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Short Communication

Al-Doped Ge as Anode Material for Rechargeable Ion Batteries: a Density Functional Theory Study

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Using first principles calculation based on density functional theory, effect of Al-doping on the adsorption and diffusion behavior of Li/Na/Mg in Ge was investigated. Results show that undoped Ge is unfavorable for Na and Mg insertion. The adsorption can be enhanced by Al-doping. Al-doping has no effect of the diffusion behavior far away from the doping sites. The result indicates that Al-doping is beneficial for the Ge as anode materials to improve the insertion of rechargeable ion batteries.

Keywords: Density functional theory, rechargeable ion batteries, Al-doping, germanium

1. INTRODUCTION

Lithium ion batteries (LIBs) as rechargeable energy storage devices are most widely used in commercial applications (such as laptop, smartphone, camera, medical apparatus and instruments)[1]. Recently, alternative energy storage devices to LIBs have achieved remarkable attention. Na-ion and Mg-ion batteries as promising rechargeable batteries are of particular interest to afford safety, environmental-friendly, abundant resources, low cost[2-5]. All kinds of investigations on promising anode materials for rechargeable ion batteries have been reported, such as group IVA elements Si, Sn, Ge [6-9]. It was reported that metal atoms diffusion in Ge is easier than in Si, the diffusivity of Li in Ge was estimated to 400 times higher than Si at room temperature [10], therefore, insertion Li, Na and Mg into Ge is more suitable for electrode materials in comparison with Si. Ge as anode materials for LIBs have been widely investigated due to its higher theoretical special capacity of 1623 mAhg^{-1} ($LiGe_{4.4}$), its theoretical special capacity is over four times than that of graphite as anode materials for LIBs (372 mAhg^{-1})[10,11]. Moreover, Ge as anode materials for Na-ion and Mg-ion batteries also has achieved more and more attention[7,12,13]. The theoretical special capacities of Ge as anodes for Na-ion batteries and Mg-ion batteries are 369 $mAhg^{-1}$ (NaGe) and 1476 $mAhg^{-1}$ (MgGe), respectively[7,8]. Although, Ge as anode materials for rechargeable ion batteries is fascinating, its volume changes of 370%, 126% and 178% for LIBs, Na-ion batteries and Mg-ion batteries during charging, respectively, which causes the serious decaying of cycle performance[6-8,14,15]. Numerous investigations have been performed to improve the cycle performance of anode materials for rechargeable ion batteries, such as nanostructures, doping, coating[9,16-18]. Zeilinger et al.[16] found that the Al-doped $Li_{15}Si_4$ as anode materials for Li-ion batteries shows a better cycle stability than $Li_{17}Si_4$ and $Li_{4.11}Si$ crystalline phases[16]. Ge/C core-shell nanostructures synthesized by Qiang et al. as anode materials for LIBs possess a good structural stability and exhibit an attractive electrochemical property.

Computer simulation is an effective method to investigate the electrochemical properties of rechargeable ion batteries and select cathode and anode materials with good electrochemical properties[19,20]. In this work, we investigated Al-doped Ge as anode materials for rechargeable ion batteries using the first principles based on density functional theory (DFT).

2. SIMULATION DETAILS

All calculations were done with 64-atom pure Ge and Al-doped Ge supercell. The defect formation energies were calculated using first principles based on density functional theory (DFT) within the SIESTA code. The PBE exchange-correlation functional and the DZ basis set were used. The cutoff of 150 Ry was used for expansion of the density. Core electrons were modeled with pseudopotentials. Brillouin-zone integrations were done with a 3×3×3 k-point Monkhorst-Pack mesh. Atoms were relaxed until the internal forces are less than 0.02 eV/Å. The diffusion behavior of metal ions in pure and Al-doped Ge was investigated using a constrained optimization.

The formation energies (E_{f_Al}) for Al doping in Ge and the adsorption energies (E_{Ads_M}) of metal (Li, Na, and Mg) atoms inserted into pure and Al-doped Ge are computed using equations (1) and (2), respectively.

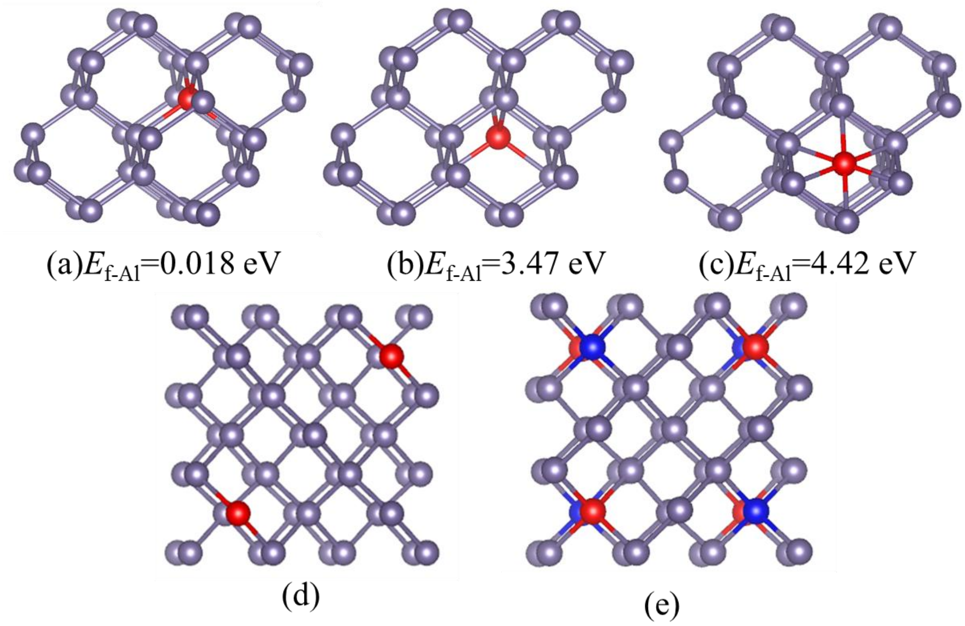
$$E_{f\_\mathrm{Al}} = E_{mGe/nAl} - E_{mGe} + nE_{Ge} - nE_{Al} \tag{1}$$

$$E_{Ads\_\mathrm{M}} = (E_{X/nM} - E_X - n_M E_M)/n_M \tag{2}$$

where m and n are atom numbers of Ge and Al in supercell, respectively. E_{mGe} and $E_{mGe/nAl}$ denotes the total energies of the perfect supercell and n Ge atoms are moved out and n Al atoms added into the supercell. E_{Ge} and E_{Al} are the energy of a Ge atom in bulk Ge and an Al atom in bulk Al. $E_{X/nM}$ is the total energy of the supercell with n metal (Li, Na, Mg) atoms are inserted into Al-doped Ge. X represents Ge_{64}, $Ge_{63}Al_1$, $Ge_{62}Al_2$, $Ge_{60}Al_4$, $Ge_{56}Al_8$, M represents Li/Na/Mg. E_M is the energy of an isolated M atom, n_M is number of M atoms.

3. RESULTS AND DISCUSSION

There are three Al doping sites in pure diamond Ge: the substitution (S), a Ge atom is replaced by an Al atom; the tetrahedral (T), an aluminum is inserted in T position, which is surrounded by four germanium atoms; and hexagonal (H), an aluminum inserted in H position, which is surrounded by a six germanium atoms, atomic configurations of these sites as shown in Fig. 1(a), (b), (c), respectively[21].


(a)$E_{\text{f-Al}}$=0.018 eV (b)$E_{\text{f-Al}}$=3.47 eV (c)$E_{\text{f-Al}}$=4.42 eV

(d) (e)

Figure 1. Three Al doping sites in diamond Ge: (a) substitution (S), (b) tetrahedral (T) and (c) hexagonal (H). Atomistic configurations of (d) 2 Al atoms doped Ge, (e) 4Al (red or blue balls) and 8 Al (red+blue) atoms doped Ge.

The formation energies of Al-doping calculated using equation (1) are also shown in Fig 1. The formation energy of the S site is much lower than that of T and H sites, which has a value of 0.018 eV, indicating the Al prefers to occupy the S site when it was doped into the Ge.

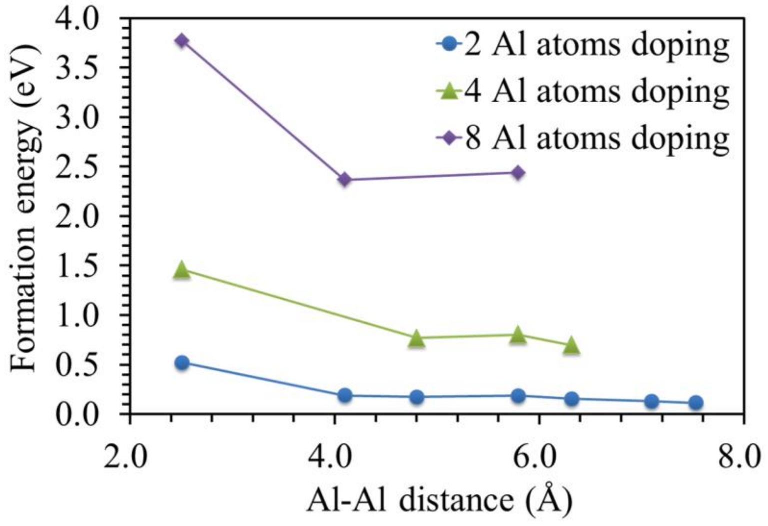


Figure 2. The formation energy Al-doped Ge as a function of Al-Al distance.

The doping of concentration Al in Ge was also investigated. To optimize the Al distribution in Ge, we calculated the formation energies of Al-doped Ge as a function of Al-Al distance. 2, 4 and 8 Al atoms doping (corresponding to doping concentration of ~3.1, ~6.2, and ~12.5 at.%) were considered. The change of formation energies as a function of Al-Al distance is shown in Fig. 2.

The formation energies decrease with increasing the Al-Al distance, indicating the weakening of the Al-Al interaction. The results suggest that the Al atoms do not tend to become clustered and they prefer to be isolated in Ge as increasing the doping concentration. So we maximized the inter-Al distances in Al-doped Ge, the atomic configuration of 2Al atoms doped Ge is shown in Fig. 1(d). And that of 4Al (red or blue balls) and 8 Al (red+blue balls) atoms doped Ge is shown in Fig. 1 (e).

The calculated adsorption energies of the Li/Na/Mg atoms in T and H sites in pure Ge are listed in Table 1.

Table 1. The adsorption energies of Li/Na/Mg occupy T and H positions in undoped Ge (in eV).

Site	Li	Na	Mg
T	-0.78	0.30	1.85
H	-0.28	1.18	2.63

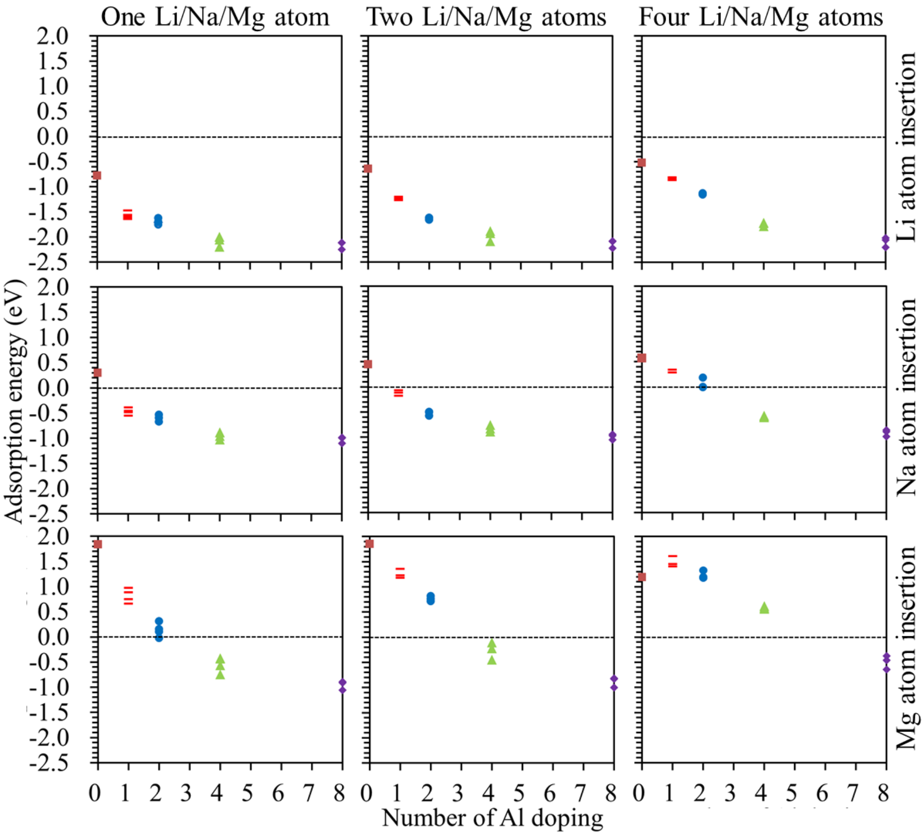


Figure 3. The absorption energies of Li/Na/Mg atoms inserted into the Al-doped Ge with different Al concentrations.

All the atoms are stable at T site than the H site in Ge. The adsorption energies of Li/Na/Mg atoms in Al-doped Ge with different Al concentration are shown in Fig. 3. And the lowest adsorption energies of are listed in Table 2. The adsorption energies are positive for Na and Mg in undoped Ge, which indicates the undoped Ge is unfavorable for Na and Mg insertion.

The adsorption energies for Li/Na/Mg atoms decrease with the increasing of Al concentrations in the Al-doped Ge. The adsorption energies decrease to negative values for a Na/Mg atom insertion as concentration of Al was increase to 2 and 4 Al atoms doped Ge. The result indicates that Al-doping is beneficial for the Ge as anode materials to improve the insertion of rechargeable ion batteries.

Table 2. The lowest adsorption energies for inserted of one Li/Na/Mg in the Al-doped Ge with different Al concentrations (in eV).

Al concentration	Li	Na	Mg
0 Al	-0.78	0.30	1.85
1 Al (~1.6 at. %)	-1.64	-0.55	0.66
2 Al (~3.1 at. %)	-1.75	-0.67	-0.02
4 Al (~6.2 at. %)	-2.05	-1.03	-0.75
8 Al (~12.5 at. %)	-2.25	-1.10	-1.06

The adsorption energies of two and four Li/Na/Mg atoms insertion into the Al-doped Ge with different Al concentrations are also shown in Fig. 3. In view of the interaction between Li/Na/ Mg atoms in the Al-doped Ge, and Li, Na and Mg atoms have the same surrounding environment in the Al-doped Ge, we maximized the distance between Li/Na/Mg atoms. The change of adsorption energies with increasing of Al doping shows the same trend as one Li/Na/ Mg atom inserted into Al-doped Ge, the adsorption energies for Li, Na, Mg decrease with the increasing of Al concentrations and become to a negative value at high doping level. The results indicate that Al-doping can improve the adsorption behavior of Ge as anode for rechargeable ion batteries.

To investigate the effect of Al doped in the Ge on the diffusion kinetics of Li, Na and Mg in the Ge, the diffusion barriers of Li/Na/Mg are calculated. According to previous report, the diffusion path of Li, Na and Mg in Ge occurs between two adjacent T site through the H site[9]. The calculated diffusion barriers of Li, Na and Mg in pure Ge are 0.51, 0.9 and 0.81eV respectively, which agrees with the results of Legrain et al.[21] and they are smaller than that in pure Si for Li, Na and Mg (0.56, 1.09 and 0.97 eV respectively). The diffusion behavior of Li, Na and Mg atoms in one Al (~1.6 at. %) and four Al atoms (~6.2 at. %) doped Ge was investigated.

The diffusion pathways of T1-T2-T3-T4 and T1-T2-T3 are shown in Fig. 4 (d) and (e), respectively, where T1, T2, T3, and T4 represent the T sites with different distances to the Al position, T1 is the nearest one with distance of 2.51 Å, and the distances between T2/T3/T4 and Al site are 2.90/4.80/6.48 Å. The diffusion energies curves as a function of diffusion distances for Li, Na and Mg are plotted in Fig.4 (a), (b), and (c), respectively. It can be seen from the figure that the Li, Na and Mg atoms tend to occupy the T site nearest to the Al site, indicting a strong interaction between them. So the diffusion barriers were increased about 0.15-0.30 eV compared to the undoped Ge, which is consistent with the previous research [22].

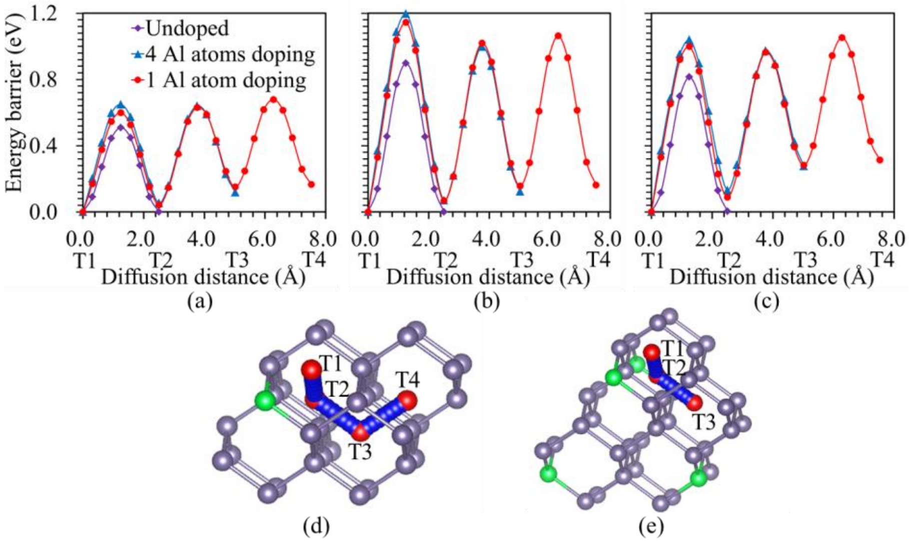


Figure 4. Diffusion energy curves of (a) Li, (b) Na and (c) Mg atoms in (d) one Al (~1.6 at. %) and (e) four Al atoms (~6.2 at. %) doped Ge.

For examples, the diffusion energies are higher through T_3 to T_4 for Li and Mg in one Al-doped (increase by 0.17 and 0.24 eV) and the highest energy barrier of Na is T_1 to T_2 in the four Al dopants (increase by 0.30 eV). The change of diffusion energies is within 0.06 eV between the T_1 to T_2 and T_2 to T_3 in 1.6 and 6.2 at.% Al concentrations. It indicates that Al doped concentrations almost have no effect on the diffusion energy barriers of Li, Na and Mg in Ge far away from the doping position.

To be good anode materials for rechargeable ion batteries, the diffusion barriers of transporting ions in the anode materials should be small, which can realize a fast charging rate. At the same time, the anode materials should have large exothermic reaction energy with transporting ions so that the anode materials have large storage capacity. All the simulation results show that the Al-doping can enhance the adsorption of Li/Na/Mg in Ge, indicating that the preferable exothermic reaction between Al-doped Ge and Li/Na/Mg atoms. At the same time the doping has no effect of the diffusion behavior far away from the doping sites. The results indicate that the Al-doped Ge is better than undoped Ge to be used as anode for rechargeable ion batteries.

4. CONCLUSION

In conclusion, effect of Al-doping on the adsorption and diffusion behavior of Li/Na/Mg atoms in Ge were investigated using the first principles based on the DFT. Undoped Ge is unfavorable for Na and Mg insertion. However, the adsorption was enhanced by increasing of Al-doping concentration. The diffusion barriers were increased about 0.15-0.30 eV for the Li/Na/Mg occupy the position nearest to the Al-doping site. Al-doping has no effect of the diffusion behavior far away from the doping sites.

These mean that the Ge doped with Al atoms can be used to promising anode materials for Li/Na/Mg ion batteries due to the crystal stability was improved.

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