ eV [39]. The calculated acceptor transition level of VCu is $0.31$ eV, which indicates that it is a p-type defect with relatively deep transition level. Other p-type defects like interstitial Cl ($\text{Cl}_i$) and Cl substituting Cu ($\text{Cl}_{\text{Cu}}$) have much larger formation energy than that of VCu, and thus they cannot contribute to p-type conductivity effectively. Our results confirmed that the p-type conductivity originates from the VCu since it has the lowest formation energy even under Cu-rich condition. However, the formation energy of VCu is also slightly less than zero near VB under Cu-poor condition, which give rise to an unphysical meaning. Nagoya et al. [40] reported in another p-type semiconductor Cu$_2$ZnSnS$_4$ that the formation energy of VCu would raise with the increasing of VCu concentration. This means that the VCu in $\gamma$-CuCl could be also thermodynamically stable up under Cu-poor condition after reaching to a fairly high concentration. If assuming 5% concentration of VCu in $\gamma$-CuCl and then using the Boltzmann distribution law, the calculated hole concentrations are $8.3 \times 10^{15}$ cm$^{-3}$ under room temperature by adopting our calculated thermal ionization energies of VCu (0.31 eV), which is in agreement with the reported low p-type conductance ($\sim 10^{-7}$ S cm$^{-1}$) from experiment. Therefore, the low p-type conductance of $\gamma$-CuCl should be ascribed to the relatively deep acceptor transition level of VCu, other than high formation energy of p-type defects, or the possible n-type compensating defects.

For the n-type defects, the transition levels of Cu, CuCl and ZnCu are $0.22$ eV, $0.30$ eV below the calculated CBM and $0.05$ eV above the calculated CBM, respectively. The results indicate that ZnCu can supply an electron to the conduction band effectively owing to its transition level inside the conduction band. However, it has relatively high formation energies under equilibrium condition. By using the non-equilibrium process like the pulsed DC magnetron sputtering [21,22], the growth of Zn-doped CuCl can break up the equilibrium state and achieve a large n-type ZnCu concentration. Since ZnCu can supply the electrons effectively, the electron concentration can reach to a high value and the Fermi energy level will move close to the CBM in the as-grown samples, which is consistent with the large electron concentration ($9.8 \times 10^{18}$ cm$^{-3}$) from the experimental report [21]. When the sample became n-type and the Fermi energy level stayed close to CBM, the defect formation energy of VCu will decrease to negative value both under Cu-rich and Cu-poor condition. It means that Cu vacancies would be formed spontaneously and may result in a compensation on electron carrier concentration gradually. Here, we pointed out that GGA or GGA + U calculations severely underestimate the band gap, however, the error on the defect formation energy may alleviate in many systems [38,41]. For instance, although GGA, GGA + U and HSE presented different band gap values, the sequences on the defect formation energies for various defects in Cu$_x$ [38] and Ga$_x$ [41] systems from different functional calculations are consistent. Therefore, the tendency on the comparison of defect formation energies between VCu and ZnCu should be reliable although our GGA + U calculation underestimates the band gap. In addition, for the defect transition levels, Lany and Zunger [42] suggest that the shallow perturbed-host state should be moved with the conduction band and the deep defect-localized state should be kept in the band gap after the revision on the band edge position. It should be still a shallow donor-type defect for ZnCu and a deep acceptor-type defect for VCu from the calculations with more accurate band gap.

In order to evaluate the possibility of the carrier compensation in Zn-doped CuCl, we have discussed the binding energy between the n-type defect ZnCu and p-type defect VCu and the diffusion barriers of these defects. The binding energy of the defect complex (ZnCu + VCu) is calculated by $E_B = (E_{\text{complex}} + \text{Epure}) - (E_{\text{ZnCu}} + E_{\text{VCu}}) [43]$, where $E_{\text{complex}}$ is the energy of the supercell containing the defect complex, $E_{\text{pure}}$ is the energy of the intrinsic supercell, and $E_{\text{ZnCu}}, E_{\text{VCu}}$ are the energies of the structures that only contain ZnCu or VCu. Our calculated binding energy for (ZnCu + VCu) is $-2.27$ eV, which indicates the n-type ZnCu and p-type VCu have a tendency to form a cluster. The formation of the neutral defect complex (ZnCu + VCu) indicates the electron carrier concentration from ZnCu will be balanced by the p-type defect VCu. The calculated diffusion barriers (Fig. 3) from a centered tetrahedron site to a nearby centered site for ZnCu and VCu are 0.63 eV and 0.38 eV, respectively. The diffusion barrier of VCu in CuCl is close to that of NaCu (0.36 eV) in Cu$_{1-x}$Ga$_x$Se$_2$, which is suggested as a faster diffuser in bulk Cu$_{1-x}$Ga$_x$Se$_2$ [44]. A rough diffusion coefficient of VCu can be determined according to the equation $D = s^2 \cdot v \cdot e^{-E_A/kT}$ [45,46], where $s$ stands for the hopping distance of a diffusion, $v$ stands for the attempt frequency and $E_A$ is taken from our calculated diffusion barrier of VCu and $kT$ is Boltzmann’s constant times the temperature. In this calculation, a typical value of 10$^{13}$ s$^{-1}$ [46,47] was used for $v$, and the temperature was set to be 300 K. The estimated diffusion coefficient of VCu is in the order of $6 \times 10^{-9}$ cm$^2$ s$^{-1}$, which is much larger than that ($\sim 10^{-12}$ cm$^2$ s$^{-1}$) of Li ion [48,49] in the famous Li-ion battery cathode LiCoO$_2$. The small diffusion barrier and large diffu-
sion coefficient of $V_{\text{Cu}}$ indicates that it can diffuse close to $Zn_{\text{Cu}}$ and form a neutral defect complex with $Zn_{\text{Cu}}$ after its spontaneous formation. These results demonstrate the intrinsic p-type defect $V_{\text{Cu}}$ can compensate the n-type conductivity effectively and the n-type conductivity in the as-grown Zn-doped CuCl should be unstable. Therefore, like other WBG semiconductors (ZnO, SnO$_2$, etc.), $\gamma$-CuCl also encounters a doping-asymmetry problem [8,9] and is hard to realize n-type with a long-term stability.

In order to illustrate the origin of the doping-asymmetry in $\gamma$-CuCl, we have investigated the band edge positions of CuCl and compared them with those from the n-type and p-type prototype compounds (i.e., ZnO for n type and Cu$_2$O for p-type). For the purpose of obtaining the band edge positions of CuCl relative to vacuum, we adopt the ionization potential of CuI (5.2 eV) from experiment [50], and then calculate the band offsets among CuCl, CuBr, and CuI. Fig. 4 presents the band edge positions and band offsets among CuCl, CuBr, CuI, ZnO, and Cu$_2$O. Our calculated results show that the valence band edge ($-5.39$ eV vs. vacuum) of CuCl is just lower than that of CuBr with $0.09$ eV and that of CuI with $0.19$ eV. Naturally, the band offset obtained from the superlattice model does not depend on the orientation of the interface. As a confirmation, here we have calculated the band offset from the superlattice oriented along (110) direction (96-atoms supercell). Our results show that the valence band offset of CuBr and CuI with CuCl are 0.09 and 0.20 eV, respectively, which is almost the same with the results from (001) oriented supercell. Our results demonstrate that this group compounds (i.e., CuCl, CuBr, and CuI) almost have the same valence band positions. From our DOS and COOP analysis, it can be explained by the VBM of these three Cu-based compounds mainly come from the 3d state of the same cation Cu and then have the similar valence band edge positions. The p-type conductivity has also been reported in CuI [53] and CuBr [54] experimentally. Based on a recently accepted doping limit rule [55], p-type doping can be achieved readily in semiconductor compounds with high VBM and n-type doping can be realized easily in semiconductor compounds with low CBM. This is the reason why the doping asymmetry exists in the WBG semiconductor, which cannot have a high VBM and low CBM at the same time. As a comparison with the band edge positions of the n-type prototype semiconductor ZnO and p-type prototype semiconductor Cu$_2$O, we found that CuI has a similar VBM position with Cu$_2$O and has a much higher CBM position than ZnO, which suggests that $\gamma$-CuCl is an intrinsic p-type semiconductor and possesses a doping asymmetry problem [8,9].

4. Conclusions

In summary, our results reveal that the VBM of CuCl comes from the antibonding state of Cu-3d and Cl-3p with the majority from Cu-3d state. Based on the calculation on defect formation energy, we find that the p-type defect $V_{\text{Cu}}$ always has the lowest formation energy under all chemical equilibrium conditions and $\gamma$-CuCl should be an intrinsic p-type semiconductor. With the Fermi level moving to n-type region, the formation energy of $V_{\text{Cu}}$ will decrease to below zero and then it can be self-formation. Combining the self-formation with the small diffusion barrier and large diffusion coefficient of $V_{\text{Cu}}$, we demonstrate that $V_{\text{Cu}}$ can compensate the n-type conductivity from the non-equilibrium Zn-doping in CuCl. The long-term stability of n-type conductivity is hard to maintain. Compared to the band edge positions with other WBG semiconductors, $\gamma$-CuCl has both high VBM and high CBM positions, which can explain the doping asymmetry in this compound.

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References