Structural and electronic properties of amorphous InSb from first principles study

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The model for amorphous semiconductor InSb (a-InSb) was constructed through the first principles calculations, based on the idea of “continuous random networks” (CRN). The results of structural parameters for a-InSb are in agreement with the available data both theoretically and experimentally. The structure of a-InSb is almost tetrahedrally bonded with a perfect average coordination number of four. Due to the influence of the disorders, the density of states for a-InSb has the smearing structure in contrast to crystalline InSb (c-InSb). As a consequence of the induction of disorders, modification phenomena occur at the band edge of a-InSb in contrast to that of c-InSb.

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1. Introduction

There has been a considerable interest in amorphous semiconductors because they have a number of interesting physical properties as well as numerous potential applications in the microelectronic and optoelectronic devices. Amorphous semiconductors have extensive advantages for the growth of amorphous films in the application of photoelectric devices and clean energy devices. Some previous studies have demonstrated that they can be successfully grown on arbitrary substrate such as glass and chinaware, and are not refined to the shape of the substrate. Also in the process of fabrication of devices, the lattice match is not necessary. Though the microscopic structure of amorphous semiconductors has been a subject of intense research for more than 30 years, the structure of amorphous semiconductors is still a great challenge in the field of computational solid state physics. In general, the two main problems need be clarified are, (1) a full characterization of the topological and chemical disorder of the amorphous network and (2) the identification of structural defects (like dangling or floating bonds). Structural studies have done to describe the microscopic geometry of amorphous III–V compound semiconductors, which are tetrahedrally bonded with each atom having four unlike atoms as neighbors, as that in the corresponding crystal. [2–5] To know the physical properties for amorphous semiconductors, one must introduce the essential structural models to obtain the desired structural information iteratively between models and experimental data.

In the present work, based on the idea of “continuous random networks” (CRN), we construct amorphous semiconductors InSb through the first principles calculations. The model containing 256 atoms was optimized, and relaxed with ultra soft-type pseudopotentials [6], based on the density functional theory. We also calculated total density (TDOS) and partial density of states (PDOS) for c-InSb and amorphous a-InSb, respectively. The influence of disorders on density of states (DOS) is discussed in detail.

2. Computational details

The continuous random networks (CRN), which were first modeled by Polk [7] describes rather well the experimental radial distribution functions of a-Ge and a-Si [3]. Shevchik [8] has pointed out that amorphous III–V compound semiconductors are probably similar to amorphous Ge in structure, which are described by CRN model with fourfold coordination for nearly every atom. For our work, the scheme to construct initial amorphous configurations of amorphous III–V compound...
3. Results and discussions

Fig. 1 shows ball-and-stick represents a-InSb sample. Based on the visual inspection, it can be clearly seen that the structure is in disorder both topologically and chemically. The structure has characteristics of excellent models of the amorphous material qualitatively. We can proceed with a more qualitatively analysis of the model. The results of total and partial pair correlation functions of a-InSb are shown in Fig. 2. The total pair correlation functions of a-InSb exhibits a strong first- and the second-neighbor peaks with a little amplitude. Moreover, the pair correlation function rapidly converges to the uniform density beyond the second-neighbor distribution. However, the like-atom partial pair correlation functions, In–In and Sb–Sb, essentially have a little amplitude at the first-neighbor distance, but exhibit strong second-neighbor peak, which provides detailed information about the short-range arrangements of atoms in the amorphous state. It can be validated from Fig. 2 and Ref.[14] that the hetero-bonds should prevail in a-InSb sample and the homo-bonds manifest themselves as small peaks at the first-neighbor peak distance in the like-atom pair correlation functions. The partial pair correlation function can provide direct evidence of the existence of wrong bonds, i.e., bonds between like atoms. We find that the first peak at 2.89 ± 0.05 Å and the second peak at 4.60 ± 0.05 Å for total pair correlation function, which are in agreement with the corresponding results of theory calculations by molecular dynamics technique [15] and experimental results by X-ray diffraction [16]. Moreover, compared with the work by Rino et al. [15], our results may be much closer to the experimental results [16].

The structure of our a-InSb sample is characterized by a predominant tetrahedral short-range order, as indicated by the value 3.97 of the average coordination number, which we define by considering all neighbors within a distance less than the first minimum \( r_m (=3.20 \, \text{Å}) \) of the total pair correlation function. The result of the average coordination number is also close to the experimental value 3.8 ± 0.3 and the theoretical value 4.23 [15,16]. It is well known that the shapes of the pair correlation functions for c-InSb are many lines at some given distances such as 2.81 Å for the nearest-neighbor In–Sb, 4.58 Å for the nearest-neighbor In–In or Sb–Sb and 5.37 Å for second-nearest-neighbor In–Sb, respectively. To make comparisons, it can be found that the distances of the first- and the second-nearest peaks are about 2.89 and 4.60 Å, respectively, which are close to that of the crystal. In Fig. 2, the first peak of InSb pair distribution function reflects the average distance of first-nearest atoms in the a-InSb structure. However, that of In–In and Sb–Sb pairs, distribution functions reflects the average distance of first-nearest wrong bonds. Wrong bonds are defects in amorphous materials and they are undesired but almost inevitable in the binary even polybasic amorphous compound. The distance of the first peak decreases for Sb–Sb, In–Sb and In–In in turn, which is similar to the relation regarding bond length of the respective crystal and pure metal. The similarity of short-range arrangements of atoms in the solids also should be shown in their physical properties.

The knowledge of fraction of wrong bonds can make us to study the information on the chemical order. And the relevant information also can be obtained by computer calculation and we can see that the average fraction of wrong bonds is 12.99%, [14] which corresponds quite closely to the “theoretical limit” of 12% for Polk-type CRN. [2,17] In a word, our model is almost tetrahedrally bonded with an almost perfect coordination of four and appropriate fraction of wrong bonds. In addition, there are structural defects that threefold-coordinated number constitutes a fraction of about 2.73% in the model. The three-coordinated atoms with dangling bonds and/or overcoordinated atoms with floating are considered as the primitive intrinsic defects in the
amorphous silicon structure. In our a-InSb sample, it also has three-coordinated atoms with a little fraction and not five-coordinated atoms.

Total and partial electronic densities of states for a-InSb and c-InSb samples are displayed in Fig. 3, respectively. The total density of states (TDOS) of InSb is similar to that of other amorphous III–V compound semiconductors and the valence bands can be roughly ascribed as three parts. They are as follows: the lowest-lying bands is composed of Sb-s like states between $-11.5$ and $-8.0$ eV, the next bands between $-6.5$ and $-3.0$ eV arises from ln s and some As p states and the top large broad peaks from $-3.0$ to 0 eV are composed of Sb p and In.

Fig. 3. Total and partial density of states for c-InSb and a-InSb, respectively. Fermi level is set to 0 eV.

Fig. 4. The density of states at band edge for c-InSb and a-InSb, respectively. Fermi level is set to 0 eV.
p states. Upon comparing TDOS and partial density of states (PDOS) of c-InSb and a-InSb, one can conclude that the main features of the spectra obviously have some dissimilarity. It is clear that the features are considerably broader in the amorphous case, which is the direct consequence of the influence of disorder both topological and chemically. Moreover, the “fine” structures of density of states in the crystalline partly disappear and become more complex in the amorphous case. In particular, there obviously occur a few peaks at the high-energy side of the low-lying band between $-9.0$ and $-8.0$ eV and at the energy range from $-6.5$ to $5.8$ eV, which cannot be found in the crystalline case. From PDOS we can find that these “new” peaks arise mainly from s states, especially the peaks between $-9.0$ and $-8.0$ eV from Sb s states and the peaks between $-6.5$ and $5.8$ eV from In s states. This result might be associated with wrong bonds.\[18–20\]

As mentioned above, the fraction of wrong bonds has a sizeable value 12.99% in the a-InSb sample. Therefore, we are inclined to believe that such “new” peaks, which occur in the TDOS of a-InSb are due to the presence of wrong bonds.

In addition to wrong bonds, there is another defect, dangling bonds with three-coordinated atoms in a-InSb sample, which also reflect the results of DOS for the amorphous case. So, we are also interested in the discrepancies of the band edge of DOS of a-InSb in contrast to that of c-InSb. In Fig. 4, one can see that the shift of the extreme of band edge makes the band gap smaller in a-InSb in contrast to that of c-InSb. From the results of PDOS, it is obvious that the band edge, not only the top of valence but also the bottom of conduction band, has the smearing structure due to disorders. Moreover, the upper valance band of s-like (In atoms and Sb atoms) PDOS shifts to the higher-side. Also the inferior conduction band of p-like PDOS shifts to the lower-energy side with a larger amplitude. We conjecture that the formation of dangling bonds may be correlative to such modification phenomenon at the band edge.

4. Conclusions

In summary, the model for a-InSb is constructed through the first principles calculations. The results of structural parameters are in agreement with the available data both theoretically and experimentally. The model obtained from our work is almost tetrahedrally bonded with a perfect average coordination number of four. Due to the influence of the disorders, the density of states for a-InSb is more complex in contrast to c-InSb. It is obvious that the band edge has the smearing structure due to disorders. As a consequence of the induction of the disorders, modification phenomena occur at the band edge of a-InSb in contrast to that of c-InSb.

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References