PHYSICAL REVIEW B VOLUME 55, NUMBER 14 1 APRIL 1997-II

Short-range order, bulk moduli, and physical trends in c-$Si_{1-x}C_x$ alloys

P. C. Kelires
Physics Department, University of Crete, P.O. Box 2208, 710 03 Heraclion, Crete, Greece
and Foundation for Research and Technology-Hellas (FORTH), P.O. Box 1527, 711 10 Heraclion, Crete, Greece

(Received 9 December 1996)

Alloys of silicon and carbon in the crystalline phase, although complex and with varying degrees of short-range order, are shown to exhibit an accurate power-law dependence of the bulk modulus B on the average nearest-neighbor separation d, over the whole composition range. The homopolar energy gap of these alloys increases with carbon content. Similar trends have only been proposed earlier for the much simpler diamond and zinc-blende semiconductors. [S0163-1829(97)03513-3]

The rapid progress in modern epitaxial techniques made it possible to fabricate complex compounds and alloys, which had been in the past considered as only hypothetical. The growth of $Si_{1-x}C_x$ alloys illustrates one of the most intriguing examples, where the extremely low solid solubility of C in Si had been overcome by nonequilibrium methods, such as molecular beam epitaxy (MBE).[1] The complexity of these ''exotic'' new materials poses a challenge to the theorist aiming to compute the most fundamental of their properties: lattice constants, bulk moduli, cohesive energies, and band gaps. Although quantum-mechanical *ab initio* calculations of total energies and forces have given excellent results when applied to simple solids, their applicability to more complex materials, where structural and compositional disorder dominates, is severely limited.

Because of these limitations, we often develop empirical formalisms in order to study a wide class of materials and to demonstrate physical trends. A decade ago, Cohen[2] proposed such an empirical model for the bulk moduli of diamond and zinc-blende (ZB) solids. The essence of this model is embodied in a simple expression which defines a power-law dependence of the bulk modulus B on the nearest-neighbor (NN) separation d. The physical considerations behind this approach is that B depends predominantly on the covalent character of the bond (exemplified by a *homopolar gap* E_h), and only weakly on *ionicity*, and that E_h scales logarithmically against lattice constants between different rows of the periodic table, as suggested by Philips.[3] Although the model has been proved to be appropriate for the simple diamond and ZB structures, one wonders whether the above ideas are more general and can be applied to complicated materials with a high degree of compositional disorder.

Here, we show that $Si_{1-x}C_x$ alloys exhibit an accurate power-law dependence of B on the lattice constant a_0 or, equivalently on the ''average'' *NN* distance d, over the whole composition range. This is quite remarkable given the complexity of these alloys, which are inherently locally disordered due to the atomic size mismatch, as well as compositionally disordered. The complexity is pronounced especially at intermediate compositions, as compared to the simple ZB form of SiC. As a consequence of the power-law dependence, it follows that the homopolar (average) gap E_h of these alloys increases with carbon content x, contrary to the intrinsic gap which has been reported to decrease. The question of short-range order (SRO) is also analyzed and quantified for all values of x.

The key point in discussing these alloys lies in the proper description of the intrinsic strain due to the huge size mismatch between Si and C. This is related to the optimum distribution of species in the network minimizing the elastic energy. In thermodynamic equilibrium the only stable phases are the equimolar perfectly ordered ZB structure and the various stoichiometric polytypes. However, it has been possible to grow metastable, defect-free, nonstoichiometric alloy layers on Si using MBE,[1,4] with carbon contents up to ~20%,[4] without the formation of silicon carbide. Thus, in our search for physical trends in this alloy series, we must consider the whole range of x, although certain values might not actually occur in the laboratory (especially under epitaxial strain). We already know that, for small carbon contents, minimization of the elastic energy is obtained if C atoms are arranged at certain distances (mainly as third NN's).[4,5] As x increases, however, compositional disorder rises because ''wrong'' (homopolar) bonds inevitably occur.

We accomplish the incorporation of C atoms in the Si lattice, or vice versa, and we attain the most favorable metastable arrangements which minimize strain, using Monte Carlo (MC) simulations in the semigrand canonical ensemble $(\Delta\mu,P,T)$ supplemented by a technique recently introduced[5] which overcomes the large formation energies and lowers the barriers for diffusion. In this approach, besides the usual random atomic displacements and volume changes, we have Ising-type flips (atom-identity switches) driven by the chemical-potential difference $\Delta\mu=\mu_{Si}-\mu_C$, which are accompanied by appropriate relaxations of first-NN atoms, away or toward the central atom undergoing the attempted switch, in order to make the flips less costly. In this way, the success rate is enhanced by as much as 50%. It should be clear that statistical averages are taken with respect to these metastable configurations, which despite that minimize strain *do not eliminate it,* since they are inherently locally strained in the neighborhood of the minority-type-atom insertion. The only strained-free configurations result from formation of SiC-like regions, but this case does not interest us, and neither is proposed by the MBE experiments at typical growth temperatures.

For the simulations we use cubic supercells of 216 atoms with periodic boundary conditions. The composition x in the

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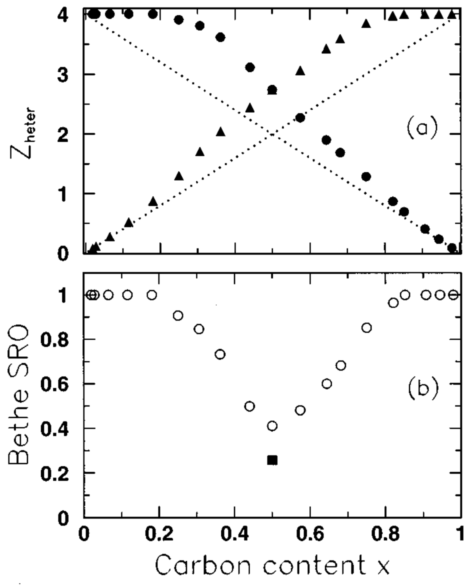

FIG. 1. Short-range order in $\mathrm{Si}_{1-x}\mathrm{C}_x$ alloys. (a) Variation of the average number of heteropolar bonds with x. Circles stand for C-Si bonds, triangles for Si-C bonds. Dotted lines denote a hypothetical random distribution of species. (b) The Bethe SRO parameter (see text) vs x. The square shows corresponding value for the amorphous stoichiometric alloy.

cell is obtained by a suitable choice of $\Delta\mu_{\text{Si}-\text{C}}$, while the pressure P and temperature $T \simeq 800$ K (a typical growth temperature) are kept fixed. The interatomic interactions are modeled via a well-tested, in similar environments,[5] empirical potential.[6] This approach is less accurate than first-principles methods, but since we are aiming at *trends*, any inaccuracies and errors are systematic and they do cancel out. Besides, the empirical approach allows for the present MC treatment, which is advantageous because strain minimization is arrived at naturally. In any *ab initio* approach one would have to find the most favorable arrangements by randomly moving atoms in the lattice in an inefficient and costly procedure.

We first discuss the question of SRO (limited to first NN's) in the series of generated samples. The relevant analysis of the extensive calculations is shown in Fig. 1. Panel (a) demonstrates how the average number of heteropolar bonds (obtained from atomic correlations at $T \simeq 800$ K) evolves as a function of x, contrasted to a hypothetical random distribution of species. Perfect heteropolar bonding ($Z_{\text{heter}} = 4$) persists for $0.24 \geqslant x \geqslant 0.82$, and then Z_{heter} is reduced for intermediate values. However, even in this region a significant amount of SRO exists. In order to quantify ordering, we utilize the concept of the nearest-neighbor correlation parameter in a binary alloy, defined as[7]

$$\Gamma_{AB} = c_A P_{AB} - c_A c_B, \tag{1}$$

which relates the probability P_{AB} of a given bond being of type A-B, to the random case where each site is independently occupied with probability c_A or c_B. [Since c_A and c_B are actually the fractions x and $1-x$ of atoms A and B in the cell, the random probability $\langle P_{AB} \rangle$ equals $(c_A c_B)/c_A = c_B$; e.g., for $x = 0.5$, $\langle P_{AB} \rangle = 2 c_A c_B = 2 \times \frac{1}{2} \times \frac{1}{2} = 0.5$.] Normalization of Γ_{AB} to maximum order results in the Bethe SRO parameter

$$\Gamma_{\text{Bethe}} = \frac{\Gamma_{AB}}{c_A P_{AB}^M - c_A c_B}, \tag{2}$$

where P_{AB}^M is the maximized probability (in the present case $P_{\text{C-Si}} = Z_{\text{C-Si}}/4$, $P_{AB}^M = 1$). Values of the Γ_{Bethe} parameter for the samples of panel (a) are drawn in panel (b). Significant SRO is preserved up to $x \simeq 0.35$ and for $x \geqslant 0.7$. The variation is smooth with a well-defined minimum at $x = 0.5$, where the parameter falls to a value somewhat less than midway between random ($\Gamma_{\text{Bethe}} = 0$) and fully ordered ($\Gamma_{\text{Bethe}} = 1$). The overall picture and the close compatibility with the structural trends, to be discussed below, show that the calculated SRO is near the optimum one. Also note that expectedly the SRO for the stoichiometric sample is higher than for amorphous SiC.[8] The reason lies in that the atomic size mismatch, which is the primary driving force for ordering in the crystal, is less effective in the amorphous material where the network has the ability to accomodate large local strains.

We now proceed to calculate the lattice constants and bulk moduli of $\mathrm{Si}_{1-x}\mathrm{C}_x$ alloys and to investigate the relationship among them. We focus our attention to *static-lattice* elastic properties (at ~ 0 K), much in the same way as done previously for amorphous carbon networks.[9] Since atom-identity flips cannot take place at such low temperatures, we generated three different metastable configurations for each x at typical growth temperatures, where the switch-success rate is significant. These were subsequently cooled to ~ 0 K at their lowest-energy configurations. At this stage, averaging over the cell dimensions gives a_0 for each configuration, and averaging over the three configurations gives a_0 for each x. The equilibrium bulk modulus $B = V(d^2E/dV^2)_{V=V_0}$ is obtained by considering a uniform expansion (compression) of the cell for each configuration and fitting points of total energy versus volume with the Murnaghan equation of state for solids. The results of our calculations as a function of carbon content x are shown in Fig. 2. (The differences in the values of a_0 or B between the three configurations are small, not exceeding the size of the symbols.) In panel (a), we observe a negative deviation from Vegard's linear rule $a_0(x) = (1-x)a_{\text{Si}} + x a_{\text{C}}$, an effect well known for ZB-SiC and attributed to charge transfer from Si to C.[10] The variation of the lattice constant with x is very well fitted with the second-order polynomial

$$a_0(x) = a_{\text{Si}} - 2.4239x + 0.5705x^2. \tag{3}$$

Note that a_0 for ZB-SiC is smaller than for the stoichiometric disordered sample (larger negative deviation). The latter is strained (mixed bonds) and cannot acquire the optimum density of the unstrained ZB form. The variation of the bulk modulus B with x in panel (b) also exhibits the same smooth trend, i.e., a downward bowing compared to the linearly interpolated values. Expectedly, the B of the stoichiometric sample is lower than that of ZB-SiC (disordered networks are softer than undistorted lattices).

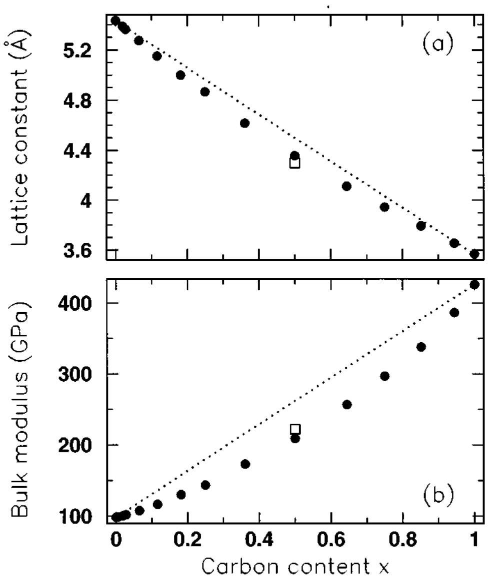

FIG. 2. (a) Lattice constants and (b) bulk moduli of $Si_{1-x}C_x$ alloys as a function of x. Dotted lines show variations according to Vegard's rule. Squares denote corresponding values for the zinc-blende SiC alloy.

A considerably deeper insight into these properties is achieved if we search for specific trends in the variation of B. Looking for such trends is preferable to study the variation of B with a_0 or, equivalently, with the nearest-neighbor distance d, instead of x. For an elemental semiconductor d is well defined, but here due to the presence of all kinds of bonds, occurring in a variety of proportions depending on carbon content x, we have to think in terms of an ''average'' $d(x)$ that reflects the actual a_0 of the sample. Thus, the best choice is to consider $d(x)=a_0(x)\sqrt{3}/4$. [Choosing $\overline{d(x)}=(1-x)d_{Si}+xd_C$ would be in conflict with the nonlinear variation of a_0.] The dependence of B on $d(x)$ is shown in Fig. 3. Panel (a) shows the linear variation, while panel (b) shows B versus d in a log-log plot. The data closely follow a straight line, which indicates that

$$B=Ad(x)^n. \tag{4}$$

A line fit through all points gives (within our numerical accuracy) for the slope n and the constant factor A the values -3.49 ± 0.02 and 1925 ± 30, respectively, when B is measured in GPa and d in Å.

The observation of this accurate power-law behavior, from these simple empirical calculations, is quite remarkable for several reasons: (a) It provides an independent verification of Cohen's proposition,[2] which was based on physical considerations, both regarding the scaling exponent n and the constant A.[11] (b) Furthermore, and most importantly, power-law behavior holds for the whole composition range of these complex alloys; i.e., B scales with d which is a function of x within a single alloy series. This is a generalization of Cohen's theory where B scales with d between different rows of the periodic table. Note that Eq. (4) does not hold if one uses the average (linearly interpolated) $\overline{d}$'s. (c) Both ZB-SiC and ''disordered'' $Si_{0.5}C_{0.5}$ follow this behavior, indicating that the respective bulk moduli and NN distances vary consistently. (d) It provides a strong test of the accuracy of our MC switching-relaxing algorithm, showing that all degrees of freedom, spatial and cellular, are properly equilibrated. So the accuracy in this power law verifies that SRO in the cells is at its optimum level. (e) Finally, it is trivial to compute B for any arbitrary carbon content x. One extracts d from $a_0(x)$ given by Eq. (3) and then B is estimated using Eq. (4). Thus, the observed trends are not just of academic interest. The knowledge and easy derivation of such structural and elastic data from simple formulas (overcoming in this way the difficulty of performing first-principles calculations for so many configurations and for such a complex material) is very helpful and essential for the description of physical properties of thin pseudomorphic epitaxial films. It is needed for the interpretation of relevant experiments, as well.

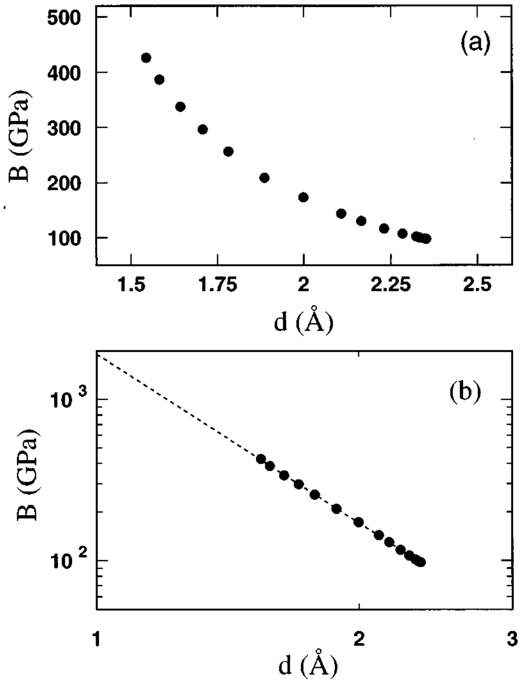

FIG. 3. The bulk modulus B as a function of the ''average'' nearest-neighbor distance d (see text) for a series of $Si_{1-x}C_x$ alloys, plotted (a) on a linear scale, (b) on a logarithmic scale. Error bars (not shown) are smaller than symbol size.

The power-law dependence of B on d immediately implies also a definite trend in the variation of the energy gap in $Si_{1-x}C_x$ alloys. According to Philips,[3] tetrahedral compounds sharing eight valence electrons per atom pair are characterized by a covalent or homopolar gap E_h and an ionic gap C.[12] Examining a series of solids of increasing ionicity (group IV→III-V→II-VI) Cohen observed[2] that the lattice constant, or d, is nearly independent of C and one should expect that B depends predominantly on E_h. Since B scales inversely proportional to the covalent-bond volume ($\sim d$; bond charge densities have roughly cylindrical shape), he suggested that

$$B=DE_hd^{-1}, \tag{5}$$

where D is a numerical constant. The $d^{-3.5}$ dependence of B follows from the argument of Philips that E_h in tetrahedral

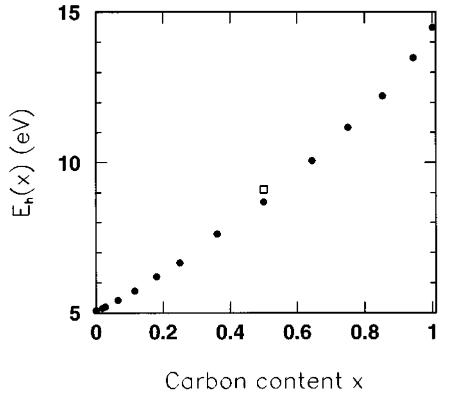

FIG. 4. The homopolar energy gap of $Si_{1-x}C_x$ alloys vs carbon content. The square shows the gap for zinc-blende SiC.

compounds scales as $d^{-2.5}$.[3] In this theory E_h plays the role of an average optical gap, like the energy gap parameter E_g in the isotropic band model of Penn.[13] Using Eq. (5) and as a level of reference the homopolar gap of Si, $E_h(\mathrm{Si})$ $(=5.07\ \mathrm{eV})$,[2] we obtain the variation of E_h with x in this series of alloys:

$$E_h(x)=E_h(\mathrm{Si})\left[\frac{B(x)}{B(\mathrm{Si})}\,\frac{d(x)}{d(\mathrm{Si})}\right]. \tag{6}$$

The results are plotted in Fig. 4. We find the E_h of carbon to be 14.5 eV, compared to 14.7 eV ($\delta E_h \simeq 1.4\%$) as determined from the experimental dielectric constant ϵ and the plasma energy E_p. Also, for ZB-SiC the calculated value (9.1 eV) agrees well with E_g obtained from Penn's model, while for $Si_{0.5}C_{0.5}$ we find a lower value (8.7 eV) as expected. The overall variation retrieves the $d^{-2.5}$ behavior, showing the reliability of our calculated bulk moduli and lattice constants [on which $E_h(x)$ in Eq. (6) is solely based].

Finally, let us point out that $E_h(x)$ increases as a function of x over the whole alloy range. This is in contrast to the behavior of the intrinsic gap which, for small carbon concentrations, has been reported by theoretical calculations to decrease,[14] attaining a minimum value at $\sim$10% of C. A possible explanation of this effect requires the average separation of bonding-antibonding states to increase, while the dispersion is such that the intrinsic gap decreases. It should be noted, however, that the lattice constants given as input to these calculations[14] were estimated using Vegard's rule, an approximation not valid in this system as shown above. This means that the cells were not completely geometrically relaxed in the correct density, and it could have as an artifact the overestimation in the reduction of the intrinsic gap. Note that recent photoluminescence studies in $Si_{1-x}C_x$/Si quantum well structures[15] found a considerably smaller shift than predicted by theory.[14] Obviously, this matter needs further investigation. In any case, our proposition for significant deviations from Vegard's law in $Si_{1-x-y}Ge_xC_y$ alloys,[5] and here in $Si_{1-x}C_x$ alloys, gains support both from recent experimental work[16] and from *ab initio* calculations.[17] Therefore, any future work should take seriously into account these deviations, especially when interpreting experimental results.

In summary, I have shown in this paper that MC simulations can provide metastable, disordered $Si_{1-x}C_x$ structures, whose bulk moduli and lattice constants obey a simple power-law behavior quite accurately. Although demonstrated for a single alloy of various compositions, the method and the accompanying analysis can be applied to other semiconductor alloys as well, in order to unravel interesting physical trends.

It is my pleasure to thank Alex Zunger, who suggested the link of my investigations with Cohen's theory, and Efthimios Kaxiras for fruitful discussions. This work has been supported in part by the HCM program of the EU, No. 0355.

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