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First-principles calculations of structure and electronic properties of aluminum doped by Ge, Sn and Pb

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ABSTRACT

Based on the first-principles calculation of plane wave ultra-soft pseudo-potential technology, the geometrical properties, impurity formation energy and electronic structures of Al doped by Ge, Sn and Pb were investigated. The structures and energies of three doped systems indicate that the formation of Ge doped Aluminum is minimum and the structure is the most stable. The impurity formation of Ge is −2.4070 eV and the system will release maximum heat, while doping with Pb will absorb heat. What's more, compared with pure aluminum, the charge distributions of central aluminum, which directly surround the impurities, are transformed from square to triangle. And this phenomenon leads that there is no covalent bond between central aluminum along the [110] direction. The charge density differences illustrate the interaction between Al and M (M = Ge, Sn and Pb) is covalent bonding. The amount of accumulated electrons shows that the system of Al−Ge possesses the strongest covalent bonding, followed by Al−Sn and final by Al−Pb. So the stability of Al-M (M = Ge, Sn and Pb) is Al−Ge > Al−Sn > Al−Pb. Additionally, according to Mulliken population analysis, it has been found that due to the incorporation of impurities elements, there are stronger repulsive effects between Al_I and the bonds between Al_I and Al_{II} is the most covalent.

1. Introduction

In recent years, aluminum alloy conductor cables have gradually begun to replace copper core cables in medium and low voltage distribution networks. However, aluminum and copper can't be directly welded, which can easily form the galvanic cell and lead to electrochemical corrosion [1]. Previous studies have found that using aluminum tin composite as intermediate transition bond is a good solution. Zhao R et al. have found that when aluminum and tin were composited, tin atom will enter the octahedral gap of the aluminum atomic cell by using XRD analysis technology [2]. And it will form a unique structure that has both face centered cubic structure and body centered cubic structure. It is a process called doping that a small amount of impurity elements or compounds are added into a kind of material matrix to transform its crystal structure, optical, thermodynamic, electronic, mechanical and magnetic properties. Doping is a quite effective and important method to obtain new materials. Nowadays, the first-principles calculations are widely used to investigate a lot of the influence of elements doping in the materials. Wen et al. have found Nd doping ZnO crystal presents the occupied states near Fermi level, which is conspicuous to strengthen the photoelectric characteristics of materials [3]. What's more, the research of Cd, Mg, Eu and Ce doping ZnO also lays a good theoretical foundation for the application of ZnO in the visible light region [4–8]. In addition, Pluengphon P et al. confirmed that when InP alloyed with Zn, Sn, Si and S, the order of absorption coefficient is Sn > Si > S > Zn and it will reduce at high pressure [9]. Mg substitution not only adjust the structural stability of $LiBH_4$ by decreasing the bonding interaction between Li and [BH], but also transform the properties from nonmetallic character (Mg-free system) to semiconducting even metallic character (Mg-doped systems) by decreasing the band gap [10]. And when Re substitutes Co_7W_6, Re will substitute the Co cites which can obviously improve the bonding strength and the stability of system [11]. What's more, doping can lead to a higher reliability for the chemical compound [12,13]. If the Cr concentration is 6.25 at.% when Cr doped in LiZnP alloy, LiZnP would be magnetic [14]. Besides, it has been found with the increase of Ni doping concentration, the magnetic properties of $BiFeO_3$ can rise obviously and it is in agreement with the experiments [15,16].

As the most abundant metal element in the earth, aluminum and its alloys show the low density, excellent electrical conductivity and good ductility. For pure aluminum, structural relaxations, which is vertical to the applied shear significantly, can decrease the ideal shear strength,

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resulting in strengths of 8–9% of the shear modulus [17]. At the strain of 16%, the theoretical tensile strength of the Al grain boundary is counted to be 9.5 GPa [18]. When the strain is less than 19%, the strain rate of the interface is equal to the interior [19]. Besides, the torsional grain boundary of aluminum has better tensile toughness than the tilted grain boundary [20]. About the formation of the intrinsic point defects, Al_V is the most easy to appear, followed by Al_O and Al_T [21]. What's more, the calculations of helium doped Al indicated that helium will occupy the octahedral interstice in aluminum due to low impurity formation energy [22,23]. In addition, there were many investigations about impurity doped in grain boundary of aluminum [24–29]. Certainly, most works focused on aluminum alloys and its compounds. As for aluminum alloys, it has been confirmed that there is an intense Si—Al bond in Al—Mg_2Si alloys [30]. In Al—Ti alloys, Al—Ti also has a covalent-like bonding [31]. According to calculations of DFT in ternary Al—Cu—Li alloys, a new stable structure $Al_6Cu_4Li_3$ is found [32]. About the research of aluminum compound, Li et al. found the direct band gap of WZ-AlN is 6.12 eV [33,34]. Moreover, the four AlN phases have a smaller plasma frequency than WZ-AlN [35]. The nanoribbon of zigzag AlN's band gap is 2.78 eV [36].

As for the doping of pure aluminum, there are little literature up to now. Only the helium doped Al has been investigated. Liu X K et al. confirmed that there is ionic interaction between helium and aluminum and the helium atom loses a small amount of electrons [22]. The helium bubble diffusion coefficient in aluminum containing a kind of metal impurity is much bigger than pure aluminum [37]. Furthermore, the increase of carbon and iron concentration will restrain the growth and the migration of helium bubbles [38,39]. But lead precipitates are able to accelerate helium bubble growth [40]. Besides, there are some researches about Al_2X which possess outstanding thermodynamic stability and magnetic properties [41]. In the Al_2X (X = Mg, Ca, Sr and Ba), Al_2Ca has the strongest bond and the most stable crystal structure [42]. What's more, the acoustic phonon in Al_2Ca mainly come from Ca [43], which is similar to Al_2X (X = Sc, Y) [44]. The above investigations mainly pay attention to the optical, thermodynamic, magnetic and electronic properties of the aluminum alloys and its compounds.

The research about aluminum doped with metal impurity is little. However, Zhao R et al. found that the unit cell of the aluminum tin layered composite material has both face-centered cubic structure and body-centered cubic structure by XRD diffraction [2]. Due to Ge, Sn and Pb in the same family, we infer Ge and Pb in the same place of the unit cell of aluminum. Consequently, based on the first-principles calculation of plane wave ultra-soft pseudo-potential technology which depend on the density function theory, we investigate the crystal structure, impurity formation energy and electronic properties of Al-M (M = Ge, Sn and Sn). We also compare the results in detail to find the difference among each other.

2. Computational details

In this work, we employed the Cambridge sequential total energy package (CASTEP) [45], which is based on density function theory, to calculate crystal structures, the impurity formation energy and electronic properties of the doped Al systems. The interaction between ion and electrons was described by the plane wave ultra-soft pseudo-potential and the calculations were adjusted by the Perdew Burke Eruzerh form of the generalized gradient approximation [46,47].

Aluminum with space group of fm3m is a face centered cubic structure, as displayed in Fig. 1 (a). It is generally acknowledged that there are two kinds of doped sites in the aluminum cell: tetrahedral site and octahedral site. However, theoretically, the atomic radius of germanium, tin and lead is much bigger than the tetrahedral interstice in aluminum. So if we add them in the tetrahedral, the lattice of aluminum would have a large distortion and a big impurity formation energy. And the structure is unstable. Consequently, we put them in the octahedral interstice, as shown in Fig. 1 (b), to calculate crystal structure, impurity formation energy and electronic properties of Al-M (M = Ge, Sn and Pb).

First of all, we set up a 3 × 3 × 3 supercell of aluminum and then add germanium, tin and lead in the centre of supercell, respectively, as shown in Fig. 1 (c). As one of the most effective methods in figuring out the optimization problems, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used to optimize the crystal structure [48]. The valence electron configurations of the atoms was set as Al $3s^23p^1$, Ge $4s^24p^2$, Sn $5s^25p^2$, Pb $5d^{10}6s^26p^2$ and the remaining electrons were determined as core electrons. The plane wave basis cutoff energy was set as 450 eV. The total energy of the atom converges was determined to be 2.0×10^{-5} eV. The displacement vector of atom, maximum atomic force and maximum stress were conducted within 2×10^{-4} nm, 5×10^{-6} eV/atom and 0.1 GPa, respectively. The *k*-point for Brillouin zone based on Monkhorst-Pack scheme [49] was all set as 4 × 4 × 4.

3. Results and discussion

3.1. Crystal structures

To distinguish the difference in the crystal structures of Al-M (M = Ge, Sn and Pb) system, the doped surpercells were optimized and the optimized results were listed in Table 1. From Table 1, it can be observed that all the crystal structures, no matter doped with any elements, have changed compared with the lattice parameters of pure aluminum, indicating that Al doped by Ge, Sn and Pb shows lattice distortion. The change in volume (3.10%) of Al—Pb is bigger than others. From periodic table of elements, it is well known that the atomic radius of lead is biggest among the doping elements. Moreover, the aluminum doped with germanium system has minimal distortion, which indicates that the Al—Ge system will be more stable than the other two doped systems.

3.2. Impurity formation energy

In the practical application, the impurity formation energy is a very significant concept. The energy required to mix a kind of material into another substance is called as the impurity formation energy, which can describe the degree of difficulty and the influence of growth environment to form impurities. Besides, it also can represent the degree of the stability of products [50,51]. Generally, the following formula can be applied to calculate the formation energy of impurities:

$$E_{for}(M) = E_{tot}(Al{-}M) - E_{tot}(Al) - E_{tot}(M)$$

Here, M is Ge, Sn or Pb. E_{for} is the final impurity formation energy; E_{tot} (Al-M) represents the total energy of aluminum doped with germanium, tin or lead; E_{tot} (Al) is the total energy of undistorted cell of aluminum. E_{tot} (M) represents the energy of isolated Ge, Sn or Pb, respectively. Therefore, it is easy to calculate the final impurity formation energy and investigate the degree of the stability of systems. The calculation results are listed in Table 2.

As is known, a negative E_{for}(M) represents exothermic and the positive one represents endothermic. From the results in Table 2, the positive results of impurity formation energy of Al—Ge and Al—Sn show that the systems would release heat to keep stability when Ge or Sn are doped into pure Al. Whereas the system of Al—Pb would absorb heat. The value of E_{for} (Ge) is the minimum, corresponding to the releasing maximum heat. According to the view of thermodynamic point, the system of Al—Ge is the most stable and Al—Pb which absorbs heat is unstable. The order of stability is Al—Ge > Al—Sn > Al—Pb. Consequently, doping germanium into aluminum is more likely than the other two doped systems due to more stable structure. The conclusions from Table 2 are consistent with the perorations from Table 1. Furthermore, after investigating the binary alloy phase diagrams of Al—Ge, Al—Sn and Al—Pb, it has been found that Al and Ge take possession of maximum solid solubility [52]. Therefore, the conclusion that germanium is