Origin of the Distinct Diffusion Behaviors of Cu and Ag in Covalent and Ionic Semiconductors

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It is well known that Cu diffuses faster than Ag in covalent semiconductors such as Si, which has prevented the replacement of Ag by Cu as a contact material in Si solar cells for reducing the cost. Surprisingly, in more ionic materials such as CdTe, Ag diffuses faster than Cu despite that it is larger than Cu, which has prevented the replacement of Cu by Ag in CdTe solar cells to improve the performance. But, so far, the mechanisms behind these distinct diffusion behaviors of Cu and Ag in covalent and ionic semiconductors have not been addressed. Here we reveal the underlying mechanisms by combining the first-principles calculations and group theory analysis. We find that the symmetry controlled *s*-*d* coupling plays a critical role in determining the diffusion behaviors. The *s*-*d* coupling is absent in pure covalent semiconductors but increases with the ionicity of the zinc blende semiconductors, and is larger for Cu than for Ag, owing to its higher *d* orbital energy. In conjunction with Coulomb interaction and strain energy, the *s*-*d* coupling is able to explain all the diffusion behaviors from Cu to Ag and from covalent to ionic hosts. This in-depth understanding enables us to engineer the diffusion of impurities in various semiconductors.

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Noble metals have been widely used in semiconductor electronic and optoelectronic devices [1]. One of their applications is as an electric contact material in semiconductor devices owing to their low electrical resistivity and supposed immunity from electromigration damage [2,3]. The four best normal metal conductors in nature are Ag, Cu, Au, and Al with a resistivity of 1.60, 1.67, 2.30, and 2.69 $\mu\Omega$ cm, respectively [2]. Compared to Al and Au, Cu offers 38% and 27% reduction, respectively, in resistivity, whereas Ag offers another 5% reduction over Cu. Thus, Cu and Ag are often considered as the logical first choices for conducting contact materials. However, in practical applications, one has to consider the diffusion of the metals into the semiconductor devices that could deteriorate the device performance. For example, the faster diffusion of Cu than Ag in Si has made Ag the better choice as a contact metal in a Si solar cell despite it being about 100 times more costly than Cu [4,5]. The high diffusivity of Cu in Si is also the reason that Al is used as the interconnect metal of Si microelectronics for over thirty years [2,3], despite Cu being much better than Al on metallic conductivity and resistance to electromigration.

On the other hand, it is surprising to find that Ag diffuses faster than Cu in more ionic compounds although Ag has a larger size than Cu. For example, in CdTe solar cells, although Cu is currently the best *p*-type dopant, it also leads to instability due to the relatively fast diffusion of Cu in CdTe. It is hence desirable if Cu could be replaced by Ag, considering Ag has a larger size than Cu; therefore, one may expect the slower diffusion of Ag than Cu and, thus, a significant enhancement of the stability of the CdTe solar cell. In addition, Ag has a shallower acceptor level than Cu due to less *p*-*d* repulsion, because the Cu *d* orbital is higher than that of Ag in energy and the acceptor level is mostly the anion *p* and Cu(Ag) *d* antibonding state; thus, it can improve *p*-type doping in CdTe. But, experimentally, this is not realized due to faster diffusion of Ag in CdTe [6,7]. The fast diffusion of Ag in ionic semiconductors is also consistent with the fact that Ag is a fast diffuser in dielectric oxides, e.g., SiO_2, preventing it from being used for (cost-insensitive) microelectronics interconnection [2,5,8]. Cu and Ag have also been widely used as interconnects or dopants in many other solar cells, including Si [9–13], Ge [14,15], GaAs [11,16], CdTe [6,7,17–21], CdSe [22–24], CdS [25], $CuInS_2$ (CIS) [26,27], Cu_2ZnSnS_4 (CZTS) [28–30], and $CH_3NH_3PbI_3$ [31,32]. In most of these cases, Cu and Ag are incorporated by the diffusion; thus, their diffusion properties have a strong influence on the device performance.

Despite the importance of Ag and Cu for semiconductor applications, the origin of the distinct diffusion behaviors of Cu and Ag in covalent and ionic semiconductors has not been fully addressed. In this work, we combine the first-principles calculations with group theory analysis to investigate the underlying mechanisms regulating the opposite trend of diffusion behaviors of Cu and Ag in a variety of semiconductors.

The magnitude of the energy barrier along the diffusion path of Ag or Cu in semiconductors is the main indicator of their diffusivity. For instance, the diffusion energy barriers of Cu in Si and Ge, deduced experimentally, are about 0.2–0.4 eV [10–12] and 0.3 eV [11,14], respectively, whereas, the energy barriers of Ag are 1.1 eV in Si [13] and 0.45 eV in Ge [15], consistent with the fact that Cu is a faster diffuser than Ag in both Si and Ge. Whereas, the experimentally measured diffusion energy barrier of Cu in CdTe is about 0.3–0.6 eV [17–19,21], and the measured value of Ag in CdTe is about 0.2 eV [20]. This is also consistent with the fact that Ag diffuses faster than Cu in CdTe, CdSe, and CdS [17–22,25], despite the size of the Ag atom is larger than that of the Cu atom. Therefore, we can understand the diffusion behavior from investigating the energy barriers of diffuser in semiconductors along the diffusion path.

Before presenting the calculated results, we first analyze the symmetry of the system (diffuser plus host semiconductor) for the diffuser moving along the diffusion path. Three typical sites along the diffusion path determine the diffusion barrier in zinc blende (ZB) and diamond semiconductors [7,33]: (i) the tetrahedral site surrounded by cation atoms, labeled as T_c; (ii) the tetrahedral site surrounded by anion atoms, labeled as T_a; and (iii) the bond center in the middle between the T_c and T_a sites, labeled as M. Whereas, for Si and Ge with diamond structure, T_c and T_a sites are equivalent and thus all labeled as T. We classify all these sites into three types of symmetries:

(i) When the diffuser Cu or Ag occupies the tetrahedral site (T or T_a or T_c) in *both* covalent and ionic compounds, the system has a T_d symmetry, which contains irreducible representations a_1, a_2, e, t_1, and t_2. At the center of the Brillouin zone Γ, the Cu (Ag) d orbitals belong to e and t_2 representations, while the host unoccupied s state belongs to the a_1 representation. Since there are no common representations between the Cu (Ag) d orbitals and the host s orbital, the s-d coupling is forbidden, i.e., $V_{s-d} = 0$.

(ii) When the diffuser Cu (Ag) stays at the M site in the full covalent diamond structure, the symmetry lowers to D_{3d}, in which the Cu (Ag) d orbitals transform as the e_g and a_{1g} irreducible representations, while the host unoccupied s orbit transforms as the irreducible representation a_{1u} (Table I). As a result, there is also no s-d coupling ($V_{s-d} = 0$) in this scenario.

(iii) When the diffuser Cu (Ag) stays at the M site in the *polar ZB structure*, the symmetry reduces to C_{3v}, in which the Cu (Ag) d orbitals belong to the e and a_1 representations, and the host s state belongs to the a_1 representation. Consequently, the Cu (Ag) d and host s orbitals could couple to each other ($V_{s-d} \neq 0$) because they have now a common representation (a_1). The coupling strength $V_{s-d} = \langle s|\Delta V|d\rangle^2/(\epsilon_s - \epsilon_d)$, which is proportional to the potential difference ΔV of the anion and cation (i.e., ionicity) and inversely proportional to the square of bond length d_0 and the energy difference $(\epsilon_s - \epsilon_d)$ between the s and d orbital energies.

TABLE I. Irreducible representations of Cu (Ag) d and host s orbitals in the T_d, D_{3d}, and C_{3v} point groups, respectively. Koster notations are shown in the parentheses for the reference. In the T_d and D_{3d} symmetry, there is no s-d coupling between the Cu (Ag) d and host s orbitals. In the C_{3v} symmetry, the s-d coupling is allowed.

Point group	Cu (Ag) d	Host s	s-d coupling ?
T_d	$t_2 \oplus e$ $(\Gamma_3 \oplus \Gamma_5)$	a_1 (Γ_1)	No
D_{3d}	$a_{1g} \oplus e_g$ $(\Gamma_1^+ \oplus \Gamma_3^+)$	a_{1u} (Γ_1^-)	No
C_{3v}	$a_1 \oplus e$ $(\Gamma_1 \oplus \Gamma_3)$	a_1 (Γ_1)	Yes

A summary of symmetry analysis is given in Table I: when the diffuser Cu (Ag) stays at the tetrahedral site there is no s-d coupling in both covalent and ionic semiconductors; when Cu (Ag) stays at the M site, the s-d coupling is also forbidden in the covalent compounds but is allowed in ionic compounds. In addition, the strength of the s-d coupling increases as increasing the compound ionicity since V_{s-d} is proportional to the difference of the anion and cation potentials. Because the allowed s-d coupling lowers considerably the formation energy of the interstitial impurity, the symmetry and ionicity, therefore, play important roles in determining the diffusion behaviors of Cu (Ag) in ionic semiconductors. Note that, although p-d coupling may also be allowed in these systems, it does not have much effect on the diffusion due to the fact that both the p and d orbitals are fully occupied.

Figure 1 compares energy change along the diffusion path of Cu, Cu$^+$, Ag, and Ag$^+$ in the group IV compounds (Si and Ge), group III-V compounds (GaAs and GaSb), and group II-VI compounds (CdS and CdSe). The computational details and calculated detailed numbers are summarized in the Supplemental Material [34]. From Fig. 1, we are able to draw the following conclusions.

In covalent group IV compounds (e.g., Si and Ge), Ag has a larger diffusion energy barrier than Cu, consistent with experimental observations that Cu diffuses faster than Ag in Si and Ge [10,11,11–15]. From Figs. 1(a) and 1(b) we can see that the diffusion energy barriers of both Cu and Ag locate at the M site. Their diffusion paths are exactly along the $\langle 111\rangle$ directions between two nearest neighbor tetrahedral sites, i.e., from the T to M to T sites as shown in Fig. 2(a). Because there is no s-d coupling, the strain energy introduced by the diffuser determines the energy landscape along the diffusion path. Along the diffusion path, the largest strain energy corresponding to the smallest space at the M site makes it the energy barrier site. Likewise, because Ag has a larger atom size than Cu, it has a larger strain energy at the barrier site and then a larger diffusion energy barrier. From Si to Ge, the diffusion energy barrier of Cu (Ag) decreases. This is because Ge has a larger lattice constant and more space at the M site and smaller elastic constants than that of Si, which results in the reduced strain energy.

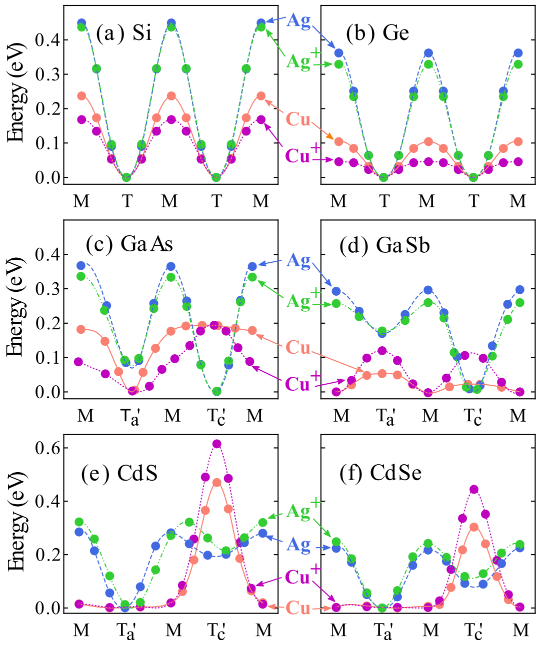

FIG. 1. The diffusion energy curves of Cu, Cu^+, Ag, and Ag^+ in the group IV compounds, Si and Ge; group III-V compounds, GaAs and GaSb; and group II-VI compounds, CdS and CdSe. The T'_a and T'_c sites for Cu and Ag diffusion are slightly different.

In ionic compounds, the diffusion paths of Cu and Ag deviate from the $\langle 111\rangle$ directions and do not cross exactly either the T_c or T_a site. We label the new sites near T_a and T_c as the T'_a and T'_c sites, respectively [Fig. 2(b)]. The deviation of the Cu (Ag) atom away from the tetrahedral sites turns on the s-d coupling, which lowers the energy. Because the deviation from the tetrahedral sites also costs strain energy, the electronic energy gain from the s-d coupling will balance this cost. The deviation increases as the s-d coupling strength increases, so the deviation of Cu is larger than that of Ag in II-VI compounds because Ag has deeper d orbitals in energy and larger atomic size, thus smaller s-d coupling than Cu.

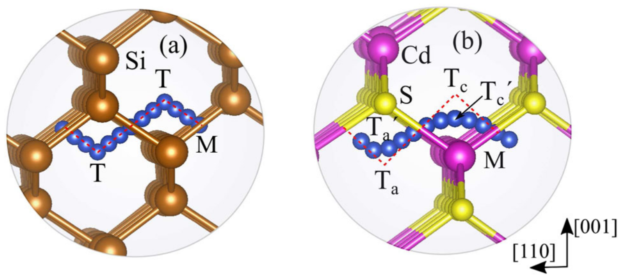

FIG. 2. The diffusion pathways of Cu in (a) Si and (b) CdS semiconductors. The red dashed lines indicate the [111] (or equivalent directions). In Si, the Cu diffusion path is exactly along the [111] (or equivalent directions). However, in CdS, it deviates from the [111] direction (or equivalent directions). We label the new sites near the T_a and T_c as the T'_a and T'_c, respectively.

In group III-V compounds, e.g., GaAs and GaSb, the s-d coupling is now allowed at the M point which reduces the energy. The s-d coupling for diffuser Cu is so strong, due to a shallow d orbital in energy and small atomic size, that its diffusion barrier is no longer at the M site in III-V compounds even though the largest strain energy is at the M point [Figs. 1(c), 1(d)]. But the s-d coupling for diffuser Ag is much weaker due to its lower $4d$ orbitals than Cu $3d$ orbitals in energy (by 2.3 eV) and larger atomic size than that of Cu. Therefore, for diffuser Ag the strain energy is still dominant over the energy gain from the s-d coupling, and the diffusion barrier is still at the M site. The charge transfer from group III cation to group V anion leads to the T'_a site being more charge negative and the T'_c site more positive relative to fully covalent group IV compounds. The Coulomb interaction lowers the T'_a site and raises the T'_c site in energy. This explains why the diffusion barrier for the Cu diffuser is at the T'_c site and the diffusion basin at the T'_a site as shown in Fig. 1(c). Whereas, because the Ag atom is so large that its induced strain energy dominates over the Coulomb energy, the Ag atom prefers the T'_c site (i.e., lower energy) relative to T'_a because the space around T'_c is larger than that around T'_a.

From group III-V to group II-VI compounds, the s-d coupling strength as well as magnitude of charge transferred from cation to anion further increase due to the increased ionicity. For diffuser Cu with high lying d orbitals, the enhanced s-d coupling significantly reduces the energy at the M site, leading it now to be almost the lowest energy site along the diffusion path [Figs. 1(e) and 1(f) for CdS and CdSe, respectively], even though the largest strain energy is still at the M site. However, for diffuser Ag, the enhancement of the s-d coupling is not so significant that the large strain energy is still predominate and, therefore, its diffusion barrier is still at the M site. The raised magnitude of the Coulomb energy from group III-V to group II-VI compounds enlarges the energy difference between the T'_c (barrier) and at the T'_a (basin) sites, leading to a larger energy barrier in the Cu diffusion path in group II-VI compounds; see Fig. 1(e). The Coulomb energy increases so significantly that the energy order is reversed between the T'_c site and T'_a for the diffuser Ag in group II-VI compounds compared with that in group III-V compounds.

Within a group of compounds, the lattice constant is larger for heavier atoms and hence the diffuser induced strain energy is smaller, leading to a smaller energy barrier if it is determined by strain energy as in the case of diffuser Ag in all the investigated compounds and the case of Cu in group IV compounds. For Cu in ionic compounds, the energy barrier is at the T'_c site and determined mainly by the Coulomb energy, and the energy basin is shifted to the vicinity of the M site due to s-d coupling. The energy barrier is smaller in heavier compounds within a group because of the reduced Coulomb energy at the T'_c site (barrier) and s-d coupling at the M site (basin) as increasing the lattice constant (Fig. 1). This also explains why for Ag the energy at the T'_a site becomes higher relative to the T'_c site from GaAs [Fig. 1(c)] to GaSb [Fig. 1(d)], and the energy at the T'_a site becomes smaller relative to the T'_c site from CdS [Fig. 1(e)] to CdSe [Fig. 1(f)]. Therefore, from GaAs to GaSb as well as from CdS to CdSe, the diffusion energy barriers of Cu (Cu^+) and Ag (Ag^+) decrease because when the lattice constant increases the strain energy decreases. Specifically, the energy barriers of Cu and Ag in GaAs are 0.19 and 0.37 eV, decreasing to 0.05 and 0.29 eV, respectively, in GaSb, and 0.47 and 0.28 eV in CdS, decreasing to 0.30 and 0.22 eV, respectively, in CdSe (Table S1).

It is a common perception that metals diffuse in solid compounds as an ion rather than as an atom [5]. As a positively charged ion, metal is smaller than when it is in a charge neutral state; thus, it is expected to be easier to pass through the compounds. From Fig. 1 we can see that the energy barrier of Cu^+ (Ag^+) is indeed slightly smaller than that of Cu (Ag) in covalent group IV compounds. Nevertheless, this common perception is not true for Cu in both III-V and II-VI compounds and Ag in II-VI compounds. For example, the energy barriers in CdSe and CdS increases from 0.30 and 0.47 eV for neutral Cu diffusion to 0.44 and 0.61 eV, respectively, for Cu^+, in contrast to diffusion in pure covalent compounds where the energy barriers of Cu^+ ion decreases compared to neutral Cu atom (Fig. 1 and Table S1). This is because in the ionic state there is a large Coulomb repulsion energy at the T'_c site and large energy gain at the M site due to s-d coupling when the conduction band is empty.

The theory developed above is robust. As a demonstration, we performed calculations for Li and Na diffusion in the semiconductor hosts. Because Li and Na have no d orbitals and no s-d coupling even in ionic compounds, we expect their diffusion trends in ionic compounds GaP and CdS are similar as Ag and Cu in covalent compounds Si and Ge. Indeed, we find that the results are as expected (Fig. S3 in the Supplemental Material [34]). In addition, we have also extended host semiconductors to GaP, SiC, and CdTe for comparison and the obtained results are shown in Fig. S4 of the Supplemental Material [34]. We can see that the results fall into the same trend as discussed above.

In conclusion, we have addressed the important roles of the Coulomb energy, strain energy, and crystal symmetry enforced s-d coupling in determining the diffusion behaviors of Cu and Ag in the common covalent and ionic semiconductors, based on the combination of the first-principles calculations and group theory analysis. In the covalent semiconductors, the s-d coupling between Cu or Ag d and host s states is forbidden and the Coulomb interaction is weak along the diffusion path; thus, the diffuser induced strain energy dominates the diffusion behavior. The diffuser Ag has a larger energy barrier than Cu due to its larger atomic size; therefore, it diffuses slower. However, in the more ionic II-VI compounds, the symmetry-enforced s-d coupling combining with Coulomb interaction makes Ag diffusing faster than Cu. Here, the s-d coupling is allowed and significantly reduces the energy at the M site, which is the diffusion barrier in covalent compounds, and the Coulomb interaction raises the energy at the T'_c site (basin in covalent compounds), making it become the diffusion barrier. Diffuser Cu has a stronger s-d coupling than Ag in ionic compounds, because Cu 3d orbitals are shallower than Ag 4d orbitals in energy; thus, it diffuses slower. The diffusion barrier in ionic compounds being raised by Coulomb interaction implies that metals with high charge states, such as Mg, Al, etc., should diffuse very slow, which is confirmed by much experimental evidence [2]. Our deep understanding of the diffusion behaviors of impurity in semiconductors discussed in this Letter would be helpful in engineering their diffusion properties.

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