Amorphous alloys of $C_{0.5}Si_{0.5}$, $Si_{0.5}Ge_{0.5}$ and $In_{0.5}Se_{0.5}$: atomic topology

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Available online 2 April 2004

Abstract

Using a recently developed ab initio molecular dynamics method based on the Harris functional to amorphize structures of semiconducting elements starting from 64 atom, periodic, diamond-like supercells, we have generated the amorphous structures corresponding to the $C_{0.5}Si_{0.5}$, $Si_{0.5}Ge_{0.5}$ and $In_{0.5}Se_{0.5}$ alloys. We report the atomic topology of the three samples and show that for the $C_{0.5}Si_{0.5}$ a few homonuclear bonds are observed; for $Si_{0.5}Ge_{0.5}$ a large number of homonuclear bonds appear, whereas for $In_{0.5}Se_{0.5}$ each Se is bonded to three In and each In is tetrahedrally bonded to at least three Se.
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PACS: 61.43.Dq; 61.43.Bn

1. Introduction

Car–Parrinello molecular dynamics (CPMD) and quenching from the melt of periodically-continued supercells with no more than 125 atoms has been the standard procedure for producing amorphous structures of semiconductors from first principles. These have several generic shortcomings: radial distribution functions (RDFs) that reproduce, at best, the first two peaks of the experimental results; structures with an excess of defects, both dangling and floating bonds; and samples without electronic and/or optical gaps when they are expected, just to mention the most relevant. However, the pioneering ab initio work of Car and Parrinello has been a landmark and undoubtedly has permeated all efforts during the past 15 years.

Their methods were first applied to amorphous silicon [1], a semiconductor that has been thoroughly studied for the last three decades, both experimentally and theoretically [2]. They were used to generate amorphous carbon [3]. Carbon is versatile due to the multiplicity of its bonding which ranges from sp^1 to sp^3 and its structure depends on the percentage of sp^1, sp^2 and sp^3 bonds. Consequently, since the density of amorphous carbon depends on the percentage of the different bonds present [4] the atomic random network of amorphous carbon depends on the density. Work on Ge based on CPMD has been less successful and results obtained do not agree as well with experiment [5]. Finally, no simulational studies of the CPMD type applied to indium or selenium have been reported to date.

Of the alloys considered in this work, carbon-silicon is the most extensively studied and a revision of the situation up to 1992 is given in Ref. [6]. The CPMD approach was applied to CSi alloys [7] and no sign of chemical ordering was found, whereas the application of *classical* methods (Tersoff potentials) [8] did reveal signs of chemical ordering. Studies of the energy gaps, using amorphous clusters have been reported [9]. Various structural studies (see Ref. [10] and references contained therein) propose different kinds of chemical order, ranging from random order to nearly complete chemical ordering. More recent experiments seem to indicate that the structure of these alloys is not chemically ordered [11] but that it contains both heteronuclear and homonuclear bonds [12].

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Since both Si and Ge do not present hybridization the situation is less versatile in their alloys than that of CSi alloys; however, several *classical* results [14] seem to indicate that homonuclear bonds may appear in these materials. The electronic structure of these alloys has been studied using a cluster approach and the behavior of the electronic gap has been analyzed [13]. For a review of amorphous silicon and their alloys, with either C or Ge, see Ref. [14].

Indium and selenium have not been studied simulationally and neither have their alloys. However, recent experimental results [15] indicate that for the 50–50 composition each Se atom is bonded to three In and each In atom has one In and three Se as the nearest neighbors.

These results motivated us to do a comparative study of these 50–50 alloys using an approach described elsewhere [16] to test its applicability for describing covalent alloys. It has already been established that for a-SiN$_x$ the method not only describes and agrees with the experimental results but can also predict new features of the amorphous atomic networks [17].

2. Method

We use FASTSTRUCTURE [18], a DFT code based on the Harris functional [19], and optimization techniques based on a fast force generator to allow simulated annealing/molecular dynamics studies with quantum force calculations [20]. We use the LDA parameterization due to Vosko et al. [21]. For the amorphization process a minimal basis set of atomic orbitals was chosen for all the samples, with a cutoff radius of 5 Å. The time step used for CSi was 6 fs, for SiGe it was 14 fs and for InSe it was 4 fs. The forces are calculated using rigorous formal derivatives of the expression for the energy in the Harris functional as discussed by Lin and Harris [22].

To generate the corresponding random networks we amorphized a crystalline diamond structure with 64

atoms in the cell, 32 of one kind and 32 of the other kind randomly distributed, with the following densities: $\rho = 1.83$ g/cm^3 for CSi, $\rho = 3.56$ g/cm^3 for SiGe and $\rho = 5.62$ g/cm^3 for InSe, data obtained from interpolating experimental results (compare to the crystalline densities: 3.17, 3.83 and 5.55 g/cm^3, respectively, [23]). The processes consist in slowly heating the crystalline samples from 300 to 2840 K for CSi, to 1440 K for SiGe and to 920 K for InSe, just below their melting temperatures, in 100 steps and immediately cooling them down to 0 K in 112 steps for CSi, 126 steps for SiGe and 147 for InSe. The atoms were allowed to move within each cell of volume (10.53 Å)^3 for CSi, (11.45 Å)^3 for SiGe and (12.23 Å)^3 for InSe, respectively, with periodic boundary conditions. We next subjected them to annealing cycles at 300 K, with intermediate quenching processes. At the end a geometry optimization was carried out to find the local energy minimum of the amorphous structures.

3. Results and discussion

In the literature the samples studied correspond to various densities. For example, in Ref. [7] the macroscopic density has been fixed at the experimental density of c-SiC. They claim that the pressure of their samples, computed a posteriori, indicates that the equilibrium volume of a-SiC is indeed very close to that of the crystal; about 2% smaller. Ref. [8] considers CSi stoichiometric samples with a density of 83% of the density of c-SiC. We believe that the density is an all important parameter since the type and number of hybridized bonds depends on this parameter and therefore the short range order will vary with the type of bonds.

In Fig. 1 we present the atomic structure of the amorphized Si$_{0.5}$C$_{0.5}$ sample. The small spheres represent carbon atoms and the larger spheres depict silicon atoms. Fig. 1(a) shows the global arrangement of the amorphous alloy, and in order to better see the tendencies of each element we present the structure of only
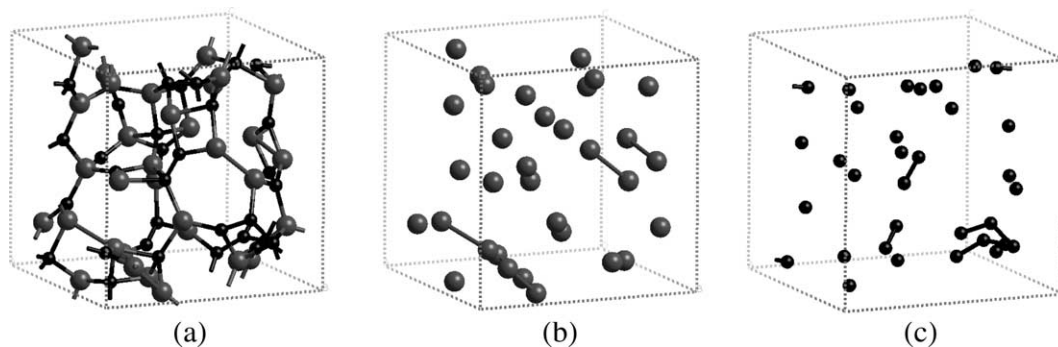

Fig. 1. Atomic topology for the C$_{0.5}$Si$_{0.5}$ sample. In (a) the two classes of atoms can be seen (Si is represented by the larger spheres). In (b) and (c) we have isolated the Si and C atomic arrangements, respectively.
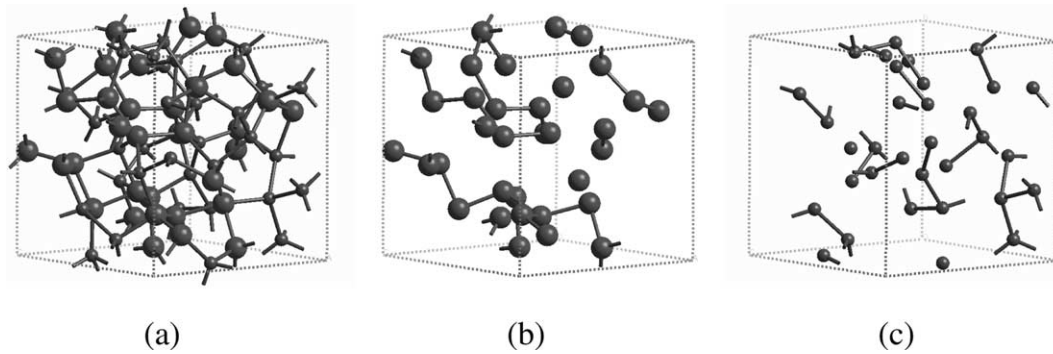
Fig. 2. Atomic topology for the $Si_{0.5}Ge_{0.5}$ sample. In (a) the two classes of atoms can be seen (in this case Ge is represented by the larger spheres). In (b) and (c) we have isolated the Ge and Si atomic arrangements, respectively.

silicon atoms in Fig. 1(b) and only carbon atoms in Fig. 1(c). It is clear that both Si and C have a slight tendency to surround themselves with atoms of their own kind indicating an incipient onset of homonuclear bonding. In Fig. 1(c) an almost complete hexagonal ring of carbon atoms can be observed.

Fig. 2 is the corresponding representation for the amorphized $Si_{0.5}Ge_{0.5}$ sample. One can observe that germanium atoms bond to germaniums and that silicon atoms bond to silicons. Both Ge and Si form chains with the same type of atoms indicating that homonuclear bonding is an important occurrence in these materials. It is clear that the behavior of $Si_{0.5}C_{0.5}$ and $Si_{0.5}Ge_{0.5}$ is different: heteronuclear bonding predominates in the $Si_{0.5}C_{0.5}$ amorphous alloy, whereas homonuclear bonding is very important in a-$Si_{0.5}Ge_{0.5}$.

The corresponding atomic structure for the indium–selenium alloys is shown in Fig. 3 where it can be observed that Se (smaller spheres), threefold coordinated, is not bonded at all to other Se atoms (Fig. 3(c)) whereas fourfold coordinated In is preferentially bonded to Se atoms (Fig. 3(b)).

It is clear that in order to determine the bonding state of the atoms in the samples studied some criterion has to be used. The bond lengths used are the values for the minima between the corresponding amorphous peaks in the partial radial distribution functions (not reported here) but the numerical values are: C–C, 1.77 Å; Si–Si, 2.69 Å; Ge–Ge, 2.81 Å; Se–Se, 2.69 Å; In–In, 3.24 Å; Si–C, 2.23 Å; Si–Ge, 2.75 Å and In–Se, 2.97 Å [24].

4. Conclusions

Our ab initio results indicate that for the bond lengths and densities considered, carbon in the SiC alloy (Fig. 1) has a tendency to form rings while silicon forms chains. Carbon, being a more versatile element bond-wise, may manifest itself in structures that have planar-like rings or chain-like arrangements, depending on the density of the sample and its concentration, so more extensive and inclusive studies are required to better understand their topological characteristics. The 50% alloy of silicon and germanium has a more noticeable homonuclear atomic structure since there are chain-like arrangements both for Ge and for Si (Fig. 2). Due to the similarity of the electronic structures of both elements we would like to advance the hypothesis that this occurrence is due to the fact that Si–Si, Ge–Ge and Si–Ge bonds are practically equally probable and therefore practically indistinguishable, so in a 50% alloy the probability of finding Si–Si nearest neighbors is the same as finding Si–Ge or
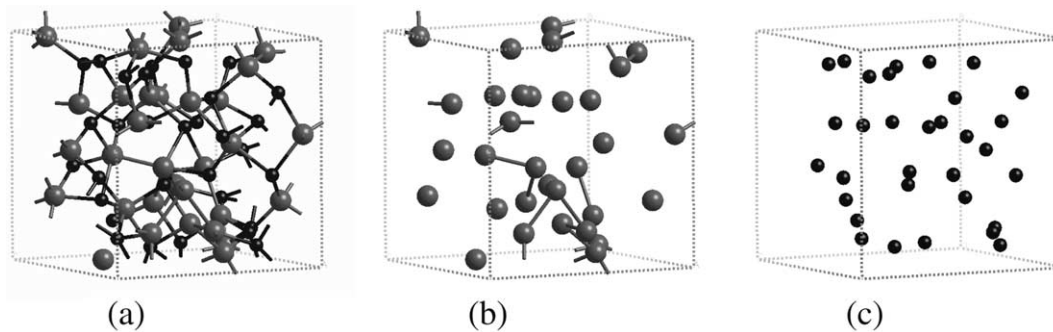

Fig. 3. Atomic topology for the $In_{0.5}Se_{0.5}$ sample. In (a) the two classes of atoms can be seen (In is represented by the larger spheres). In (b) and (c) we have isolated the In and Se atomic arrangements, respectively.

Ge–Ge. Studies are under way to analyze the solidity of our hypothesis.

Very recent experimental results [15] for indium–selenium amorphous alloys seem to indicate that in these materials, homonuclear bonding is not the most common bond and that, at least for the 50% alloy, each selenium atom is bonded to three indium atoms and each indium atom has one In and three Se atoms as its nearest neighbors. Our simulational results indicate, in fact, that Se is threefold coordinated with *all* In atoms, and fourfold coordinated In is bonded to at least three selenium atoms and one indium, and some times to four seleniums (Fig. 3) in agreement with Ref. [15].

Acknowledgements

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