Electronic and Structural Properties of a Twin Boundary in Si

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A second-order twin boundary in Si, of the $\Sigma 9$ type, is investigated with first-principles density-functional theory and with an empirical tight-binding model. Of two proposed reconstructions studied, the one supported by recent experiment is energetically favored, with less bond stretching than the other. A conduction-band-edge interface electronic state associated with bond-angle strains is found. A phonon resonance, the interfacial analog of a Rayleigh mode, is predicted; Raman spectroscopy should be able to detect it.

Grain boundaries, interfaces between two crystal grains with different orientations, are present in almost all real solids. As discussed in a recent review,[1] modern advances in materials science have for the first time permitted the controlled and clean preparation of specific grain boundaries,[2] paving the way for studies of the physical properties of these internal interfaces.

This paper presents a theoretical study of a grain boundary which is very common in multiply twinned Si crystals, the so-called "$\Sigma 9$" boundary.[3] We examine two proposed models[3] for the atomic reconstruction of this boundary. Although neither model contains dangling bonds, we find one model (the "glide-plane" model) to have better formed bonds near the boundary, and to suffer from much less boundary strain, than the other model (the "mirror-plane" model). The glide-plane model is thus favored energetically; this supports the results of recent experiments.[2] We also present electronic band calculations (the glide-plane model appears to have localized interfacial states associated with the conduction-band edge), as well as tentative results on grain-boundary phonons (an interfacial analog of the Rayleigh wave is found).

We have applied two different methods to this problem: (1) density-functional theory within the local-density approximation (LDA), using a local orbital basis and norm-conserving pseudopotentials[4]; and (2) the semiempirical tight-binding total-energy method.[5] The present work represents the first application of a first-principles technique to twin boundaries in crystals. LDA calculations of similar quality have recently appeared for stacking faults in Si,[6] and the $\Sigma 9$ boundary has previously been studied by an empirical method very closely related to ours.[5]

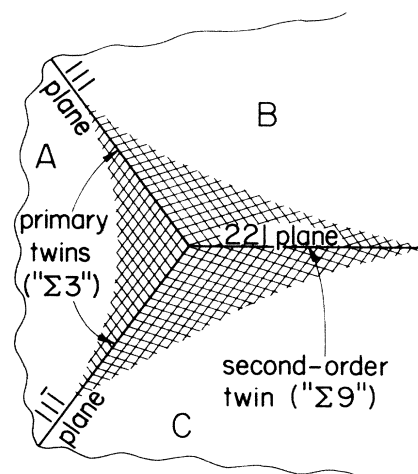Figure 1 illustrates how the $\Sigma 9$ boundary occurs nat-

FIG. 1. Multiple twinning and the $\Sigma 9$ boundary. Very common in polycrystalline growth in semiconductors is the formation of a "primary twin" ($\Sigma 3$) across a (111) plane. However, a grain may twin across crystallographically distinct (111) planes to produce new grains of several different orientations; in the figure, grain A twins across its ($1\bar{1}1$) plane to form grain B, and across its (111) plane to form twin C. (The view is down the [$1\bar{1}0$] axis.) The (111)-type planes containing the [$1\bar{1}0$] axis are sketched in each grain, indicating their relative orientation. A definite misorientation results between grains B and C, $38.94°$, and the boundary between them is a twin of a definite type. It is called a second-order twin or $\Sigma 9$; the plane common to both grains is of a (221) type.

urally in multiple twinning. ($\Sigma 9$ has also been made synthetically.[1]) The easy planes for twinning in semiconductors are of the (111) type; when a single grain twins across two crystallographically inequivalent (111) planes (forming so-called "$\Sigma 3$" twins[3]), the resulting two grains are misoriented by 38.94° and the boundary between them is a "second order" twin,[2] the $\Sigma 9$.

Figure 2 shows two different reconstruction models which have been proposed[3] for $\Sigma 9$. The first has a glide-plane symmetry and has a sequence of five- and seven-membered rings very reminiscent of the Si(111) 2×1 surface reconstruction. The second has a mirror symmetry and contains a linear sequence of seven-, six-, and five-membered rings. Recent high-energy electron microscopy[2] finds a glide-plane symmetry at the boundary, favoring the first model.

The first step of our calculation is to find the equilibrium atomic geometry for the two reconstructions.
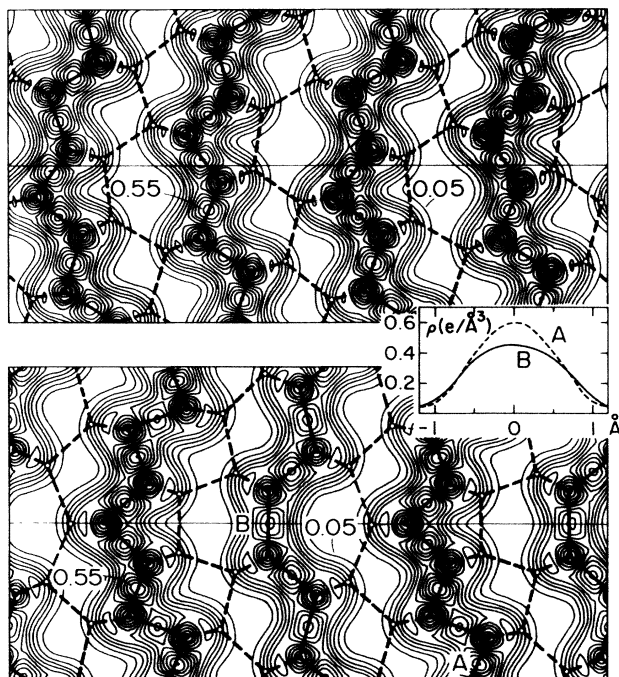

FIG. 2. Relaxed atomic structure and charge density for two different models for the $\Sigma 9$ boundary. Top: the glide-plane reconstruction. Bottom: the mirror-plane reconstruction. Both are views down a [110]-type axis; they are periodic in this direction with period $a = 4.07$ Å. Half of the atoms lie in the plane shown (solid circles), and half lie in a plane translated $a/2$ in the [110] direction (open circles). The valence density calculated within LDA is shown; contour spacing is 0.05 $e/\text{Å}^2$. In the mirror-plane reconstruction, some interface bonds are significantly weaker than bulk bonds; the inset, a plot of the charge density along the two indicated bonds A (bulklike) and B (in the boundary), shows that the bond charge is reduced by $\approx 25\%$ in the interface.

Because of the computational complexity of this task, we assign it to the semiempirical tight-binding method. This technique in its various modifications has proved successful in describing exotic crystal structures, surfaces, clusters, and boundaries.[5] To explain it briefly, the Si energy bands are fitted with a standard four-orbital sp^3 nearest-neighbor hopping model; the total energy is taken as the sum over the band energies minus the double-counting terms and electron-ion terms which are modeled as a sum of pairwise interactions. We have determined the minimum-energy state for both structures within this model, permitting both relaxations of atoms within the unit cell and changes in the grain-boundary thickness. Symmetry-breaking distortions are allowed for, but do not occur.

We extensively study the resulting equilibrated structures using a first-principles density-functional theory.[4] We use the local-density approximation with a Ceperley-Alder exchange-correlation functional and norm-conserving pseudopotentials of the Hamann-Schlüter-Chiang type. The Gaussian basis set consists of two s orbitals, three p's, and the three d's, which have full tetrahedral symmetry.[4] These orbitals have been shown to give well-converged results for the bulk crystal.[4] As a test, we have used this basis set to compute the energy of ST-12, a complex crystal phase with distorted tetrahedral bonding and odd-membered rings of bonds, making it similar to $\Sigma 9$. We find its energy to be 0.06 eV/atom lower than diamond Si, in good agreement with the plane-wave result of Biswas et al.[7] (0.04 eV/atom).

All the computations are carried out with use of a supercell technique, in which pairs of copies of the grain-boundary plane are repeated periodically normal to the plane, so that a fully periodic structure is obtained. We studied both 36-atom and 40-atom supercells, corresponding to boundary plane spacings of about eight (111) atomic layers. Unless otherwise stated, the results quoted below will be for the 40-atom cell.

As Table I shows, the LDA calculation, as well as the tight-binding model, definitely favors the glide-plane reconstruction over the mirror-plane one, even when the uncertainty due to supercell effects (± 50 ergs/cm^2) is accounted for. Various experimental techniques are available for obtaining interface energies[9]; to our knowledge, none have yet been applied to the present boundary. The boundary energy for the glide-plane model converts into 0.17 eV per bond crossing the interface. This is small relative to the ~ 2.4-eV bond energy in Si—the bonds across the interface are well formed. It is also about a factor of 6 lower than a typical surface creation energy for Si[5]; on the other hand, it is an order of magnitude larger than the energy of a stacking fault.[6]

The total valence charge plotted in Fig. 2 shows why

TABLE I. Comparison of the interfacial energies and volume change for the glide-plane and mirror-plane reconstructions, and phonon frequencies for the glide-plane model. The experiment (Ref. 2) quoted for the volume change is for Ge; Si is reportedly (Ref. 8) very similar. Both the interface energy and the volume change favor the glide-plane model. Δa is the difference between the equilibrium position of a typical atom in the tight-binding and in the local-density calculations, projected along the phonon normal-mode displacement.

Calculation scheme	Interfacial energy (ergs/cm^2)			Volume change[a] per unit boundary area (Å)			Phonons-GPM[b] (meV)	
	GPM[b]	GPM[c]	MPM[b]	GPM[b]	GPM[c]	MPM[b]	$\hbar\omega_1(\Delta a_1 \leq 0.05$ Å$)$	$\hbar\omega_2(\Delta a_2 \leq 0.05$ Å$)$
Local-density approximation	240	290	910	d	+0.05	d	12.3	15.5
Tight-binding total energy	120	210	665	+0.04	+0.05	−0.11	11.1	14.1

[a]Experiment (Ref. 2): +0.26 ±0.13 Å.
[b]36-atom cell.
[c]40-atom cell.
[d]Not investigated thoroughly.

the mirror-plane reconstruction is unfavorable. While in the glide-plane reconstruction every bond charge is virtually identical to a bulk bond, in the mirror-plane reconstruction some of the near-boundary bonds are significantly weaker than bulk bonds. The inset of Fig. 2 shows that one particular bond (bond B) in a six-membered ring inside the boundary has a 25% smaller bond charge than a bulk bond (bond A). This weakening is associated with a 5% stretching of bond B; no bond in the glide-plane model is stretched or compressed by $\geq 1\frac{1}{2}\%$.

Considerable care has been taken to assure the accuracy of the LDA calculations:

(1) Self-consistency is always achieved such that the total energy is converged to 0.005 eV per interface bond.

(2) Calculations have been carried out with both 36-atom and 40-atom supercells. The interface energy, volume change (see Table I), and charge density are all satisfactorily converged.

(3) We have checked the convergence of our results with respect to basis-set size (extra d orbitals were added to grain-boundary atoms) and Brillouin-zone sampling (mesh was increased from three per irreducible sector to eight). While absolute energies are affected, relative energies are not; in both cases, phonon frequencies are unchanged to within 1%.

(4) Most important, we have checked that the tight-binding and LDA equilibrium structures agree. It is computationally impossible for us to check agreement in every structural degree of freedom (18 for the 36-atom cell). We have therefore devised a scheme which probes the most important degrees of freedom: Within the tight-binding model we diagonalize the dynamical matrix to find the interface phonon eigenfrequencies and eigenvectors. Using the LDA, we then calculate the changes in the total energy resulting from moving the grain-boundary atoms along the eigenvectors corresponding to the lowest-lying Γ_1^+

phonon frequencies. We reason that it is for these softest modes that the structure as obtained with the tight-binding method is most likely to be in error.

As the table indicates, our calculations show that the tight-binding relaxed structure is already very close to equilibrium, with typical additional atom motions of < 0.05 Å for these lowest-lying modes and bond-length changes < 0.01 Å. In addition, we find frozen phonon frequencies in extremely close agreement with those obtained by diagonalization of the tight-binding dynamical matrix.

The second of the phonons listed in Table I is of significant physical interest. Analysis of the atomic motions shows it to be an interfacial analog of the surface Rayleigh mode. This mode is Raman active; to our knowledge, a Raman measurement has never been performed for a grain boundary.

Figure 3 shows our results for the electronic energy bands of the glide-plane model for $\Sigma 9$. There are no electronic states deep inside the gap, which is expected since the grain boundary contains no dangling bonds. Shallow states do occur, that is, bands in the gap associated with the conduction- or valence-band edges. Unfortunately in a supercell geometry it is impossible to distinguish unambiguously between localized and extended states.

However, an examination of the conduction-band-edge state (Fig. 3, middle) shows that it is definitely an interface state. Its charge density is mostly localized in the backbond regions of atoms with strongly bent bonds. Preliminary measurements[10] have not detected carrier traps at this interface, but we expect that other probes (photoluminescence, perhaps) should reveal the presence of this conduction-band-edge localized state.

The charge density of the valence-band-edge state, on the other hand, shows no tendency to be localized at the interface (Fig. 3, bottom). We expect that a more accurate theory (a much larger supercell calcula-
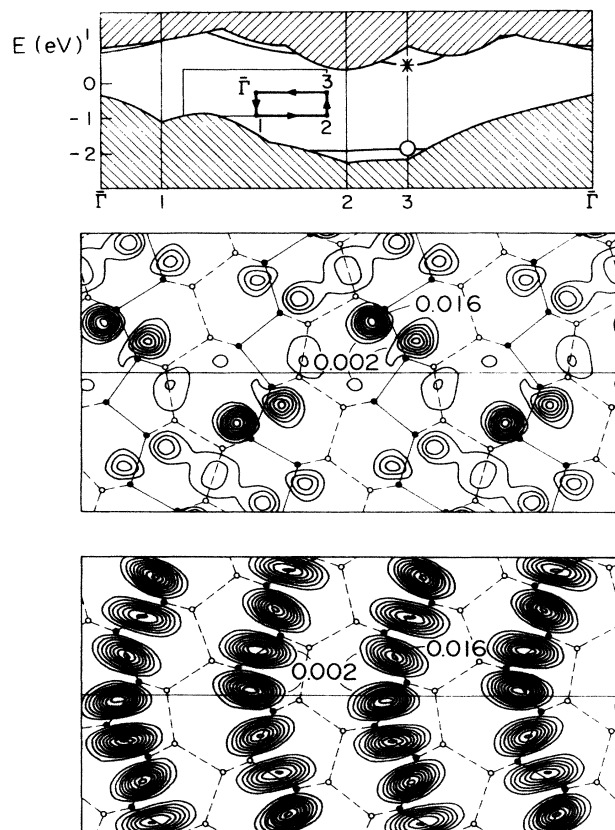
FIG. 3. Interfacial electronic structure near the fundamental gap. Top: energy bands calculated within the LDA. The projection of the bulk bands are hatched; inset: the interfacial Brillouin zone and the wave vectors which have been plotted. Bands appear to emerge from the continuum from both the conduction- and the valence-band edges. Middle: A study of the charge density of one of the conduction-band-edge states (asterisk) shows that it is indeed localized to the interface, with charge residing mainly in the backbonds in regions of large bond-angle strain. Bottom: The charge density of one of the valence-band-edge states (open circle) indicates that this state is not localized to the boundary.

tion or a Green's-function calculation) would push this state inside the bulk continuum.

To summarize, we have presented the first LDA cal-culation of the electronic and structural properties of a twin boundary, the $\Sigma 9$ in Si. Complemented by an empirical tight-binding total-energy model, the calculation proves that the glide-plane reconstruction is energetically favored over the mirror-plane reconstruction, showing that strains and the concommitant disturbance of chemical bonds is much less in the former than in the latter. We have identified an interesting phonon mode, the interfacial analog of a surface Rayleigh mode, and propose a Raman experiment to study it. We also predict a conduction-band-edge localized electronic state.

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