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Evaluation of the Stillinger-Weber classical interaction potential for tetragonal semiconductors in nonideal atomic configurations

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A classical potential incorporating two- and three-body interaction terms has recently been introduced by Stillinger and Weber (SW) for simulation of the liquefaction transition of silicon. The equilibrium mechanical properties of this potential are determined and found to agree well with experimental values. The potential also seems to be adequate for problems involving computation of defect energies, such as the stability of strained-layer superlattice interfaces. However, inadequate treatment of configurations with low coordination number makes modeling of the epitaxial growth of (111) silicon impossible. Simple modifications of the SW potential form do allow for (111) epitaxial growth, but the earliest stages of growth then become unphysical.

INTRODUCTION

Computer simulation of the dynamic structural properties of covalently bound materials has always represented a very difficult problem. No physically reasonable pair potential can stabilize the open structures characteristic of covalent crystals, and more realistic potentials have until recently been computationally intractable. However, recent work in solid-state-device physics has resulted in considerable interest in the growth and stability of systems consisting of many thin layers of different semiconductors or metals. Examples would include quantum-well devices and strained-layer superlattices (SLS).[1] Such devices depend on the controlled growth of high-quality semiconductor layers as little as a few atoms thick. Theoretical understanding of stability properties and conditions which allow growth of such systems is, at present, very limited. Accordingly, the author has been involved in an effort to study theoretically, on an atomic scale, the growth and stability properties of tetrahedral semiconductor SLS structures (especially Si-SiGe systems). An essential step in such a project is the development of a physically reasonable interaction potential which will reproduce the bulk properties of the class of material of interest (tetrahedral semiconductors), and also allow atomic interactions in nonideal geometries, such as are encountered in study of stability or growth, to be properly modeled.

POTENTIALS FOR COVALENT CRYSTAL GROWTH

A standard approximation scheme for the interaction energy of a system of N identical particles is to express this energy in terms of sums of all possible one-body, two-body, three-body, etc., interaction terms. Thus, the potential energy would be represented by

$$\Phi(1,\ldots,N)=\sum_i f_1(i)+\sum_{\substack{i,j\\(i<j)}} f_2(i,j)+\sum_{\substack{i,j,k\\(i<j<k)}} f_3(i,j,k)+\cdots \quad (1)$$

The utility of this representation depends on the rapid convergence of the energy as the order of the interaction terms increases. As discussed earlier, a pair potential is invalid for simulation of open covalent structures. To maintain reasonable computational tractability, Eq. (1) will be truncated after the three-body term. The one-body term is ignored in the remainder of this paper, since it is primarily concerned with external forces.

The standard phenomenological implementation of the n-body expansion for binding energy is the valence force-field representation.[3] This method involves expansion of the binding energy in terms of small radial and angular atomic displacements from the crystalline equilibrium positions. Such an expansion is reasonable for describing physical properties in which only small displacements from equilibrium positions are involved, such as phonon properties, but is totally inadequate for simulation of growth or of defective systems, for which atomic configurations arise which cannot be mapped onto such a description of the interaction potential in a natural way. One must therefore choose another implementation which allows for treatment of arbitrary positions and coordination numbers.

The simulation of growth of a crystal from the vapor imposes especially strong constraints on the structure of the interatomic potential. Adatom-surface interactions are characterized by small coordination numbers relative to the bulk. In addition, the details of the process of growth are strongly influenced by the behavior of the interaction potential at distances larger than the equilibrium interatomic spacing. Thus, the "tail" of the potential must have a reasonable structure and magnitude for growth processes to be correctly modeled. Analysis of stability properties of a strained lattice system also provide a strong test of the model potential, although not as stringent as do the growth simulations. The stability analysis requires that defect energies be correctly evaluated. Since atomic configurations around defects are nonideal (typically possessing coordination numbers of 3 or 5 for a tetragonal semiconductor), the interaction potential must be accurate in such geometries to be useful for stability analysis.

THE STILLINGER-WEBER SILICON POTENTIAL

The Stillinger-Weber (SW) potential is in the form of Eq. (1), which is truncated to include only the two- and three-

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body terms.[2] The energy and length units are scaled so that the minimum in the two-body potential occurs at $r=2^{1/6}$ and that the largest two-atom binding energy is -1. They require that f_2 be a function only of radial distance, and that f_2 be a function only of radial distance, and that f_3 possess full translational and rotational symmetry. The scaled pair potential has the form

$$f_2(r)=\begin{cases} A(Br^{-p}-r^{-q})\exp[1/(r-a)], & r<a \ , \\ 0, & r>a \ . \end{cases} \quad (2)$$

Here a sets the range of the potential, B is adjusted so that the potential minimum occurs at the desired value, and A is set so that the value of f_2 at the potential minimum is -1. The values chosen for simulation of the melting of silicon were $A=7.0496$, $B=0.60222$, $p=4$, $q=0$, and $a=1.8$ (where the equilibrium spacing is 1.1225). This potential cuts off at $r=a$ smoothly, thus avoiding generation of artifacts in the simulations.

The three-body term f_3 is required to have rotational and translational symmetry. It therefore can be expressed as a symmetrized sum:

$$f_3(ijk)=h(ijk)+h(jik)+h(jki) \ , \quad (3)$$

where $h(ijk)$ will depend on the distances r_{ij}, r_{jk}, and the angle θ_{ijk}. Provided that both radii are less than a, h has the following form:

$$h(r_{ij},r_{jk},\theta_{ijk})=\lambda\exp[\gamma(r_{ij}-a)^{-1}+\gamma(r_{jk}-a)^{-1}] \times(\cos\theta_{ijk}+1/3)^2 \ , \quad (4)$$

otherwise h is zero. The angular term discriminates in favor of the ideal tetrahedral geometry without excluding the possibility of other configurations as a valence force-field treatment would. SW assigned these parameters the values $\lambda=21$, $\gamma=1.2$.

Stillinger and Weber chose this set of parameters based on several criteria. They first required that the diamond structure be the most stable periodic configuration at zero temperature and pressure, which is of course the situation in real silicon. They then required that the melting point and the liquid structure of the melt be in reasonable accord with experiment. They were quite successful in reproducing the desired properties of the melt, but their potential does not result in the diamond to β-tin phase transition at high pressure (or indeed any phase transition). This raises a question concerning the quality of the structural (and mechanical) energy calculations in the solid.

One can determine the accuracy with which this potential model's bulk mechanical properties near equilibrium by expanding the potential energy about equilibrium positions and then comparing with experimental fits to valence force-field approximations. This expansion gives expressions for an energy term associated with bond-length changes and another corresponding to bond bending. The bond-stretch energy is given by

$$\Delta E=C_0(r-r_0)^2/2r_0^2 \ , \quad (5)$$

and the bond-bending energy is given by

$$\Delta E=C_1(\delta\theta_{ij})^2/2 \ , \quad (6)$$

where r_0 is the equilibirum bond length, $\delta\theta_{ij}$ is the variation in the bond angle, and C_0 and C_1 are the bond-stretch and bond-bending coefficients, respectively. Experimental fits of these parameters for silicon yield $C_0=55$ eV and $C_1=3.2$ eV.[3] When the SW potential is expanded near equilibrium, we find that $C_0=61$ eV and $C_1=2.64$ eV. This agreement is surprisingly good considering that no mechanical information was used in determining the model parameters.

It appears that the SW potential provides us with a rather good model for both the properties of molten silicon and the bulk properties of solid silicon. In addition, the SW potential predicts a vacancy formation energy of 4.64 eV, which compares very well with quantum-mechanical calculations, which would predict a value of about 4.5 eV.[4] This leads us to believe that defect energies will be reasonably well treated by the SW potential, which may therefore be used for analysis of stability properties. However, to determine the suitability of this potential for simulation of crystal growth, we must examine the potential-energy surface which adatoms adsorbing from the vapor would encounter as growth of the first monolayer proceeds.

The case of homoepitaxial growth on the (111) surface of silicon is investigated in detail here. On this surface alternate atoms have dangling bonds which will interact with the vapor adatoms. The various surface reconstructions which have been observed by low-energy electron diffraction and other techniques on the (111) silicon surface are ignored, since no reconstruction occurs on this surface in the SW model. This is a direct result of limiting attractive interactions to the two-body term; a three-body term with attractive interactions may stabilize surface reconstructions. The surface potential seen by the initial adatom was then calculated for the (111) SW Si surface. This showed that the initial equilibrium position for an adatom is not directly above a surface atom with a dangling bond, as would be expected in a valence force-field calculation, but rather is equidistant from three surface atoms with dangling bonds. Thus, the energy gained by multiple bonding is larger than the energy lost by bond bending in this configuration. This agrees with qualitative quantum arguments.[5] Further computations of the potential for a surface with a few adatoms reveals that new adatoms will continue to adsorb in analogous positions on the original surface until the dangling bonds are used up. In the absence of surface domains this will occur at a surface coverage of $\frac{1}{3}$ monolayer.

The homoepitaxial growth of SW silicon on a (111) surface thus proceeds in a physically reasonable manner up to a nominal coverage of $\frac{1}{3}$ monolayer, given only that the substrate is held at a sufficiently high temperature for surface diffusion to readily occur. The growth process has been modeled to this point and beyond using a Monte Carlo technique developed by the author and used previously to study growth of Lennard-Jones SLS systems.[6] The qualitative picture deduced from the surface potential calculations is confirmed for coverages less than $\frac{1}{3}$ monolayer. After this point, however, additional adatoms must produce local reconstructions of the adatom structure so that a layer of (111) silicon can result. Such reconstructions depend critically on the accuracy of the SW potential for atomic configurations with very low coordination numbers (1,2). Unfortunately, these configurations are not handled well by the SW potential. The Monte Carlo growth routine shows that (111) silicon growth does not occur properly after the first $\frac{1}{3}$ monolayer, but rather an essentially amorphous structure is built up. Thus, the SW potential is insufficiently accurate for physically realistic simulation of crystal growth, despite

being quite suitable for bulk properties and probably adequate for stability analyses.

MODIFICATIONS OF THE SW INTERACTION POTENTIAL

The SW potential cannot be used to model crystal growth processes. Possible modifications will now be considered, both to the parameter set and to the potential itself, which might result in a useful description of growth from the vapor. One might force the growth of the tetragonal structure by making this structure energetically more favorable, either by increasing the size of the three-body term in general or by altering the three-body term to increasingly favor the tetragonal structure over other atomic configurations. The first possibility was checked by repeating the earlier analysis while changing λ from 21 to 60 (a smaller change is inadequate). Increasing the size of the three-body term does result in growth of (111) silicon. However, the initial adatoms no longer bond simultaneously to three silicon atoms, but adsorb in the final (111) configuration bound to a single surface atom, which is unphysical. Moreover, the change in λ was accomplished at the expense of the accuracy of the bulk equilibrium material properties, since the lattice is now a factor of 3 more rigid against bond bending than before. This results in a liquid-crystal–like melt and bulk equilibrium properties entirely different than those of silicon (notably, the phonon spectrum is drastically altered).

Although this simple alteration of the SW parameter set does not result in a physically reasonable interaction potential for silicon growth, it is possible to make the tetragonal structure more favorable without changing the equilibrium properties by changing the form of the potential. Specifically, a fourth-order angular term was added to Eq. (4).

$$h(ijk)=\lambda\{\gamma[(r_{ij}-a)^{-1}+(r_{jk}-a)^{-1}]\}\times[(\cos\theta_{ijk}+\tfrac{1}{3})^2+\epsilon(\cos\theta_{ijk}+\tfrac{1}{3})^4] \quad , \tag{7}$$

where ϵ controls the relative strength of the fourth-order angular term. Clearly, for θ near the tetragonal value, the fourth-order term is vanishingly small, and thus has no effect on the equilibrium properties. However, it favors the tetragonal local geometry more than does the original form of the potential, and thus may lead to realistic growth simulations. Upon testing this potential in the Monte Carlo growth routine, we find that (111) silicon growth occurs properly for ϵ above 10. However, this value for ϵ again corresponds to the value for which the initial adatom equilibrium positions change from triply bound to singly bound, indicating that the effort to grow reasonable (111) silicon within the general form of the SW potential results in unphysical early stages of epitaxy.

DISCUSSION

We have demonstrated that the Stillinger-Weber potential for silicon, in addition to the intended purpose of modeling molten silicon, provides a rather accurate model of the bulk mechanical properties of silicon, at least in the regime of small displacements. Unfortunately, although the potential does prove accurate enough in nontetrahedral geometries to do a reasonable job of modeling defect structures, explicit implementation of a continuous-space growth simulation procedure combined with energetic considerations reveals that the SW potential is inadequate for the characteristic geometries which arise during growth from the vapor, and that simple modifications of the SW potential do not change this situation.

More recently, other potentials for silicon having the general form of Eq. (1) truncated to two- and three-body terms have been introduced by Biswas and Hamann (BH),[7] and by Tersoff.[8] Both of these potentials attempt to include more information concerning the local environment surrounding the bonds of immediate interest, and are also fit to the large quantum-mechanical data base which exists for silicon. The result is that these potentials give more accurate results when applied to standard geometries, and are also transferable to a wider range of unconventional geometries. Thus, the BH and/or the Tersoff potentials are likely candidates for accurate simulation of the growth process. An indication that this is true is that both potentials yield reasonable reconstructions on silicon surfaces.[7,8] We are currently evaluating these potentials as to their suitability for growth simulation, but this will take some time, owing to the complexity of the continuous-space simulation routine.

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