



First-principles molecular dynamics study on structural and electronic properties of amorphous germanium carbide



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ABSTRACT

We study the structural and electronic properties of amorphous GeC alloy using the first-principles molecular dynamics simulation. With melting-quenching technique, we obtain the microscopic atomic structure of amorphous GeC alloy from a $2 \times 2 \times 2$ supercell of zinc-blende (ZB) GeC cubic cells. Obvious phase separation is found in the final amorphous structure. The average partial coordination number, average total coordination number, and average bond length are deduced from the RDFs of our structure, and 4.33 and 3.59 coordinations are obtained for Ge and C respectively. Average bond length of 1.46 Å, 2.02 Å, and 2.55 Å are calculated for C–C, Ge–C, and Ge–Ge, respectively. The bond angle distributions are analyzed for different types and great deviation from the ZB structure (109.47°) is observed. The density of states of our modeling shows that the disorder and defects in amorphous GeC have an important effect on the electronic properties. Besides the original sp^3 hybridization, new sp^2 and p -orbital bonding characters of Ge and C atoms are also found.

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1. Introduction

Alloys of group IV elements have attracted great interests for their uses in hetero-structure devices due to their narrow optical band gap. Besides $Si_{1-x}Ge_x$ and $Si_{1-x}C_x$ films [1–4], many research has also been done on $Ge_{1-x}C_x$ films for applications in optoelectronics, and infrared optics [5,6]. A variety of techniques were employed to deposit $Ge_{1-x}C_x$ films, such as chemical vapor deposition [7,8], plasma deposition [9,10], and reactive sputtering [11–14], and amorphous films were primarily obtained in the experiments. There are still great challenges in preparation of crystalline films due to the large difference in atomic radii of C and Ge in spite of some reports on crystalline [15] or nanocrystalline $Ge_{1-x}C_x$ films [16]. Even for the amorphous film, its electrical, optical, and mechanical properties are sensitive to the preparation process [17], which was attributed to the delicate changes in the atomic bonding and configuration in the film under different deposition processing. Chemical bonding and amorphous structure properties of $Ge_{1-x}C_x$ have been widely explored by experiments and sp^3 hybrid bonds between C and Ge were discovered [1,18–21], but the atomic configuration in the film still remains to be studied. Radial distribution function (RDF) is usually used to describe the atomic configuration in disordered system or amorphous materials, and measurements of scattering intensity of X-ray or neutron are common used methods for studying RDF [22,23]. While theoretically, first-principles molecular dynamics (MD) calculation is also a preferred method that has been

widely employed to generate amorphous materials like α -Si [24,25], α -SiGe [26], α -BP [27], α -AlGaN [28] and α -MgZn [29] etc. As stoichiometric crystalline GeC have been widely studied via first-principles calculation concerning its structural, chemical bonding, and physical properties [30,31], there are seldom researches of these properties on amorphous GeC (α -GeC). Since it is difficult to analyze the atomic structure and bonding characters of α -GeC in experiment, we adopt a MD calculation to investigate the microstructure of α -GeC, which will provide some insights to the experimental process.

In the paper, first-principles MD method was used to generate the α -GeC and the RDF, chemical bonding, and structural properties of the α -GeC were analyzed. In addition, the electronic properties of α -GeC were also investigated. We introduced the technical details, calculation method and theory in Section 2, and then presented and discussed the results in Section 3. Finally, a summary was made in Section 4.

2. Methods and computational detail

Melting-quenching (M-Q) method was employed to construct the structure for α -GeC. First, a liquid structure of GeC was established by melting a 64-atom supercell of crystalline GeC with zinc-blende (ZB) structure at 4000 K. Then the liquid structure was quenched to 300 K and thus the resulted structure was used as the amorphous structure of GeC at room temperature. Both the melting and quenching processes were implemented by MD simulation of the movements of the Ge and C atoms with 2000 steps (3fp/step). In order to keep the temperature and volume constant, we used the NVT ensemble during the MD simulation and the Nosé–Hoover thermostat was used in the NVT ensemble to keep the temperature [32].

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First-principles MD method based on density functional theory (DFT) was employed during the simulation process, which can better describe the interactions between atoms and has high accuracy in spite of a little time-consuming compared with the widely used methods of tight-binding theory and empirical functions that have high computational efficiency yet less accuracy [33]. DFT calculations were performed on the CASTEP platform. The atomic trajectories can be followed during the simulation process and the changes in chemical bonds with each step can be seen, which helps us understand the results more easily. Plane-wave ultrasoft pseudopotential (USP) was used for the interaction between valence electrons and atomic core and generalized gradient approximation (GGA) due to Perdew–Burke–Ernzerhof (PBE) [34] was used for the exchange–correlation effects. The USP introduced by Vanderbilt allows the calculation to be performed with the lowest possible cutoff energy for the plane-wave basis set. A cutoff energy of 380 eV was used for the plane wave expansion and the Brillouin-zone integration was performed over the $3 \times 3 \times 3$ grid size using the Monkhorst–Pack scheme for optimization. Only Γ point was used during the MD simulation. In the analysis of the electronic properties, the partial density of state (PDOS), which is based on Mulliken population analysis and allows the contribution from each energy band to a given atomic orbital to be calculated, is displayed for C-2s, C-2p, Ge-4s, and Ge-4p, respectively.

3. Results and discussion

3.1. The structural properties

Fig. 1 presents the structures for the original ZB-GeC (a) and the *a*-GeC (b) obtained with M-Q method. It can be clearly seen that the characteristic long-range order of ZB-GeC disappeared in the structure of *a*-GeC. In the meantime, many original Ge–C bonds broke and new Ge–Ge and C–C bonds were formed, which resulted in the change of the coordination of Ge and C atoms in *a*-GeC and caused aggregation of C and Ge atoms. Phase separation will finally occur as a result of the aggregation. Similar phenomena were also observed for other IV–IV compound semiconductors in which their instability towards decaying into their elemental constituents or into random alloys was observed [35]. As for GeC, the structure instability is mainly attributed to the large lattice mismatch and the resulting cost in elastic energy as carbon incorporated into germanium, which has been proved both by experiments and by theoretical calculations [15,35–38].

The atomic structure of *a*-GeC was quantified via its RDF $g_{\alpha\beta}(r)$ of atomic species α and β , which in this case represents Ge and C respectively. It is a measure of the probability of finding atom β at a distance of r away from the given reference atom α and is calculated according to Eq. (1) [26], where the number density of species β is described as $\rho_{\beta} = N_{\beta}/V$, N_{β} is the total number of atom β , and V is the cell volume.

Term $\langle n_{\alpha\beta}(r, r + \Delta r) \rangle$ in Eq. (1) means the average number of atom β confined in the shell between radii r and $r + \Delta r$ centered at atom α .

$$g_{\alpha\beta}(r) = \frac{\langle n_{\alpha\beta}(r, r + \Delta r) \rangle}{4\pi r^2 \rho_{\beta} \Delta r} \quad (1)$$

The average partial nearest coordination number, the average total nearest coordination number and the average bond length then can be deduced.

Fig. 2a and b shows the RDFs of the *a*-GeC and ZB-GeC, respectively. The three peaks at ~ 1.5 Å, ~ 2.0 Å, and ~ 2.5 Å in Fig. 2a represent the nearest neighbors of C and Ge corresponding to C–C, Ge–C and Ge–Ge bonds of the amorphous structure, respectively. While the first two peaks in Fig. 2b, representing the nearest neighbors of C and Ge in ZB structure, are located at ~ 2.0 Å which is also the length of Ge–C bond, and at ~ 3.25 Å which represents both the nearest distance between Ge/Ge pair and the distance between C/C pair. The third peak in ZB-GeC is the second neighbors of Ge/C. So the main peak of Ge–C bond doesn't change much in the two structures, except that the one for *a*-GeC has a larger full width at half maximum (FWHM) which is related to the variation of Ge–C bond length and will be discussed in Fig. 3. The distances of the nearest C/C pair and Ge/Ge pair changed from ~ 3.25 Å in ZB-GeC to ~ 1.5 Å and ~ 2.5 Å for *a*-GeC due to the collapse of ordered ZB structure and formation of C–C and Ge–Ge bonds in *a*-GeC.

By analyzing the RDFs, the average bond lengths C–C, Ge–C, and Ge–Ge in *a*-GeC can be calculated using Eq. (2) [26], where R is the position of the first minimum after the first main RDF peak. The average bond lengths of C–C, Ge–C, and Ge–Ge for *a*-GeC are calculated to be 1.46 Å, 2.02 Å, and 2.55 Å, respectively.

$$\bar{r}_{\alpha\beta} = \frac{4\pi\rho_{\beta}}{n_{\alpha\beta}} \int_0^R g_{\alpha\beta}(r) r^2 dr \quad (2)$$

Fig. 3 shows the distribution of bond length for the *a*-GeC. The FWHM of Ge–Ge peak (0.28 Å) is larger than that of Ge–C peak (0.22 Å) which has a larger FWHM than C–C peak (0.17 Å), which means that the Ge–Ge bond is more changeable than C–C bond and thus contributed much to the formation of disordered structure in *a*-GeC.

By integrating the corresponding RDF curve up to the cutoff radius R , the average partial nearest coordination number $n_{\alpha\beta}(R)$ can be obtained from Eq. (3) [26].

$$n_{\alpha\beta}(R) = 4\pi\rho_{\beta} \int_0^R g_{\alpha\beta}(r) r^2 dr \quad (3)$$

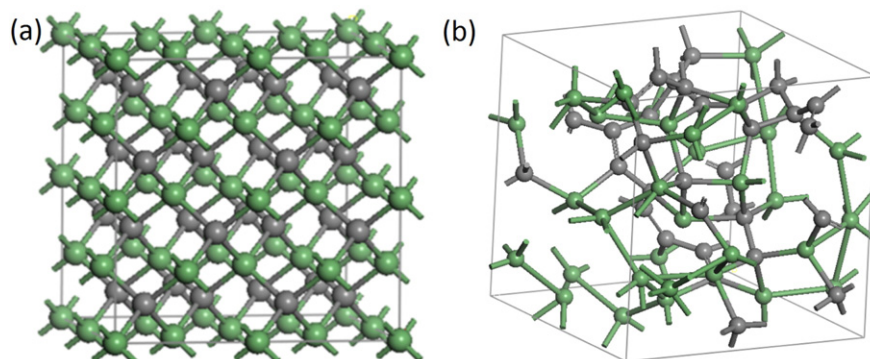


Fig. 1. Atomic model for the stoichiometric (a) ZB-GeC and (b) *a*-GeC obtained using MD method (with Ge in green and C in grey).

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