New Extended Point Defect Structure in Diamond Cubic Crystals

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In the course of atomistic simulations of the dislocation array at the Ge/Si(001) interface, we have generated a new closed symmetric defect structure comprising eighteen atoms that may be found in a variety of circumstances including dislocation intersections and grain boundaries. The structure maintains tetrahedral bonding with reasonable changes in bond lengths and angles, and may have interesting electronic properties. At the Ge/Si interface, these extended point defects may reach a very high planar concentration of $\sim 10^{12}/\text{cm}^2$.

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The unique electronic and optical properties of strained multilayers depend critically on the structure of the interface. As a result, there is considerable interest in defect structures that may form to accommodate the lattice mismatch in strained heterostructures. We present here a new extended point defect structure predicted by numerical simulations that may occur at dislocation intersections at the Ge/Si(001) interface and in other boundaries. We believe that these are the first realistically scaled atomistic simulations of misfit dislocations and their possible intersections in semiconductor heterostructures. In the real physical problem modeled by the simulations, these eighteen-atom defects would form a square lattice with $a=96$ Å. We call the new structure the "dreidl" after the child's top that it resembles [1].

In the perfect diamond cubic and zinc blende structures, the atoms form sixfold rings viewed along $[1,\pm 1,0]$. Commonly observed defect structures are alternating fivefold and sevenfold rings, joined to form a figure of ten atoms with two shared by the pentagon and the heptagon. These occur, for example, in the core of the $(a/2)[1,1,0]$ edge dislocation [2,3], in the 90° partial dislocation [4], at the Si(111)-(2×1) surface [5], and in the Σ9 twin boundary [6,7]. In each case, the atoms retain tetrahedral coordination with modest changes in bond lengths and somewhat larger changes in bond angles. Figure 1 shows this fivefold plus sevenfold structure at the core of the $(a/2)[1,1,0]$ edge dislocation in Si.

There is almost precisely a 4% mismatch between the lattice constants of Ge and Si. When a film of Ge is grown epitaxially on an Si(001) substrate, the misfit strain can result in the formation at the interface of a regular two-dimensional array of edge dislocations with Burgers vectors $(a/2)[1,\pm 1,0]$. The experiments show that they are undissociated perfect edge dislocations, rather than partials [8].

We have done classical molecular dynamics simulations of this dislocation array for rather large microcrystals (~20000 atoms). These simulations for a 2D grid of dislocations at the interface of two misfitting crystals go beyond any previous classical simulations of dislocations by looking at large-scale periodic structures observed experimentally. Without describing the calculations in great detail, rectangular crystals of Ge and Si were constructed with axes long $x=[1,-1,0]$, $y=[1,1,0]$, $z=[0,0,1]$. The Ge crystal contained 48 layers along x and y, and the Si crystal 50 layers to match it in size. Each had 16 layers along z. The Ge crystal was then placed on top of the Si crystal, and to save computer time, the sample was preheated to dispose the system to form edge dislocations at the center along $[1,\pm 1,0]$.

The minimum energy structure of the dislocation grid was obtained by a sequence of simulated annealing runs followed by conjugate gradient minimization. Periodic boundary conditions were applied along x and y, and free surfaces along z. Two many-body empirical potentials were employed, namely, those of the Stillinger and Weber form [9,10] and of Tersoff [11]. Both potentials have been widely used, and give good agreement with bulk properties, e.g., the lattice constant, cohesive energy, and crystal structure. Furthermore, the latter has recently been shown to give reasonable agreement with *ab initio* total-energy pseudopotential calculations of the structure of the 90° partial dislocation in Si [4]. Computationally, however, these potentials cannot simply be plugged in to

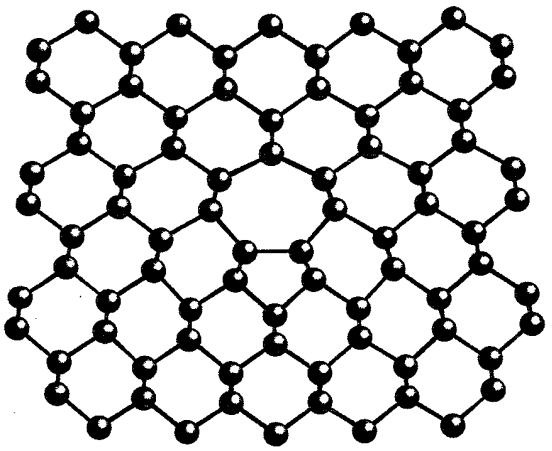

FIG. 1. The fivefold+sevenfold rings at the core of the $(a/2)[1,1,0]$ edge dislocation in diamond cubic semiconductors. The [001] direction is vertical and [110] horizontal. These results were generated by simulations in a small sample of 922 atoms of Si.

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simulate arbitrary problems because they have such short range, particularly the Tersoff model. A key step in our annealing procedure appears to have been an initial series of time steps with Stillinger-Weber at low temperature, rescaling the velocities every time step to damp the very large forces present at the center of our initial sample. An earlier run beginning at high T generated and locked in an amorphous structure at the interface.

Since the pentagon-heptagon structure is so ubiquitous, it is likely that combinations and intersections of it will also occur. Such is indeed the case for the array of dislocations in Ge/Si. The simulations yield orthogonal edge dislocations, each with the fivefold plus sevenfold core structure, with the core of one displaced above the other by one layer $a/4$ along [0,0,1]. At their intersection, they form the closed symmetric structure shown in Fig. 2, the dreidl. The fivefold rings join at the bottom, the sevenfold at the top. Although it is not completely obvious in the figure, every atom has fourfold coordination. The dreidl has one twofold rotation and two inequivalent mirror planes, and thus belongs to the point group $2mm$. At the outset of these calculations, we did not have in mind any particular structure for the dislocation intersections. In hindsight, its symmetry and tetrahedral bonding make the structure shown in Fig. 2 very believable.

With the Stillinger-Weber potential, the bond lengths in the dreidl differ by -5% to $+9\%$ from their perfect crystal values, and the angles differ from the tetrahedral angle $\arccos(-1/3)=109.47°$ by -12% to $+24\%$. Sensibly identical distortions are obtained with the Tersoff potential; the largest change in bond length for the latter is $+10.5\%$ compared to $+8.8\%$ for Stillinger-Weber, for example. These changes are slightly larger than those for the fivefold plus sevenfold rings at the cores of the individual dislocations. Five to six layers away from the dreidl along the dislocation cores, the largest changes in bond lengths and bond angles are (7–8)% and 20%, respectively, for both potentials. We have done simulations of single edge dislocations in Ge/Si(001) with the two-atom core wholly in the Ge film just above the interface, straddling the interface, and entirely in Si just below. These indicate that the fractional changes in bond lengths and angles in the core are determined primarily by its fivefold plus sevenfold ring structure rather than its location in Ge, Si, or at the interface.

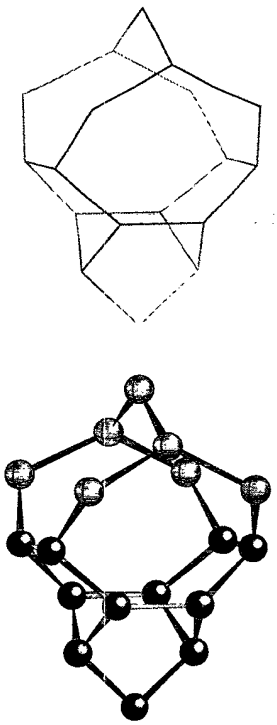

FIG. 2. The dreidl, the closed symmetric structure of eighteen atoms predicted by simulations to occur at the intersection of $(a/2)[1,\pm1,0]$ edge dislocations in Ge/Si. The [001] direction connects the bottom Si atom and the top Ge atom.

The changes in energy due to strain for individual atoms in the cores of the individual dislocations in the array are (5–6)% or less, while in the dreidl, where they are superimposed, the changes are at most (9–11)%. These are percentages of the calculated potential energies per atom in the perfect crystals, which are 4.33 and 3.85 eV for Si [9] and Ge [12] for potentials having the Stillinger-Weber form, and 4.63 and 3.84 eV for Si and Ge with the Tersoff potential, so the largest changes in energy are about 0.2 eV for single dislocations and 0.4 eV in the dreidl. It is somewhat difficult to compare total strain energies for intersecting and nonintersecting dislocations because the values for both depend on location and the numbers of atoms included. However, if we compare the strain energy of the dreidl with that for two pairs of fivefold plus sevenfold single dislocation cores along the [1,−1,0] and [1,1,0] directions at the Ge/Si interface, which is the simplest alternative, we find the intersection is energetically favored by 0.5–0.6 eV. Since these orthogonal dislocations do not interact except in their core regions, this may not be an unfair comparison.

To place these numbers in context, the *ab initio* calculations for the 90° partial in Si [4] yielded changes in bond lengths of as much as $-3.2\%,+5.4\%$ and in bond angles of $-12\%,+26\%$. The largest change in bond energy in the *ab initio* study of the $\Sigma9$ boundary in Si by DiVincenzo *et al.* [7] is 7.1%. The calculated strains and strain energies in the dreidl are somewhat larger, as should be expected at the intersection of two dislocations, but they are not unreasonable and instead may offer the possibility that the defect may have interesting electronic states.

It is a consequence of the way the simulations were done that the dislocation cores and the dreidl straddle the interface, with eleven Si atoms and seven Ge atoms in the latter. The experiments find the dislocations wholly within the Ge film [8]. In the electron micrographs, the cores of the individual dislocations are shown consistently

TABLE I. Calculated and experimental values for the elastic constants in units of 10^{12} dyn/cm^2. The model potentials used are those of Stillinger and Weber (SW, Ref. [9]), Ding and Andersen (DA, Ref. [12]), and Tersoff (T, Ref. [11]).

		SW	T	Expt.
Si	c_{11}	1.514	1.425	1.658
	c_{12}	0.764	0.753	0.639
	c_{44}	0.564	0.690	0.796
	K	0.710	0.775	0.904
		DA	T	Expt.
Ge	c_{11}	1.383	1.385	1.285
	c_{12}	0.509	0.444	0.483
	c_{44}	0.588	0.668	0.668
	K	0.704	0.754	0.733

in the Ge film at the interface. For dislocations that do not intersect, variations in offsets greater than $6(a/4) = 8.3$ Å would be required, and these are not observed. In the simulations, the core structures could be moved up or down relative to the interface by the simple expedient of replacing Si atoms with Ge or vice versa. However, the Stillinger-Weber and Tersoff potentials are not really well suited to study the energetics as a function of core location along [0,0,1] because, for Si, each gives a smaller value than experiment for the particular combination of elastic constants that determines the strain fields and energies outside the core of a dislocation.

The integrated elastic strain energy per unit length of a dislocation at a radius R is [13]

$$E = (Kb^2/4\pi)\log(R/r_0),$$

where b is the Burges vector, r_0 is the core radius, and K is a combination of the elastic constants. For a [1,1,0] edge dislocation in an fcc (or zinc blende) lattice,

$$K = (C_{12}+c_{12})\{c_{44}(C_{12}-c_{12})/[c_{11}(C_{12}+c_{12}+2c_{44})]\}^{1/2},$$

$$C_{12} = [c_{11}(c_{11}+c_{12}+2c_{44})]^{1/2}.$$

Table I compares our calculated values for the elastic constants for the several potentials [14] with the experimental values. The calculated and measured values of c_{ij} appear to agree reasonably well for Ge, less so for Si where the largest discrepancy is -29% for c_{44} with Stillinger-Weber and $+18\%$ for c_{12} with Tersoff. For K, the combination appropriate for dislocation energetics, each softens Si relative to Ge, Stillinger-Weber by 22%, and Tersoff by 11%, and each gives nearly identical values for K_{Si} and K_{Ge}. In short, neither potential will favor location of the dislocation grid in the Ge film as preferentially as would a potential that more accurately predicted the measured difference of about 20% in the K's. We believe this will not affect the atomic structure in the cores of the dislocations or at their intersections. This was proven to be the case for individual edge dislocations for both potentials and for the 90° partial calculation with the Tersoff potential [4].

It is interesting to speculate how the presence of these large "point" defects might influence the electronic and mechanical properties of the interface. Because there are no dangling or extra bonds, it may be conjectured by analogy with the 90° partial [4] that electronic states localized at the dreidl will not penetrate deep into the band gap. However, the simulations predict larger changes in bond lengths and strain energies in the dreidl than those reported [4–7] for the linked fivefold plus sevenfold ring structure, so the possibility of electronic states deeper in the gap cannot be dismissed. *Ab initio* calculations to explore this question are under way. In addition, impurities can segregate to dislocations, altering the properties of both the bulk material and, in this case, the interface. In the open volume at the top of the defect, hard sphere estimates with radii of 1.2 Å for Si and Ge show space for an interstitial atom with a radius of nearly 2 Å.

The electrical properties of semiconductors are controlled by point defects, at densities as low as 10^{11}/cm^3 in Si at room temperature. In this connection, it is worth emphasizing that the distance between dislocations in the array is ~ 100 Å, and that the concentration of dreidls would be $\sim 10^{12}$/cm^2 at the Ge-Si interface, forming a square lattice. For a film with twenty layers of Ge, or about 30 Å, this translates to a 3D density of $\sim 3\times 10^{18}$/cm^3, which is large enough to significantly affect device performance. The dreidl may also occur in grain boundaries and at walls separating domains in surface reconstructions. Two experimental methods that might be used to search for its existence are x-ray scattering and photoluminescence.

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[1] Dreidl (rhymes with cradle): "a 4-sided toy marked with Hebrew letters and spun like a top in a game of chance" [*Webster's Ninth New Collegiate Dictionary* (Merriam-Webster, Springfield, MA, 1989)].

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