Configurational and Electronic Properties of Amorphous Semiconductors

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The configurational properties of a-Si, a-Ge and a-$Si_{1-x}C_x$ have been studied by Monte Carlo simulation methods. A special attention is given to the selection of the interatomic potential. The calculated networks for the a-Si and a-Ge systems are found to be nearly the same with only a small scaling factor of difference for the bond distances and nearly the same bond angles. In the case of a-$Si_{1-x}C_x$ we find that all C sites are 4-fold coordinated, whereas the coordination of Si varies between 3 and 6. The increase of x in a-$Si_{1-x}C_x$ increases the amount of 5-fold Si sites and decreases the amount of 4-fold Si sites indicanting an increase of the disorder. With the geometrical structures generated by the Monte Carlo simulation a quantum mechanical investigation is made of the electronic structure of a-Si. Using the INDO method for a cluster "supermolecule" composed of 35 Si atoms saturated with hydrogen atoms the density of states of a-Si is simulated. Configuration interaction calculation is also performed to disciiss the optical absorption spectrum of a-Si.

I. Introduction

Amorphous semiconductors represent an important area in condensed matter physics. This subject has been extensively studied both theoretically and experimentally not only because of its technological importance but also because of its interesting physical properties[1].

A necessary requisite to any microscopic study of disordered semiconductors is the knowledge of their atomic structure. Experimentally, disorder means that one can measure only average properties and an accurate determination of the individual atomic coordinates is impossible. Yet a quantitative characterization of the atomistic disorder, i.e, an accurate microscopic model of the disordered network, is a prerequisite for any quantitative theoretical approach to the properties of these systems. Reliable models of disordered structures can be generated from an accurate description of the interatomic potential energy surface, using statistical simulation methods based on Molecular-Dynamics (MD)[2] or Monte Carlo (MC) techniques[3].

Here, we present results of simulations of the following systems: amorphous Si (a-Si), amorphous Ge (a-Ge) and amorphous SiC (a-$Si_{1-x}C_x$ with x up to 0.1). We use a MC algorithm and the interatomic potential developed by Tersoff[4].

Once an amorphous structure has been obtained by simulation it is possible to study the electronic structure using conventional non-relativistic quantum mechanical methods. In particular, our interest in the optical spectra of amorphous materials demands a careful analysis of the electronic excited states. Besides the transition energies it is important to obtain the relative intensities of the corresponding electronic absorption. For that matter we use the self-consistent-field approach within the intermediate neglect of differential overlap approximation followed by configuration interaction, the so-called SCF-INDO-C1 method[5], and adopt a "supermolecule" approach. Further details are given in the next section.

II. Method

To study the configurational structure we have used the continuous- space MC method. A reliable description of the atomic interaction is provided by using an empiric interatomic potential. Details on the functional

form and parameter values of the potential are postponed to subsection II.2.

The MC simulations are made with cubic boxes of 216 atoms. The problem of surface effects can be overcome by implementing periodic boundary conditions using the minimum image convention[6].

In order to generate the atomic arrangement in a-Si, the ideal configuration of the diamond structure was melted using a constant temperature and pressure (NPT) MC procedure. This simulation was performed at 3000 K since the experimental melting point for Si is 1683 K but the calculated melting point for Si modelled by the Tersoff potential is 2547 K[7].

After the system was thermalized at 3000 K, which required about 10000 MC steps, the temperature was decreased to 2500 K and the system was thermalized again. This process is repeated down to 300 K and only then the a-Si coordinates are generated. In the cases of a-Ge and a-Si_1–,C, we used similar procedures.

Having the structure generated by the MC simulation it is possible to perform an analysis of the electronic structure.

II.1 Electronic structure calculations

To make the electronic structure calculations we adopt the INDO method. A Hartree-Fock (HF) self-consistent field calculation is first performed on the ground state. The HF orbital energies are used to calculate the density-of-states (DOS). In this one-particle picture the discrete set of energy levels are used to simulate the DOS of the bulk by convoluting Gaussian-type functions around each discrete energy level with a given width[8]. In all calculations performed here we used a Gaussian width of 0.5 eV.

It is not possible to include all the 216 atoms in these analysis because of computational limitation. Then, we consider a representative portion including 35 atoms as a "supermolecule". These atoms are selected by choosing randomly an atom in the 216-atom cell and looking for its 34 nearest neighbors. Now we have again to deal with feigned surface effects. Then we saturated the dangling bonds of the supermolecule with hydrogen atoms[9]. This procedure must not be confused with real hydrogenation, which is common in amorphous semiconductors.

The HF states are used next to generate the excited states by configuration interaction (CI). Using single-electron promotion with reference to the HF wavefunction around 400 excited states are generated and allowed to interact by diagonalizing the Hamiltonian matrix in this basis. This immediately gives the corresponding excitation energies. In addition, as all CI states come from diagonalization of the same CI matrix the corresponding eigenstates of the CI hamiltonian form an orthonormal set and this allows the determination of the transition moments. Thus the corresponding intensities are calculated from the oscillator strength. In all cases here the oscillator strength has been obtained using the length form. The optical spectrum is finally obtained by convoluting Lorentzians around the transition energies using the oscillator strength for the intensity[10]. This procedure is very convenient for large systems where a state-to-state analysis is neither possible nor desirable.

11.2 The interatomic potential

To model the interaction between the atoms we have used the Tersoff potential (TP). In this scheme the energy is a sum of pairlike interactions, but the coefficient of the attractive term depends on the local environment, giving a many-body potential. The functional form of the energy E is given by

$$E = \sum_i E_i = \frac{1}{2}\sum_{i \neq j} V_{ij}$$

$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \tag{1}$$

Here E is the total interatomic energy of the system. The indices i and j run over the atoms of the system, and r_{ij} is the distance from atom i to atom j.

The function f_R represents a repulsive energy due to atomic wave function overlapping, and f_A represents an attractive pair potential to give interatomic binding. These functions are chosen to be exponentials, as in a Morse potential

$$f_R(r_{ij}) = A_{ij}\exp(-\lambda_{ij} r_{ij})$$

$$f_A(r_{ij}) = -B_{ij}\exp(-\mu_{ij} r_{ij}) \tag{2}$$

with

$$A_{ij} = (A_i A_j)^{1/2} \ , \ B_{ij} = (B_i B_j)^{1/2}$$

$$\lambda_{ij} = (\lambda_i + \lambda_j)/2 \ , \ \mu_{ij} = (\mu_i + \mu_j)/2 \tag{3}$$

The function f_C is a cutoff function, that limits the range of the potential and it has the form

$$f_C(r_{ij}) = \left\{ \begin{array}{ll} 1 & , r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2}\cos[\pi(r_{ij} - R_{ij})/(S_{ij} - R_{ij})] & , R_{ij} < r_{ij} < S_{ij} \\ 0 & , r_{ij} > S_{ij} \end{array} \right\} \quad (4)$$

with

$$R_{ij} = (R_i R_j)^{1/2} \ , \ S_{ij} = (S_i S_j)^{1/2} \ , \quad (5)$$

and a continuous value and derivative for all r_{ij}, and goes from 1 to 0 in a small range between R_{ij} and S_{ij}. R_{ij} and S_{ij} are chosen to include only first neighbor interaction for most structures of interest.

The bond order function, b_{ij}, has the form

$$\begin{aligned} b_{ij} &= \chi_{ij}(1 + \beta_i^{n_i}\zeta_{ij}^{n_i})^{-1/2n_i} \\ \zeta_{ij} &= \sum_{k\neq i,j} f_C(r_{ik})g(\theta_{ijk}) \\ g(\theta_{ijk}) &= 1 + c_i^2/d_i^2 - c_i^2/[d_i^2 + (h_i - \cos\theta_{ijk})^2] \end{aligned} \quad (6)$$

where θ_{ijk}, is the bond angle between bonds ij and ik.

The parameters in the potential were determined by fitting to a data base consisting of ab *initio* results. This data base included the cohesive energy, bulk modulus and bond length in the diamond structure and the cohesive energies in the dimer and in the bulk politypes FCC, BCC, β-tin, simple cubic and simple hexagonal. For Si and Ge we use the parameters given in reference [4] and for C that given in reference [11].

The present approach has the advantage of statistical precision and allows the use of large cells to model the disordered material. In contrast, *ab initio* MD are restricted to short simulation times, small cells (about 60 atoms), fixed volumes and the use of only the Γ-point for the integration in the Brillouin-Zone.

III. Results and discussion

III.1 a-Si and a-Ge: atomic arrangement

The configurational structure of a-Si as obtained with the MC method in which the atoms interact via the TP has already been published[12]. Here we first briefly revisite this problem as an initial test for the MC computational code that we developed. Our results are indeed in agreement with the Tersoff results[12]. In this subsection we shall also present our results for the configurational structure of a-Ge.

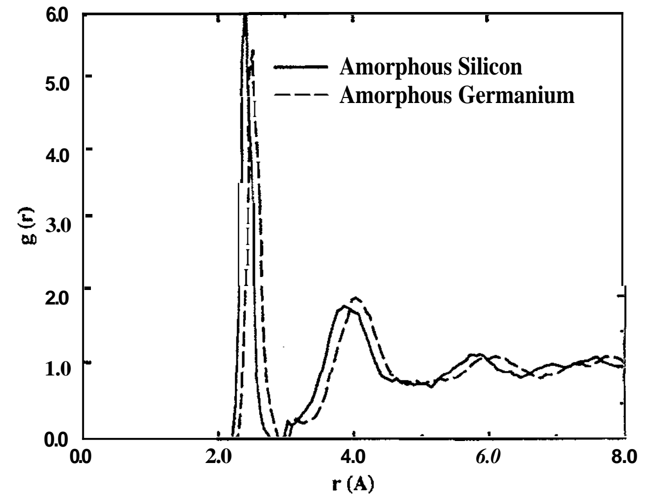

Figure 1: Radial distribution functions for a-Si (solid lines) and a-Ge (dashed lines).

In the Fig. 1 we show the radial distribution functions (**RDF**) for these systems. A very pronounced peak at 2.41 Å for a-Si and 2.52 Å for a-Ge indicates that the systems have a short range order as expected for covalent disordered systems.

In the Fig. 2 we show the angular distribution functions for a-Si and a-Ge. The distributions are centered around the angle of 109.5 degrees (vertical line in the plot). This is the angle of the bonds in crystalline Si and Ge.

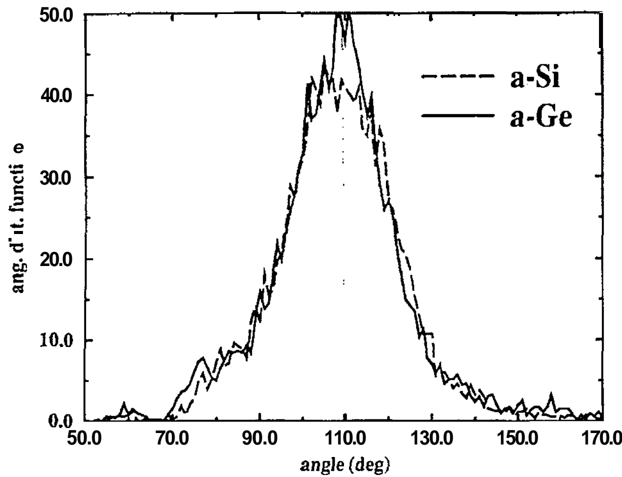

Figure 2: Angular distribution functions for a-Si (solid lines) and a-Ge (dashed lines).

In the Table I we compare our results with that obtained within the Car-Parrinello scheme (CP)[13] and experimentally[14,15,16]. In the case of a-Ge there is not, to our knowledge, *ab-initio* MD results in the literature. We compare the mean first-neighbor distance, $\bar{R}_1$, the standard deviation of bond lengths, σ_{R_1} the average coordination, N_C, the mean bond angle, $\bar{\theta}$, and the standard deviation of bond angles, σ_θ.

Table I: Mean first-neighbor distance, R_1, standard deviation of bond lengths, u ¬, average coordination, N_C, mean bond angle, $\bar{\theta}$, and standard deviation of bond angles, σ_θ for amorphous Si and amorphous Ge. Our results are compared with both CP[13] and experimental results[14,15,16].

		R_1 (A)	σ_{R_1} (10^{-2} Å)	N_C	θ (deg)	σ_θ (deg)
a-Si	Our	2.41	8.1	4.10	108.6	12.1
	CP	2.38	9.0	3.96	108.1	13.4
	Exp.	2.36	7.4	4.05	108.4	9.9
a-Ge	Our	2.52	4.9	4.15	108.3	15.8
	Exp.	2.463	7.4	3.68		

The results presented in Table I and Figs. 1 and 2 show that the geometrical pattern of a-Ge and a-Si networks are nearly equal with only a small scaling difference in bond lengths.

111.2 a-Si$_1$-,C,: atomic **arrangement**

The atomic arrangements of stoichiometric SiC, i.e, a-Si$_1$-,C, with x = 0.5 have been studied both experimentally[17] and theoretically[18]. However the understanding of the atomic arrangements of a-Si in which a small amount of C atoms is included is still missing. In this subsection we present our results obtained with the MC simulations for a-Si$_1$-,C, with varying x up to 0.1.

In the Fig. 3 we show the RDF for the systems that we have studied compared with the RDF of a-Si.

Analysis of the RDF of Fig. 3 in terms of partial correlation functions, shows that the first and second peaks at 1.62 Å and 1.95 Å are due to C-C correlation. We note that when the concentration of C is 2% or 5% the peak at 1.62 Å is missing. The third peak at 2.4 Å is due to Si-Si correlation and the fourth peak at 3.05 Å is due to Si-C correlation.

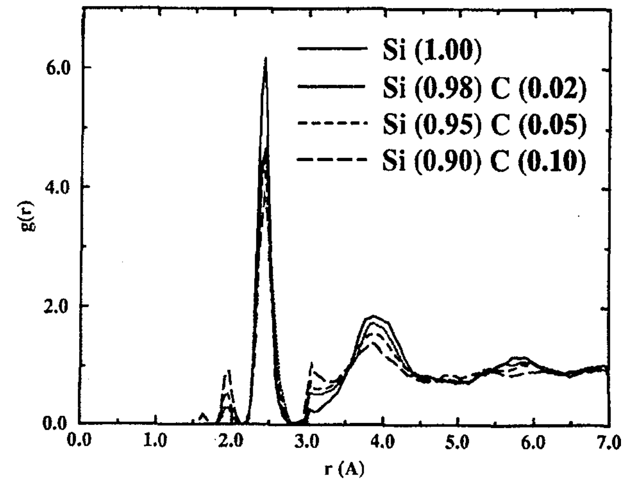

Figure 3: Radial distribution functions for a-Si (solid lines). a-$Si_{0.98}C_{0.02}$ (dotted lines), a-$Si_{0.95}C_{0.05}$ (dashed lines) and a-$Si_{0.9}C_{0.1}$ (long dashed lines).

In all simulations made here we obtain that the C atoms are always tetracoordinated. However our results for the coordination of the Si atoms range between 3 and 6. In the Table II we compare the amounts of tri, tetra, penta and hexacoordinated Si sites for each C content studied here.

We note that the increase of C concentration in a-$Si_{1-x}C_x$ increases the amount of 5-fold sites and decreases the amount of 4-fold sites. This is indicative of an increase in the disorder of the system.

Table II: Percentage of Si sites in a-Si1-,C, calculated with coordination three, four, five and six.

x	3-fold	4-fold	5-fold	6-fold
0.00	0.0	90	9.3	0.7
0.02	0.0	78	21.5	0.5
0.05	0.5	75	24	0.5
0.10	2.5	70	27	0.5

111.3 a-Si: electronic structure

In this subsection we present the results for the electronic structure calculations of a-Si. In the Fig. 4 we compare our calculated DOS for a-Si and crystalline Si (c-Si). We see that the peaks in the DOS are broadened when changing from the crystalline to the amorphous systern. In the case of a-Si we see a small peak in the DOS near the energy of 0 eV. This peak is related to a very localized state and this state is due to an overcoordinated (5-fold) site. The large gaps in the Fig. 4 are due to the frozen orbital approximation using the HF scheme. The inclusion of relaxation is made in the CI method and improves the results. In the Table III we show the difference in energy between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) obtained at the HF calculation. We also show the calculated optical gap, obtained here from the calculated first excitation energy in the CI model, for the case of a-Si and c-Si. As the HOMO-LUMO energy difference corresponds to a frozen orbital picture it gives values for the energy gap that are too large in a cluster model. Only for the infinite system the relaxation energy can be neglected. A simple way to include the relaxation of the unoccupied orbitals is to perform a CI calculation with single excitation. As Table III shows the relaxation is large for c-Si and very large for a-Si. The final theoretical estimate of the corresponding optical energy gap is improved by the inclusion of the relaxation energy although it is still somewhat too large. We note that, experimentally, in the case of a-Si there is the formation of a pseudogap at the Fermi Energy. The value of the energy gap value of c-Si is 1.2 eV. For all the difficulties involved in the calculation of total energy the essential aim in obtaining energy gap is to analyze the general trend. This feature is nicely reproduced in our model (Table III).

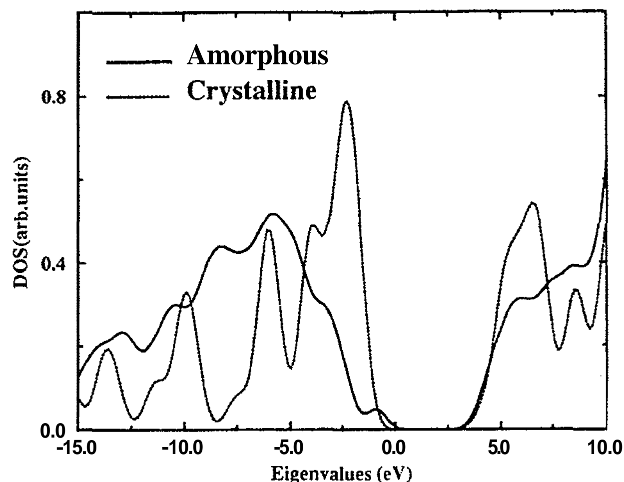

Figure 4: Calculated density-of-states of amorphous (solid line) and crystalline Si (dotted line).

Table III: Calculated HOMO-LUMO energy difference and optical gap (in eV) for amorphous and crystalline Si.

	HOMO-LUMO	Optical Gap
c-Si	5.80	3.45
a-Si	5.06	1.54

The Fig. 5 shows the calculated optical absorption spectrum for a-Si and c-Si using the SCF-INDO-C1 procedure described in the section II. In the low-energy side one notes an almost rigid shift of 1.0 eV for the intense transitions. However for the case of the amorphous system the natural disorder gives absorption intensity to formally dipole forbidden transitions.

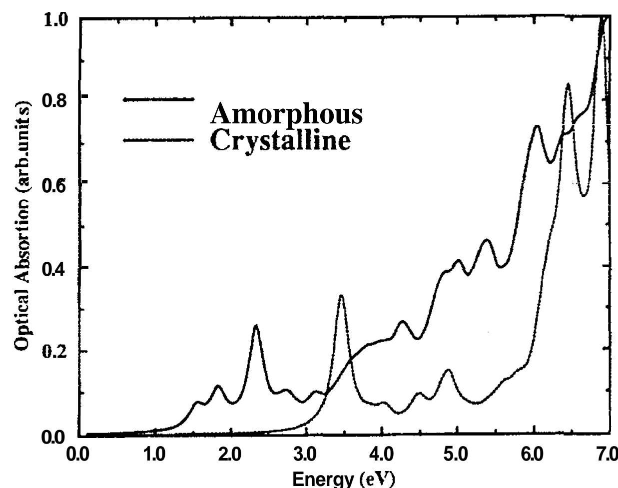

Figure 5: Calculated optical absorption of amorphous (solid line) and crystailine Si (dotted line).

IV. Final remarks and conclusions

We have simulated the configurational structures of a-Si and a-Ge. We find that the difference between these two calculated structures is only a small scaling factor for the bond lenghts but with essentially the same network pattern as given by the angular distribution functions.

We have also studied the case of a-$Si_{1-x}C_x$, x = 0.02, 0.05 or 0.10. We find that the C atoms are always tetracoordinated, but the Si atoms can have coordination 3, 4, 5 or 6. The amount of Si atoms that are tri and pentacoordinated increases when the concentration of C increases in the samples. This indicates an increase in the disorder of the system.

These calculated geometric structures are used to obtain the electronic properties of a-Si, particularly the density-of-states and the optical absorption spectrum. Further studies of the electronic structure of a-Ge and a-$Si_{1-x}C_x$ are being made in our group.

Acknowledgements

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