

First-Principles Study of Cu_9S_5 : A Novel p-Type Conductive Semiconductor

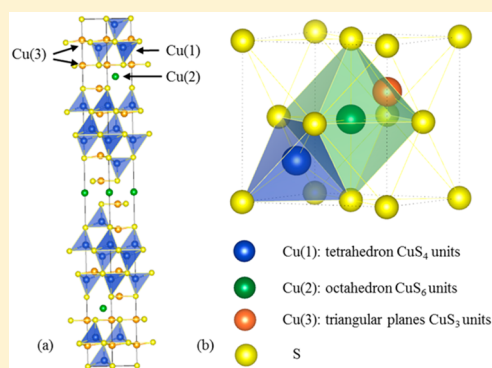
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Supporting Information

ABSTRACT: Cu_9S_5 (digenite) is a p-type semiconductor with excellent electrical conductivity, high mobility of copper ions, and high work function. When used as the back electrode of CdTe solar cells, a high power conversion efficiency (PCE) is obtained. Density functional theory (DFT) method was used to study the structural and electronic properties of Cu_9S_5 in this work. From the calculated band structures, we find that the Fermi level of the Cu_9S_5 slightly crosses the valence band by about 0.08 eV below the valence band maximum (VBM), indicating a high hole concentration and potential high electrical conductivity as a p-type semiconductor. It is also found that the crystal structure of Cu_9S_5 remained stable with a few Cu atoms diffused away, which introduces a p-type doping effect. Finally, we give a quantitative discussion on why CdTe solar cells with Cu_9S_5 as the back electrode shows the high PCE.



INTRODUCTION

Copper sulfides (Cu_{2-x}S , $0 \leq x \leq 1$) have attracted great interest due to their different stoichiometry, complex structure, and unique physical and chemical properties as earth-abundant materials.^{1–3} Copper sulfides have several stable solid phases with the stoichiometric compositions varying in a wide range from copper-rich Cu_2S to copper-deficient CuS . There are several known phases at room temperature, such as chalcocite (Cu_2S), djuleite ($\text{Cu}_{1.96}\text{S}$), digenite (Cu_9S_5), anilite (Cu_7S_4), and covellite (CuS).^{4,5} All of these copper sulfides are intrinsically p-type semiconductors due to the copper vacancies in the crystal lattice.⁶ Depending on the Cu contents and temperature, their crystal structures and electronic properties are different.^{7,8} Copper sulfides have a wide range of potential applications in photocatalysis, solar cells, photothermal conversion, sensors, superionic materials, and lithium-ion batteries and even have been used as a photothermal agent to kill cancer cells.^{4–6,9–14} In particular, because of their low cost, environmental friendliness, and variable band gaps in the range of 1.2–2.4 eV, they are considered to be one of the most likely future sustainable energy materials.¹⁵

Among them, Cu_9S_5 has two stable existing phases: low-digenite (below 364 K) and high-digenite (above 364 K). When the temperature is increased over 364 K, the position of the Cu atom in the crystal structure changes from ordered states to disordered states.¹⁶ Cu_9S_5 has many excellent performance qualities, such as excellent electrical conductivity, high mobility of copper ions, high work function, and novel photothermal conversion efficiency.¹⁷ We recently used Cu_9S_5 (low-digenite) as the back electrode of a CdTe thin-film solar

cell.¹⁸ Compared with CdTe solar cells using metal as the back electrode, it reduced the contact potential barrier greatly and promoted a high power conversion efficiency (PCE, 11.3%). However, in this experimental work, the detailed mechanism of reducing the contact potential is not given. There are some theoretical studies on copper sulfides such as the solid–liquid hybrid phase of high-chalcocite Cu_2S ,¹⁹ covellite (CuS),²⁰ and Cu_{2-x}S ,²¹ but the study of Cu_9S_5 is still lacking. Up to now, all we know about the character of Cu_9S_5 is from experiments, such as the direct band gap (1.5 eV) obtained from optical absorption measurements.²² However, the Cu_9S_5 in that work is a chemically deposited semiconductor thin film composed of Cu_9S_5 nanocrystals (~ 19 nm), indicating that this gap could be too large as a result of the quantum confinement effect. Moreover, the optical gap would be less than the fundamental gap that does not include the exciton binding energy in the role of the excitonic effect, which makes it difficult to determine the real band gap by experiments. Thus, it is highly desirable to implement a theoretical study of the structural and electronic properties of Cu_9S_5 and the property of it when used as the back electrode of CdTe solar cells. In the present work, we performed a detailed study of Cu_9S_5 by using density functional theory (DFT) calculations and explained why CdTe cells with Cu_9S_5 as the back electrode under the help of Au films as an assistant back electrode show a very high PCE.

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METHODS

Geometry optimization and electronic properties are calculated by using a projector-augmented wave (PAW)^{23,24} pseudopotential as implemented in the Vienna ab initio simulation package (VASP).²⁵ To ensure the accuracy, a 550 eV cutoff energy is chosen for the plane-wave basis, and the Cu 3d and 4s, S 3s and 3p electrons are included as the valence electrons in the calculations. The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is adopted.²⁶ The geometry optimization is performed until the remaining forces become less than 10^{-2} eV/Å and the energy between two successive step is less than 10^{-5} eV. Brillouin zone integrals are approximated using the method of Monkhorst and Pack,²⁷ and a $7 \times 7 \times 2$ k-point set is used for geometry optimization and $21 \times 21 \times 6$ to get the densities of states (DOSs).

It is well-known that local density approximation (LDA) and GGA functionals systematically underestimate Kohn–Sham band gaps (compared to experimentally determined values), whereas the Hartree–Fock method systematically overestimates them. As a hybrid functional can correct the self-interaction errors (SIEs) for both Cu and S atoms, it often gives reasonably accurate predictions of band gaps. In this case, Heyd–Scuseria–Ernzerhof (HSE06)²⁸ is chosen for the predictions of band gaps. The computationally economical method GGA+ U ²⁹ is used to get more details of electronic structures, which tends to provide a d^{10} configuration for Cu and can provide a relatively accurate band gap. Hence, we adopt $U = 3, 5, 7, 9, 11, 13$, and 15 eV for tests. The best U parameter is determined by comparing the GGA+ U results with the benchmark of HSE06 results.

RESULTS AND DISCUSSION

The lattice of the low-digenite conventional cell is identified as a hexagonal phase (R3-MH) based on a fcc sublattice of S (Figure 1). The S atoms form an approximate elongated close A–B–C–A–B–C stacking packed lattice along the z direction. The structure is similar to that of cubic chalcocite (Cu_2S), but only 9/10 of the Cu sites are occupied, leading to a strong p-type doping effect.²¹ Cu atoms are located in three kinds of positions: tetrahedron CuS_4 units (Cu(1), blue), octahedron CuS_6 units (Cu(2), green), and triangular plane CuS_3 units (Cu(3), orange), with distribution percentages of 44.4, 44.4, and 11.1%, respectively. Cu(2) has the longest Cu–S bond (2.78 Å) (Table S1) and forms a layered arrangement.

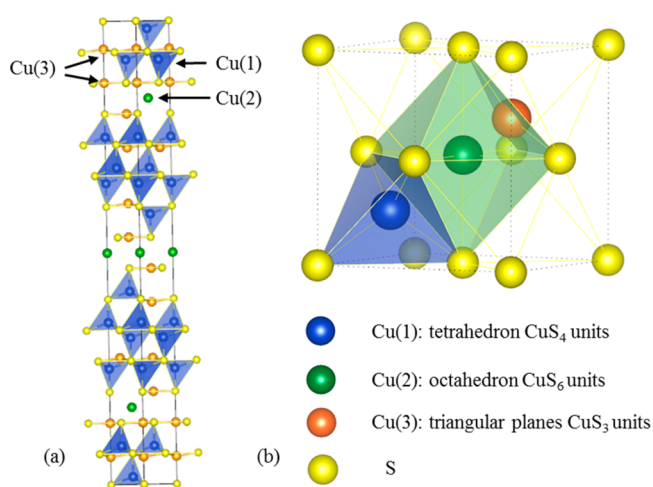


Figure 1. (a) Crystal structure of Cu_9S_5 with a low-temperature phase. (b) The fcc sublattice of S and possible distribution position of Cu in the S fcc sublattice.

Cu S_6 units (Cu(2), green), and triangular plane CuS_3 units (Cu(3), orange), with distribution percentages of 44.4, 44.4, and 11.1%, respectively. Cu(2) has the longest Cu–S bond (2.78 Å) (Table S1) and forms a layered arrangement.

Compared with the experimental values for lattice parameters, the LDA calculated lattice parameters $a = b$ are overestimated by 0.016 Å, and the lattice parameter c is underestimated by 0.869 Å (Table S2). By contrast, GGA underestimates $a = b$ by 0.54 Å and overestimates c by 0.192 Å. Compared with the above two methods, the GGA+ U method gives more accurate structural parameters (Table S2). As shown in Table S2, lattice parameters $a = b$ differ from the experimental values by -0.23 , -0.10 , and 0.03% when $U = 11, 13$, and 15 eV, respectively. Therefore, $U = 15$ eV gives the best estimation of $a = b$ with respect to experimental measurements. The c lattice parameter differs from the experimental value by 0.12, 0.22, and 0.22% when $U = 11, 13$, and 15 eV, respectively. Therefore, the best estimation for c is given under $U = 11$ eV. The volume differs from the experimental value by -0.34 , 0.02, and 0.27% when $U = 11, 13$, and 15 eV, respectively; therefore, the best estimation for volume is given under $U = 13$ eV.

The electronic structures of Cu_9S_5 were studied next. As shown in Figure S1, standard LDA/GGA cannot open a band gap with the conduction band minimum (CBM) almost overlapping the valence band maximum (VBM), but the GGA+ U method can open a band gap. With the increasing U value, the VBM and Fermi level remain almost unchanged, and CBM shifts upward, leading to an increased band gap. Figure 2a,b shows the band structure and the density of states (DOS) of Cu_9S_5 under HSE06, respectively, which exhibit a gap of 0.610 eV. In addition, the Fermi level slightly crosses the valence band by about 0.08 eV below the VBM, indicating a high hole concentration and potential high electrical conductivity for this system. This can be attributed to the fact that the Cu vacancies introduce holes in Cu_9S_5 . A similar phenomenon that the Fermi level lies below the VBM is also observed for Cu_2S [20] and CuS [19]. Technically, the band gap should be zero at levels of theory because the Fermi level crosses the valence band. However, we still consider the “band gap” (the energy difference between the two seemingly disconnected manifolds of bands in the vicinity of the Fermi level) in this work. Because optical transitions can only take place between unoccupied and occupied states, and assuming that only vertical transitions occur, the “band gap” that we define here can still make sense.

Among all of the calculated band structures with different U values by the GGA+ U method, it is also observed that the Fermi level slightly crosses the valence band, indicating that Cu_9S_5 is a p-type degenerate semiconductor. When the U value is increased up to 9 eV (Figure S2), an acceptable direct “band gap” of 0.637 eV appearing at the Γ point is obtained (Figure 2c), which is close to the HSE06 value of 0.610 eV. The U value of 15 eV gives good estimation of the lattice parameters, while reproducing the HSE06 band gap requires a U value of 9 eV. Considering that a U value of 15 eV is too large and we mainly focus on the electronic properties, a U value of 9 eV was used for both structure optimization and band structure calculations in our further calculations in this work, and this value also provides a relatively accurate electronic structure and avoids the large computing cost by HSE06. From the partial density of states (PDOS) of Cu_9S_5 (Figure 2d), it can be seen that the VBM is predominantly composed of Cu 3d orbitals and S 3p orbitals, and the Cu 3d orbital does not show a

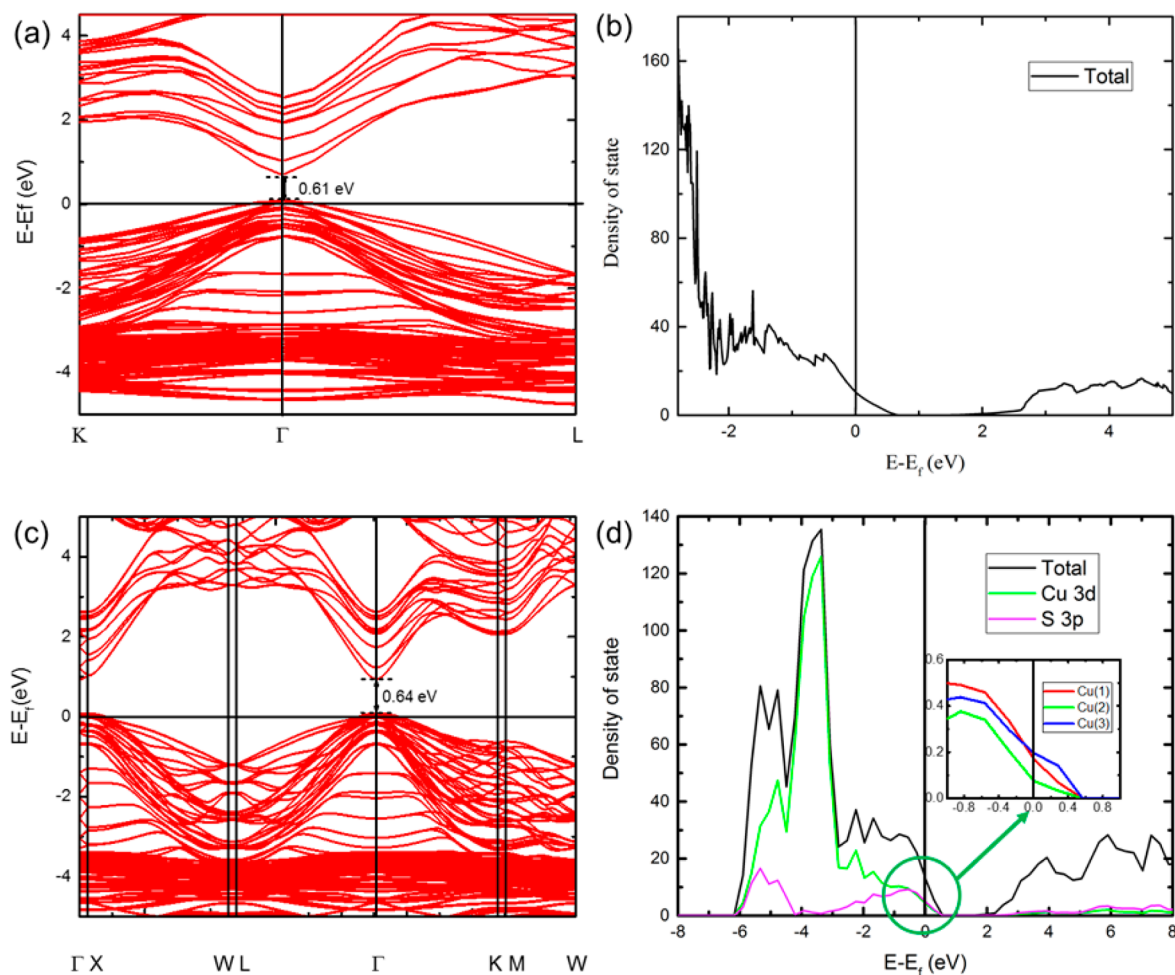


Figure 2. DFT-calculated electronic structures of Cu_9S_5 : (a) Band structure by the HSE06 method, (b) DOS by HSE06, (c) band structure by the GGA+ U ($U = 9$ eV) method, and (d) PDOS by the GGA+ U ($U = 9$ eV) method. The contributions of three types of Cu atomic orbitals in the vicinity of the Fermi level are shown in the inset.

significant downward shift with respect to the Fermi level. A similar phenomenon is also observed for Cu_2S ,²¹ CuS ,²⁰ and CuBr .³⁰ The PDOS in the vicinity of the Fermi level shows that the highest occupied state is mainly composed of a Cu 3d state and S 3p state, indicating that the conduction of Cu_9S_5 relies on the transition metal Cu 3d orbitals and S 3p orbitals. From the PDOS of different Cu atoms (inset in Figure 2b), we also found that Cu(2) (octahedral central Cu) has the least contribution to the total DOS near E_f with respect to Cu(1) (tetrahedral central Cu) and Cu(3) (trigonal central Cu). As we known, hole concentration can be calculated as follows

$$N = \int_{-\infty}^{E_v} (1 - f_B(E)) g_c(E) dE \quad (1)$$

where $f_B(E)$ is the Fermi distribution function and can be described as $\frac{1}{1 + \exp(\frac{E - E_f}{k_B T})}$ (E_f is the Fermi energy, k_B is the

Boltzmann constant, and T is temperature) and $g_c(E)$ is the DOS at energy E . Thus, Cu(2) has the least contribution to hole concentration in Cu_9S_5 and may also have the least contribution to the electrical conductivity.

It is reported that Cu_9S_5 is a superionic conductor with high Cu ion conductivities.⁶ When Cu_9S_5 is used as the back electrode of a CdTe solar cell, there is Cu diffusion from Cu_9S_5 to CdTe, forming a gradient-doping region that greatly reduces

the contact potential barrier.¹⁸ As a result, copper vacancies would be formed in Cu_9S_5 . The formation energy of one Cu vacancy was calculated as follows

$$E_{\text{form}} = E_{\text{vacancy}} + \mu_{\text{Cu}} - E_{\text{perfect}} \quad (2)$$

E_{vacancy} and E_{perfect} are the total energies of the Cu_9S_5 supercell with one Cu vacancy and without a Cu vacancy, respectively, and μ_{Cu} is the chemical potential of the Cu atom. Note that the chemical potentials depend on the experimental conditions (oxidizing conditions or reducing conditions). Under extreme oxidizing conditions, μ_{Cu} satisfies the constraint of $\mu_{\text{Cu}} + \mu_{\text{S}} = E_{\text{tot}}[\text{CuS}]$, in which $E_{\text{tot}}[\text{CuS}]$ is the total energy of bulk CuS and μ_{S} is equal to 1/8 of the total energy of the bulk S_8 in the solid phase. On the other hand, under extreme reducing conditions, μ_{Cu} is equal to the total energy of the fcc Cu. As shown in Figure S3, the Cu(2) (octahedral central Cu) vacancy has the smallest formation energy, indicating that they are more likely to diffuse away to form Frenkel defects of Cu vacancies.

Thus, it is worth studying the electronic structures of Cu_9S_5 with Cu(2) vacancies. We removed one, two, and three octahedral central Cu atoms in a crystal unit cell and found that after structure relaxation the crystal structure stays stable, with S atoms remaining on a fcc sublattice and Cu atoms remaining in the original position, except that planar triangles of the central Cu atom near the removed octahedral central Cu atom

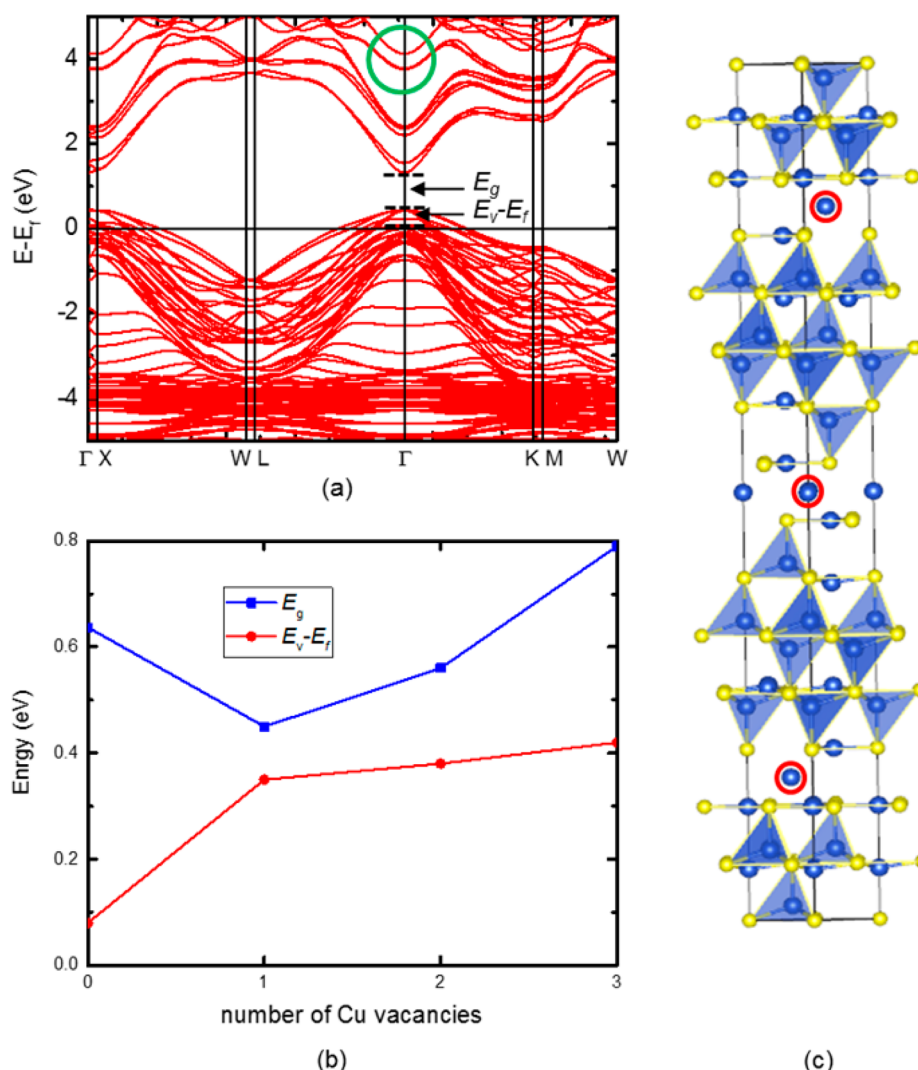


Figure 3. (a) Calculated band structure of Cu_9S_5 with three Cu vacancies. (b) E_g and $(E_v - E_f)$ as a function of the number of Cu vacancies. (c) Unit cell of Cu_9S_5 with three Cu vacancies, as highlighted with red circles.

moved to a nearby tetrahedral center. The phonon bands of the Cu_9S_5 structure with no vacancy, one Cu vacancy, two Cu vacancies, and three Cu vacancies are plotted in Figure S4. No obvious imaginary mode can be seen in the first Brillouin zone, suggesting that Cu_9S_5 with no vacancy, one vacancy, two vacancies, and three vacancies are dynamically stable. From Figure S3, it can be seen that the formation energy of the Cu(2) vacancy is negative, indicating that Cu_9S_5 with defects of Cu vacancies is thermodynamically favorable. The band structure of Cu_9S_5 with three vacancies of octahedral central Cu is shown in Figure 3a. Compared with the band structure of Cu_9S_5 without Cu vacancies, their band structures are similar, and the “band gaps” of the structure with one and two Cu vacancies are smaller and the “band gap” of the structure with three Cu vacancies is larger. For Cu_9S_5 with vacancies, the VBM shifts upward and the “band gap” is slightly increased with the number of vacancies. This can be attributed to the fact that the increased Cu vacancies can be considered as a hole-doping; therefore, the Fermi level shifts downward. In addition, there is a defect state, as highlighted by the green circle. We also calculated Cu_9S_5 with one charged defect; as shown in Figure S5, its band structure is very similar to the band structure of Cu_9S_5 with one neutral defect, expect that its VBM shifts up

slightly by about 0.04 eV and the CBM shifts down by about 0.19 eV. The “band gap” (E_g) and the degree of the Fermi level (E_f) shift ($E_v - E_f$) as a function of the number of copper atomic vacancies are shown in Figure 3b. We can see that ($E_v - E_f$) increases greatly with the first octahedral central Cu vacancy formed, while more Cu vacancies can only increase ($E_v - E_f$) slightly. Figure S6 shows that hole concentration enhances greatly with the increase of Cu atom vacancies, which would benefit the electrical conductivity if the electrical conductance (σ) remains nearly unaffected. Interestingly, the “energy gap” (E_g) first decreases with the first Cu vacancy formed and then increases with the increase of Cu vacancies. This can be attributed to the fact that with the first Cu vacancy formed, the introduced hole-doping induces a built-in electric field in the layered structure, which shifts the energy levels of Cu–S bonds to higher energies and leads to a reduced “energy gap”. Meanwhile, as shown in Table S3, the lattice parameters decrease with the increase of Cu vacancies, indicating a reduced fcc sublattice of S and enhanced Cu–S bonds, which would enlarge the “energy gap”. When the second Cu vacancy is formed, this effect becomes more serious and surpasses the effect of a built-in electric field and leads to the increased “energy gap” in Cu_9S_5 .

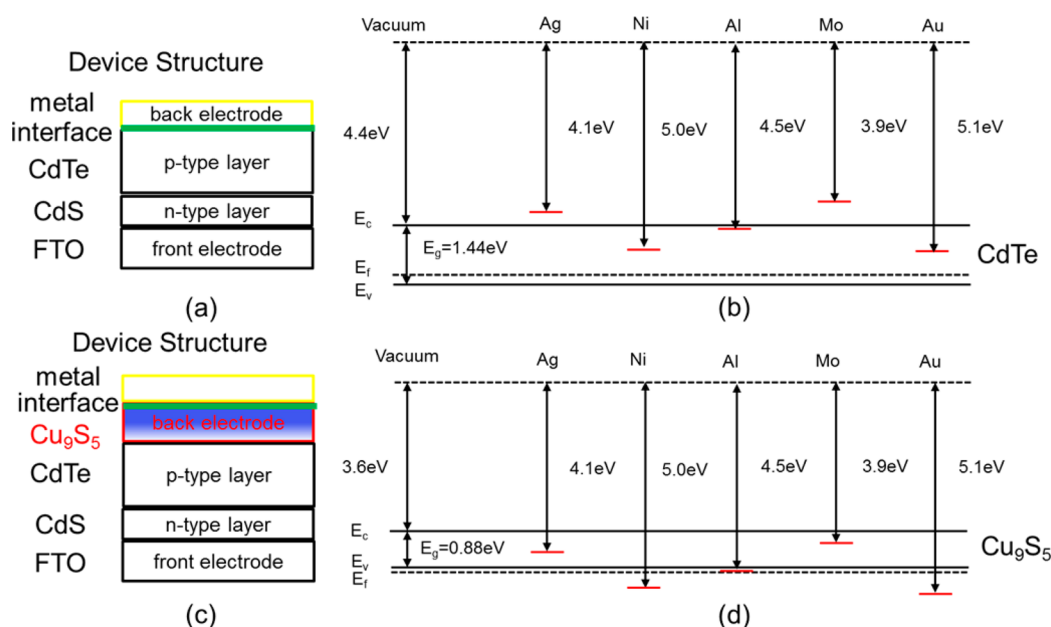


Figure 4. (a) Device model of the traditional CdTe solar cell with metal as the back electrode (FTO/CdS/CdTe/metal). (b) Calculated band alignment of CdTe contacted with different metals. (c) Device model of our newly developed CdTe solar cell with Cu_9S_5 as the back electrode and metal as the assistant back electrode (FTO/CdS/CdTe/ Cu_9S_5 /metal). (d) Calculated band alignment of Cu_9S_5 contacted with different metals.

We also calculated other elements' doping cases, such as to replace Cu atoms with K and Ag and to replace S atoms with N. From the calculated band structures, we can see that all of the above doping cases will lead to a similar hole-doping as Cu vacancies, as shown in Figure S7. The values of $(E_v - E_f)$ for N, K, and Ag doping are 0.199, 0.124, and 0.126 eV, respectively, which are all smaller than the value (0.35 eV) for one Cu vacancy doping. All of the above doping cases (one Cu vacancy, N, K, and Ag doping) can be viewed as aliovalent ion doping, compared to the original Cu-ion (average +1.11 valence state) in Cu_9S_5 . Due to the degree of aliovalence between the Cu vacancy (zero valence state) and Cu-ion being the biggest among them, the value of $(E_v - E_f)$ for Cu_9S_5 with one Cu vacancy is the largest. In addition, as shown in Table S4, lattice parameters of N-doping decrease like the Cu vacancy, which may be attributed to the N–Cu bond strength being stronger than the S–Cu bond. In contrast, the Ag-doping leads to an increase of lattice parameters because Ag^+ is bigger than the Cu-ion. Though the lattice parameter $a = b$ is decreased by a little, the lattice parameter c is increased by a large degree for K doping, also due to the much bigger K^+ radius.

We finally discuss the application of Cu_9S_5 as the back electrode for CdTe solar cells. The device models of the traditional CdTe solar cell and our recently developed CdTe solar cell with Cu_9S_5 as the back electrode and Au as the assistant electrode¹⁸ are shown in Figure 4a,c, respectively. As CdTe in a (110) orientation has a high stability and is commonly used in experiments,^{31–34} we chose the (110) surface as the normal surface for CdTe. Metals in a (100) orientation were chosen in order to match CdTe-(110) well. In the same way, Cu_9S_5 in a (100) orientation was chosen because of its small lattice mismatch with metal-(100).

The calculated work function of CdTe is 5.2 eV, very close to the experimental values of 5.0–5.7 eV.³¹ Owing to its intrinsic high work function (bigger than the work function of most metals), it is hard to form a good Ohmic contact with metal back electrodes. Instead, CdTe forms a Schottky barrier when

contacting with the representative Ag, Ni, Al, Mo, and Au electrodes (Figure 4b), which would degrade the performance of solar cells. The calculated work function of Cu_9S_5 is 4.5 eV, slightly smaller than the experimental value of 5.12 eV.¹⁸ On the basis of this experimental value, the work function of Cu_9S_5 is the closest to the work function of CdTe. Moreover, as mentioned above, there is Cu diffusion from Cu_9S_5 to CdTe, which would form a gradient-doping region to reduce the contact potential barrier. Meanwhile, as shown in Figure 4d, the work function of Cu_9S_5 is smaller than that of Ni and Au; therefore, Cu_9S_5 can form an Ohmic contact with Ni and Au because the Fermi level of Ni and Au is lower than the VBM of Cu_9S_5 . This explains the experimental results that CdTe solar cells with Cu_9S_5 as the back electrode and Au as the assist electrode show greatly improved PCE.¹⁸

As we discussed above, Cu_9S_5 is a self-doped p-type semiconductor with a relatively high carrier (holes) concentration. Besides the above application as the back electrode of CdTe solar cells, there are also some other potential applications for Cu_9S_5 : (1) Arising from the highly concentrated p-type carriers in vacancy-doped Cu_9S_5 , Cu_9S_5 can exhibit localized surface plasmon resonances, as demonstrated by Burda et al.³⁵ This can induce a high photothermal conversion efficiency, leading to Cu_9S_5 being applied for potential photothermal materials. For example, Tian et al. synthesized hydrophilic plate-like Cu_9S_5 nanocrystals and used them as a new photothermal agent, which showed a 25.7% heat conversion efficiency for photothermal ablation of cancer cells in vivo.¹⁷ (2) Because Cu_9S_5 exhibits good electronic conductivity and high hole concentration (the effective mass of holes is generally much larger than that of electrons, which contributes to the Seebeck coefficient), it can be used as a promising thermoelectric material.¹⁶ (3) Because Cu_9S_5 exhibits good conductivity and high work function as a p-type semiconductor, it may also be used as contact electrodes for field effect transistors.

CONCLUSIONS

In conclusion, we have studied the structural and electronic properties of Cu_9S_5 using DFT calculations. It is found that the Fermi level slightly crosses the valence band by about 0.08 eV below the VBM, indicating a high hole concentration and potential high electrical conductivity as a p-type semiconductor. The crystal structure of Cu_9S_5 remains stable with some of the octahedral central Cu atoms diffused away, and the Cu vacancies would introduce an extra p-type doping effect. Finally, we found that the work function of Cu_9S_5 is the closest to the work function of CdTe and smaller than those of Ni and Au. The above explains why CdTe cells with Cu_9S_5 as the back electrode and the help of Au films as an assistant back electrode show a very high PCE.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07843.

Details of the calculated results, band structure, and supplementary tables and figures (PDF)

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Notes

The authors declare no competing financial interest.

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