Chemical Trends of the Band Gaps in Semiconducting Silicon Clathrates

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Abstract

We have calculated the band structures of $M_8Si_{38}Ga_8$ (M: Na, K, Rb, and Cs) using the density-functional theory with the generalized gradient corrected local density approximation. They are indirect semiconductors with the calculated gaps from 0.45 to 0.89 eV, the gaps becoming wider with the promotion to the heavier encapsulated guest alkali atoms. These are comparable to the calculated gap of 0.65 eV of crystalline Si with the diamond structure.

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1. Introduction

Since the proposal by Adams et al. [1] of Type-I silicon clathrate as a wider band gap semiconductor than Si with the diamond structure (di-Si), vast of studies have been devoted to synthesize this type of compounds by incorporation of impurity atoms to stabilize this structure. For example, Nolas et al. succeeded in synthesizing germanium type-I clathrates and proposed that they are attractive as thermoelectric materials since the rattling motion of guest atoms will reduce the thermal conductivity [2]. However, semiconducting silicon clathrates have not been intensively studied until M. Imai et al. recently synthesized $K_8Ga_8Si_{38}$ and confirmed that this is a semiconductor[3]. Its estimated band gap is rather narrow. In this article, we concentrate on alloys of silicon clathrates $M_8Si_{38}Ga_8$, which contains substitutional Ga atoms and encapsulated guest alkali atoms (M), and clarify the effect of M on the band gaps using first-principle calculations.

2. Calculation Methods and Structures Considered

Electronic structure calculations have been done for Si$_{46}$ and $M_8Si_{38}Ga_8$ (M: Na, K, Rb, and Cs) using the code of CASTEP, which is based on the density functional theory (DFT) with the pseudopotential generated by the

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scheme of Vanderbilt. We also conducted calculations of di-Si and Si$_{38}$Ga$_8$ for comparison. Local density approximation with generalized gradient correction (GGA) was used for the approximation to the exchange-correlation term of the DFT.

In order to determine the crystallographic parameters (lattice constants and fractional coordinates of atoms), geometrical optimization using total energy minimization algorithm has been performed by the Broyden-Fletcher-Goldfarb-Shannon optimization procedure. As initial parameters for optimization of Si$_{46}$, we used predicted parameters by Adams et al.[1]. As for M$_8$Si$_{38}$Ga$_8$, 50% of Si 6c sites (3 atoms) and 20% of Si 24k sites (5 atoms) were assumed to be substituted by Ga, in accordance with the observed site occupancies of K$_8$Ga$_8$Si$_{38}$ and Rb$_8$Si$_{38}$Ga$_8$ by Kröner et al.[4,5]. It should be noted that introduction of this assumption means that the effect of random distribution of atoms was disregarded.

Convergence of an optimization mode is controlled by the following criteria: The energy change between two steps, the root-mean-square (rms) force on movable atoms, the rms displacement of atoms in Cartesian coordinates, and the rms stress tolerance must be smaller than 1meV, 10$^{-10}$ N, 10$^{-4}$ nm, and 0.1GPa, respectively.

The band structure (BS) calculations have been performed for optimized structures near their Fermi levels ($E_F$) along several high-symmetry lines in the Brillouin zone. The energy zero of the BS diagrams given below is taken at the top of the valence bands.

3. Results and Discussion

At first, results of the optimization for di-Si and Si$_{46}$ are described. Predicted lattice constant of di-Si (a=0.538nm) is ca 1% smaller than the observed one (a = 0.543nm), as is usually experienced in DFT-LDA(or -GGA) calculations. Predicted lattice constant of Si$_{46}$ (a=1.003 nm) is 3% smaller than Adams et al’s prediction (a=1.0355 nm). This is perhaps because their calculation is based on tight-binding method, which has a tendency to underestimate the overlap of bonding electrons.

As for electronic structures of di-Si, the valence band maximum (VBM) is at $\Gamma$ (0 0 0) and the conduction band minimum (CBM) is along the line from $\Gamma$ to X (1/2 0 1/2), which is in accordance with the previous calculation [6].

The calculated indirect gap is 0.65eV.

![Si$_{46}$ Band Structure](image)

Fig.1  Band Structure of Si$_{46}$

The results for Si$_{46}$ are shown in Fig.1. Both of VBM and CBM are along the line from $\Gamma$ (0 0 0) to X (1/2 0 0) and the direct gap is 1.315eV. Thus, ca 0.7eV opening of the Si band gap was reproduced, though absolute gap values are different from those of previous calculations [1, 7]. This fundamental gap becomes narrower to 1.11eV if eight silicon atoms are substituted by Ga and hypothetical Si$_{38}$Ga$_8$ is formed, where Fermi level lies in the VB. Introduction of eight alkali metal atoms compensates holes and make M$_8$Si$_{38}$Ga$_8$ a semiconductor, as shown in the calculated band structure of K$_8$Si$_{38}$Ga$_8$ (Fig.2). This is consistent with the anticipation from the simple rigid band model. However, it should be noted that directness of the
gap will be lost and the predicted gap value is narrower than the fundamental gap value of the hypothetical Si$_{38}$Ga$_8$ above referred.

![Figure 2: Band structure of K$_8$Si$_{38}$Ga$_8$](image)

The calculated band gaps (Eg’s) of M$_8$Si$_{38}$Ga$_8$ are shown in Fig. 3 as a function of the cell volumes. As is shown, Eg’s are increased with the promotion to the heavier elements, but tendency of saturation is seen. To understand this behavior, we considered two factors which would determine gap values of M$_8$Si$_{38}$Ga$_8$.

![Figure 3: Calculated band gaps of M$_8$Si$_{38}$Ga$_8$ (M: Na, K, Rb, and Cs)](image)

One is a cell-volume effect of Si clathrate. It is predicted that di-Si will have negative coefficient of the pressure dependence of the band gap [8]. A similar effect would work in case of Si$_{46}$ clathrates.

Another effect is the charge transfer by electropositive alkali metals to Si. As shown in Fig. 4, valence bands (VB) of K$_8$Si$_{38}$Ga$_8$ are mainly composed of atomic orbitals of Si and Ga while conduction bands (CB) are of those of alkali metals. We have already shown the tendency that the gap values of alkali-metal monosilicides are increased as their ionicities are increased [9]. The similar effect would work in the present case. That is, more electropositive elements will raise the energy level of CB, resulting in wider Eg.
In order to estimate overall effect of encapsulated guest alkali atoms, we also have performed calculations of $E_g$ dependence of Si$_{46}$ on cell-volume. Variation of $E_g$ of M$_8$Si$_{38}$Ga$_8$ could be qualitatively understood by these factors, which will be described elsewhere.

4. Conclusion

Band structures of M$_8$Si$_{38}$Ga$_8$ (M: Na, K, Rb, and Cs) were calculated using the density-functional theory with the generalized gradient corrected local density approximation and it was found that they are indirect semiconductors. The calculated gaps become wider with the promotion to the heavier encapsulated guest alkali atoms from 0.45 to 0.89 eV. They are comparable to 0.65 eV, that of crystalline Si with the diamond structure.

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