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Small-angle X-ray scattering of two-phase atomistic models for amorphous silicon–germanium alloys

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ABSTRACT

The present work deals with a detailed analysis of the small-angle X-ray scattering in amorphous silicon–germanium alloy using the simulation technique. We envisage the two-phase alloy model consisting in a mixture of Ge-rich and Ge-poor domains at the nanoscale. By substituting Ge atoms for Si atoms in a continuous random network, compositionally nanoheterogeneous alloys are generated with various composition-contrasts between the two phases. After relaxing the as-generated structure, we compute its radial distribution function, and then we deduce by the Fourier transform technique its X-ray scattering pattern. Using a smoothing procedure, the computed small-angle X-ray scattering patterns are corrected for the termination errors due to the finite size of the model, allowing so, for the first time at our best knowledge, a rigorous quantitative analysis of this scattering. Our simulation shows that the relative alloy composition of the two phases is a determinant parameter for the occurrence of small-angle X-ray scattering. A composition-contrast threshold, independent of the overall composition of the alloy as well as the relative volume fraction of the phases, has been demonstrated. Thus, two-phase silicon–germanium alloy with composition-contrast smaller than 0.3 behaves as compositionally homogeneous alloy in the context of small-angle X-ray scattering experiment. Our simulation also shows that the experimentally derived characteristics of the compositional heterogeneity in the alloy, such as radius of gyration and correlation volume, are composition-contrast dependent; they are generally smaller or equal to the actual values.

1. Introduction

Amorphous silicon–germanium (a-$Si_{1-x}Ge_x$) alloy is one of the most promising narrow-gap semiconductors for use in multi-junction amorphous solar cells. Indeed, the optical band gap of a-$Si_{1-x}Ge_x$ alloy can be easily tuned (from 1.7 to 1.0 eV) by increasing the germanium rate, allowing so an efficient absorption of radiations over a broad band of the sunlight spectrum, resulting therefore in a more efficient and more stable solar cells [1–6]. As with all materials, the microstructure controls the electronic as well as the optoelectronic properties, so understanding and controlling the structure of a-$Si_{1-x}Ge_x$ alloy are crucial to its technological applications.

Many experimental studies have been reported in the literature in order to explore the structure of these alloys locally and at the nanoscale. Extended X-ray absorption Fine-structure (EXAFS) has been used to investigate the local structure of a-$Si_{1-x}Ge_x$ alloys [7–11]. Some studies showed that the local environment of Ge atoms is completely random whereas others suggested an inhomogeneous

distribution of Ge atoms in Ge-rich films. To examine the structure of a-$Si_{1-x}Ge_x$ alloys at the nanoscale, the small-angle X-ray scattering (SAXS) technique was used. Several SAXS data carried out for hydrogenated a-$Si_{1-x}Ge_x$ films [12–18] argue in favor of a heterogeneous microstructure at the nanoscale. This heterogeneity was interpreted as due partly to the presence of voids and/or hydrogen-rich clusters in hydrogenated amorphous films. More detailed nanoscale structural analysis has been reported by Goerigk and Williamson [19–21] for a series of hydrogenated a-$Si_{1-x}Ge_x$ films using the anomalous small-angle X-ray scattering (ASAXS) technique. The contribution of structural heterogeneities such as voids has been successfully separated from the total diffracted intensity. The remaining ASAXS has been successfully interpreted in the context of a two-phase model which consists on a mixture of Ge-rich and Ge-poor domains with correlation lengths in the nanometer range.

On the other hand, some theoretical studies have been reported in the literature to aid at the interpretation of the EXAFS data for a-$Si_{1-x}Ge_x$ alloys [22–26]. These efforts have been focused on the analysis of the microstructure of these alloys at the local scale. Theoretical analysis of the SAXS data for these alloys has been undertaken only recently and, for the first time at our best knowledge, in our research group [27,28]. Nanoporous atomistic models for a-$Si_{1-x}Ge_x$ alloys were generated by substituting Ge atoms for Si atoms in nanoporous paracrystalline

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network for a-Si developed previously in our group [29]. Alloy networks with uniform distribution of Ge atoms, and others with heterogeneous one were generated to study the effect of the compositional heterogeneity. We have shown that nanoporous atomistic models for a-Si$_{1-x}$Ge$_x$ alloy account for the SAXS observed experimentally for some samples. More interestingly, the compositional heterogeneity leads to an enhancement of this scattering. However, the coexistence of both types of heterogeneities on the one hand, and the parasite effects at small scattering angles due to the finite size of the models, on the other hand, have inhibited a rigorous quantitative analysis of the SAXS patterns of these atomistic models. The problem of troublesome effects due to the finite size of the structural model was recently resolved in our analysis of the SAXS in nanoporous atomistic models for a-Ge [30]. Indeed, a smoothing procedure was proposed to get rid of the truncation effects allowing so a rigorous quantitative analysis of the SAXS patterns of nanoporous a-Ge. This work has encouraged us to revisit the problem of the SAXS in a-Si$_{1-x}$Ge$_x$ alloys in more detail and, mainly, from a quantitative point of view.

Our present work deals with a detailed analysis of the SAXS in atomistic models for a-Si$_{1-x}$Ge$_x$ alloys. Our main focus is on the effect of compositional heterogeneity only, on the small-angle scattering in these alloys. Thus, we consider compositionally heterogeneous atomistic models without nanovoids.

2. Computation method

The present investigation is based on the class of continuous random network atomistic models generated with the Wooten–Winer–Weaire bond switching algorithm by Barkema and Mousseau [31], resulting in N-atom model with periodic boundary conditions. A 4096-atom model was provided to us by the courtesy of Professor Normand Mousseau; it is contained in a cubic supercell of 47 Å edge. A 32,768-atom model was derived from the 4096-atom network by a simple duplication (eight times) in the three directions of space, resulting in a cubic supercell of 94 Å edge. By substituting Ge atoms for Si atoms in the preceding a-Si networks, structural models for a-Si$_{1-x}$Ge$_x$ alloys are constructed. A homogeneous alloy (one-phase model) with alloy composition x is generated by substituting a corresponding fraction of Si atoms selected at random throughout the a-Si network. To generate a heterogeneous two-phase model, the substitution procedure is carried out in two steps. First, Ge atoms are substituted randomly for Si atoms within non-overlapping spherical volumes of predefined radii and with a predefined Ge fraction x_α; this constitutes the α-phase. Then, Ge atoms are substituted randomly for Si atoms in between these spherical volumes with a different predefined Ge fraction x_β; this constitutes the β-phase. A representative of the resulting structures is demonstrated in Fig. 1, showing two ball and stick networks of a-Si$_{0.9}$Ge$_{0.1}$ alloy: a homogenous one-phase model (Fig. 1(a)) and a heterogeneous two-phase model (Fig. 1(b)).

Once the structural model for a-Si$_{1-x}$Ge$_x$ alloy is generated, we proceed to its relaxation. The structural relaxation is accomplished by the minimization of the total strain energy of the network. In the present work, the anharmonic Keating model proposed by Rücker and Methfessel [32] was used. Within the framework of this model, the strain energy of the system is given by:

$$V = \sum_{i,j}\alpha_{ij}\left(\overrightarrow{r}_{ij}\cdot\overrightarrow{r}_{ij}-r_{ij}^{0^2}\right)^2 + \sum_{i,j,k}\beta_{ijk}\left(\overrightarrow{r}_{ij}\cdot\overrightarrow{r}_{ik}+\frac{1}{3}\,r_{ij}^0 r_{ik}^0\right)^2. \quad (1)$$

The first sum in this expression is on all atoms i in the supercell and their four nearest-neighbors specified by j. The second sum is on all atoms i and pairs of distinct neighbors. $\overrightarrow{r}_{ij}$ and $\overrightarrow{r}_{ik}$ are the vectors connecting atom i with its first-neighbors j and k, respectively. r_{ij}^0 is the unstrained $i-j$ bond length; $r_{ij}^0 = 2.35$, 2.40 and 2.45 Å for Si–Si, Si–Ge and Ge–Ge bonds, respectively. The force constants α and β
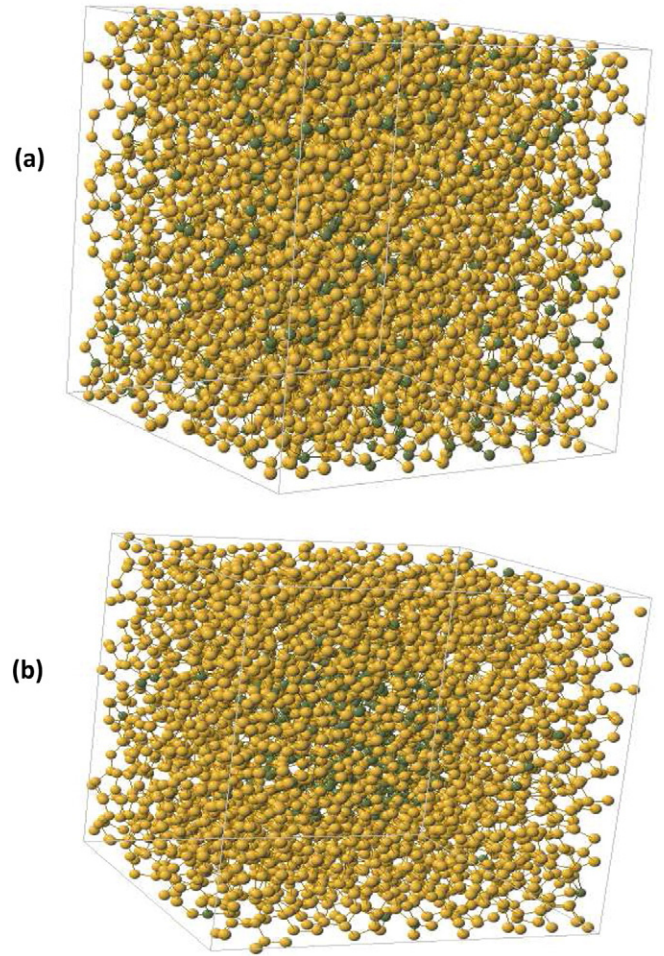
Fig. 1. Ball and stick models of a-Si$_{0.9}$Ge$_{0.1}$ alloy: (a) a one-phase model, and (b) a two-phase model in which the α-phase is formed by a single sphere of composition $x_\alpha = 0.7$. Yellow spheres denote Si atoms, and green spheres show Ge atoms.

essentially describe the bond-stretching and bond-bending restoring forces, respectively; their dependence laws are given by [32]:

$$\alpha_{ij} = \alpha_{ij}^0\left(\frac{r_{ij}^0}{r_{ij}}\right)^4 \quad (2)$$

and

$$\beta_{ijk} = \beta_{ijk}^0\left(\frac{r_{ij}^0\, r_{ik}^0}{r_{ij}r_{ik}}\right)^{\frac{7}{2}}. \quad (3)$$

The total strain energy given by Eq. (1) is minimized by an iterative conjugate gradient method starting with initial configuration in which all the atoms in the supercell are randomly displaced from their original positions. In this relaxation procedure, variations of the supercell sizes are allowed.

Now, given the equilibrium coordinates of all the atoms of the relaxed network, its structural characteristics can be easily computed, mainly the atomic pair correlation functions. The partial pair correlation function, $g_{ij}(r)$, is defined by the relationship:

$$dN_{ij}(r) = 4\pi r^2 n_0 c_j g_{ij}(r)dr \quad (4)$$

where $dN_{ij}(r)$ is the average number of atoms of j-type confined in the spherical shell of radii r and $r + dr$ centered at an atom of i-type taken