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Correlation between atomic structure and localized gap states in silicon grain boundaries

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Tight-binding molecular-dynamics simulations of a typical high-energy grain boundary in silicon show that its equilibrium atomic structure is similar to that of bulk amorphous silicon and contains coordination defects. The corresponding electronic structure is also amorphouslike, displaying gap states mainly localized around the coordination defects, where large changes in the bond-hybridization character are observed. It is proposed that such coordination defects in disordered high-energy grain boundaries are responsible for the experimentally observed gap states in polycrystalline Si. [S0163-1829(98)07308-1]

It is well known that the electrical properties of polycrystalline Si are dominated by localized electronic states in the band gap closely connected with the presence of grain boundaries (GB's). Such gap states can act as traps for charge carriers, thereby altering the electrical nature of the material. For example, in the case of *p*-*n* junctions for solar cells[1] the GB's provide effective recombination centers for the light-generated charge carriers, thereby reducing device performance.[1,2] Optical and electronic measurements on fine-grained Si films indicate the presence of exponential band tails penetrating into the band gap and narrow continua of states located deeper in the band gap.[3–5] The band tails are thought to be connected with structural disorder,[6] through either the smearing of bulk states or the appearance of ''shallow'' gap states (i.e., new states at the band edges). The deep gap states, in turn, are usually attributed to either dangling bonds (i.e., threefold coordinated Si atoms) or to segregated impurities. Unfortunately, the fact that polycrystalline Si always contains sizable amounts of hydrogen and other impurities is a significant difficulty for the experimental investigation of the effect of GB's on the electronic properties. The structural and electronic properties of ideally pure GB's are, therefore, a subject particularly suitable for computer simulations.

Recent empirical-potential molecular-dynamics (MD) simulations of large-unit-cell Si GB's, either grown from the melt or annealed at high temperature, and subsequently cooled to $T=0$ K,[7] revealed a common, highly disordered GB structure of uniform thickness (typically ~ 5 Å) and energy. By comparison with the zero-temperature relaxed input structure of these same GB's, the high-temperature annealed structure had a lower GB energy, thus representing the thermodynamic ground state. Moreover, the universal, ''confined amorphous'' structure of these GB's was found to be very similar to that of bulk amorphous Si (*a*-Si); in particular, a small fraction of coordination defects was found to exist in this equilibrium structure. Here we propose that these coordination defects are the origin of the experimentally observed gap states in polycrystalline Si. Our analysis is based on a tight-binding (TB) study of the correlation between the structural and electronic properties of a representative high-energy GB in Si. In agreement with the empirical-potential simulation results,[7] we find that the GB structure obtained after high-temperature annealing is highly disordered and has a lower energy than the corresponding zero-temperature relaxed structure. Moreover, the electronic density of states (DOS) of atoms in the GB region displays the typical features of *a*-Si, namely, the smearing of the valence *s* and *p* subbands and a flat conduction band, and several localized gap states. By computing the site- and orbital-projected local DOS, we demonstrate that the presence of gap states in the electronic structure is strictly correlated to the presence of coordination defects in the atomic structure. Moreover, from the relative occupations of the *s* and *p* orbitals we conclude that gap states arise from the change in the hybridization character of the local bonding around such coordination defects.

Previous electronic-structure simulations of Si GB's based on zero-temperature static relaxation have mainly focused on symmetric-tilt boundaries,[8–10] known to have a relatively low energy compared to large-unit-cell, high-angle twist GB's.[11] The main result of these studies is that such GB's, are relatively ordered and hence do not contribute deep gap states to the DOS. Similar simulations of twist GB's in Si (Ref. 12) and Ge (Ref. 13) revealed, by contrast, more disordered structures, containing coordination defects and exhibiting a broad continuum of gap states. It therefore appears that, although the highly disordered, high-energy GB's represent only a minor component of a well-annealed coarse-grained microstructure, their pronounced electrical activity may dominate the electrical behavior of rather pure polycrystalline Si. Such a dominance should become even more pronounced in fine-grained (10–50 nm) microstructures, in which a much larger fraction of high-energy GB's should be present.[14] Electrical measurements have, indeed, demonstrated a significant increase in the density of gap states with decreasing grain size.[4] These observations suggest that insights into the electrical behavior of polycrystalline Si can be obtained from an understanding of the *high-energy* GB's.

As pointed out in earlier studies,[7] from a purely geometric point of view the twist GB's on the (001) plane of the Si diamond lattice are representative of virtually all high-energy GB's, since two out of four bonds (50%) of each GB atom involve partners across the interface, while the remaining two bonds are within the same grain. This results in high GB energies, compared to the GB's on the two densest planes [i.e., (011) and (111)], in which only one bond per atom is directed across the interface. Based on these findings,[7] we choose the (001) $\phi=43.6°$ (so-called $\Sigma 29$) twist boundary as a typical high-energy GB for our TB-MD simulations; this GB has a planar unit cell $\Sigma=29$ times larger than the primitive planar unit cell of perfect-crystal (001) planes. Similar simulations will be performed also on the (001) $\phi=36.9°$ ($\Sigma 5$) twist GB, which, as will be shown, displays all the basic features of the $\Sigma 29$ GB; however, its smaller planar unit cell will enable us to expose more clearly the correlation between atomic and electronic structure.

In all our simulations we consider a three-dimensionally periodic supercell with 24 (001) planes, containing two identical GB's separated by 12 (001) planes. The z dimension of the simulation cell is then equal to $L_z=6a_0$, while the x and y dimensions are equal to $L=(\frac{29}{2})^{1/2}a_0$ and $L=(\frac{5}{2})^{1/2}a_0$ for the $\Sigma 29$ and $\Sigma 5$ supercells, containing 696 and 120 atoms, respectively; $a_0=5.43$ Å is the Si lattice parameter. To describe the covalent bonding in Si we use an orthogonal TB Hamiltonian based on the minimal sp^3 basis set;[15] this TB parametrization is known to give a good description of Si point-defect properties.[16] Although less accurate than a fully *ab initio* model, the TB formalism is nevertheless capable of describing in a simple and intuitive way the physics of covalent bonding and rehybridization in the presence of disorder, thus capturing the basic correlation between atomic structure and electronic properties. Moreover, MD simulations of such large systems as the $\Sigma 29$ GB are presently out of each for *ab initio* techniques.

The input supercell configurations for the two GB's were obtained by high-temperature equilibration followed by cooling to, and relaxation at, zero temperature[7] using Tersoff's empirical potential.[17] These configurations were then subjected to TB-MD annealing at $T=700$ K, followed by cooling to, and relaxation at, $T=0$ K with TB quantum-mechanical forces. The relaxation was terminated when the largest force was smaller than 0.03 eV/Å. Stress relaxation in the z direction perpendicular to the GB plane was allowed in both the Tersoff and TB cycles while keeping the xy-plane dimensions fixed so as to mimic embedding of the GB between bulk material.

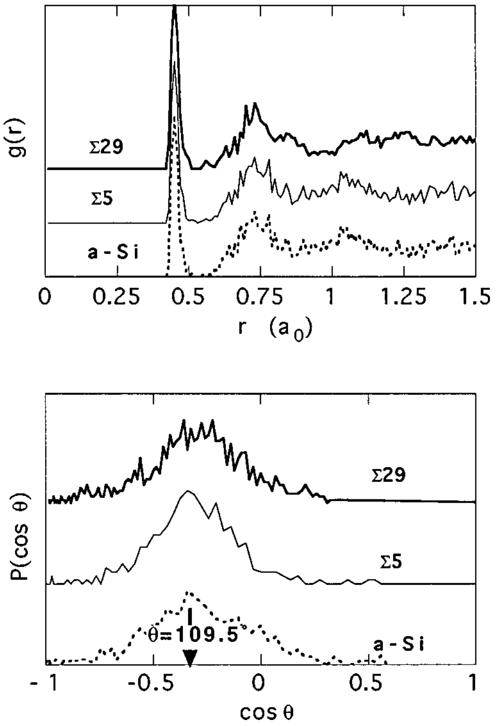

FIG. 1. Pair distribution function (upper panel) and bond-angle distribution function (lower panel) averaged over the atoms in the planes adjacent the $\Sigma 29$ and $\Sigma 5$ grain boundaries. Dashed lines are the corresponding distribution functions for a-Si. The arrow in the lower panel indicates the crystalline-Si tetrahedral angle of $\theta=109.5°$.

The high-temperature-annealed $\Sigma 29$ and $\Sigma 5$ GB's, display a disordered structure extending over a width of about 5 Å. Figure 1 shows the pair distribution function $g(r)$ and the bond-angle distribution function $P(\cos\theta)$, for the atoms comprised within the disordered region $\pm a_0/2$ from the GB of both GB's. Both sets of curves are very similar to the same distributions for a-Si (dotted line in Fig. 1), also obtained with the procedure described above. These GB's have excess energies of $E_{\mathrm{GB}}=1846$ and 1497 mJ/m^2, respectively. Both values are about 14% lower than the corresponding zero-temperature relaxed GB energies, in agreement with the value of about 10% energy lowering obtained by empirical-potential simulations on several high-energy GB's.[7] The average coordination in the GB regions is 4.05, somewhat lower than the empirical-potential value of 4.21,[7] but in good agreement with *ab initio*[18] and TB (Ref. 19) results for a-Si. All the above TB-MD findings confirm the previous empirical-potential results,[7] thus supporting the notion that high-energy GB's in Si, indeed, exhibit a universal, confined-amorphous structure under thermodynamic-equilibrium conditions.

We now turn to the study of the electronic properties of these confined-amorphous GB's. The electronic structure is calculated by sampling the **k** space of the relaxed GB supercell, using the $\mathbf{k}=0$ Γ point for the $\Sigma 29$ GB, and with a uniform mesh corresponding to about 2000 points in the ir-

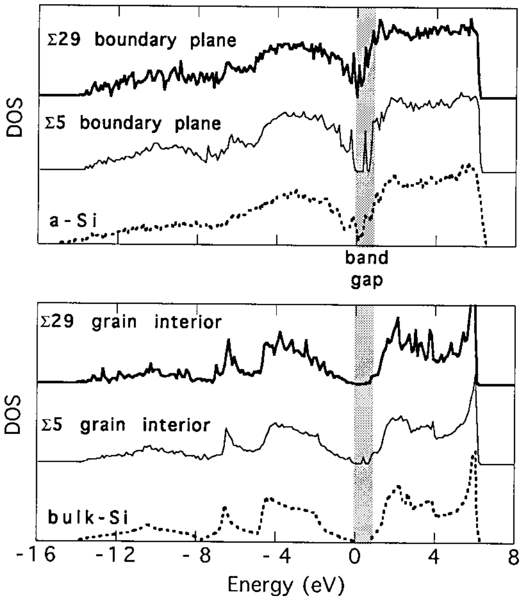

FIG. 2. Upper panel: Electron DOS averaged over the atoms in the Σ29 and Σ5 grain boundaries; the dashed line corresponds to the *a*-Si DOS. Lower panel: Electron DOS averaged over the atoms in the planes at a distance $\pm a_0$ from the grain boundaries; the dashed line corresponds to the crystalline-Si DOS. The shaded region indicates the crystalline-Si band gap (0.0–0.78 eV).

reducible Brillouin zone of the diamond lattice for the Σ5 GB. Energies are measured with respect to the top of the valence band in the perfect crystal. The bottom of the conduction band (also defining the band gap) for this TB representation lies at 0.78 eV.

Figure 2 shows the local DOS averaged over the atoms in the disordered GB structure (top panel), and in the perfect-crystallike planes (bottom panel) at $z \sim \pm a_0$ from the GB, for both the Σ29 and the Σ5 GB's. By comparison with the *a*-Si DOS (also shown in the top panel of Fig. 2), obtained with the same **k**-space sampling density as above, it can be seen that the GB region is, indeed, amorphouslike also from an electronic-structure point of view. The local DOS shows the broadening of the valence *s* and *p* subbands (centered at about -10 and -4 eV, respectively, in the perfect crystal), characteristic of *a*-Si;[20] the conduction band is almost flat, in agreement with x-ray-absorption measurements on *a*-Si.[21] Only minor features of the perfect-crystal DOS persist in the GB local DOS, such as the small *s*-*p* mixing peak at about -6 eV. Several peaks in the band-gap region are visible; their origin will be discussed in more detail below. By contrast, the local DOS of atoms in the planes at $z \sim \pm a_0$ is practically identical to that of crystalline Si, also shown in the bottom panel of Fig. 2, with only very minor signatures of the gap states; the latter are mostly due to finite-size effects.

The correlation between the atomic structure of the GB and the gap states appearing in the GB local DOS can be elucidated by computing at each atom a localization index for the eigenvalues corresponding to the gap-state energies. The localization index $L_{n,i}$ for the *n*th eigenvalue at atom *i* is defined as $L_{n,i} = \Sigma_\alpha |c_{n,i\alpha}|^2$, and gives the probability for atom *i* to contribute to that eigenvalue. $L_{n,i}$ is thus equal to $1/N$ for a fully distributed state in a supercell with *N* atoms, and equal to 1 if the state is entirely localized on atom *i*; we will consider a state to be at least partially localized whenever $L_{n,i} \geqslant 0.15$. By summing $L_{n,i}$ over the atoms in each GB for the eigenvalues corresponding to the sharp gap peaks in the GB local DOS, values of $\Sigma_i L_{n,i} \sim 0.5-0.7$ are obtained, indicating a distinctive localization of the gap states at the GB regions.

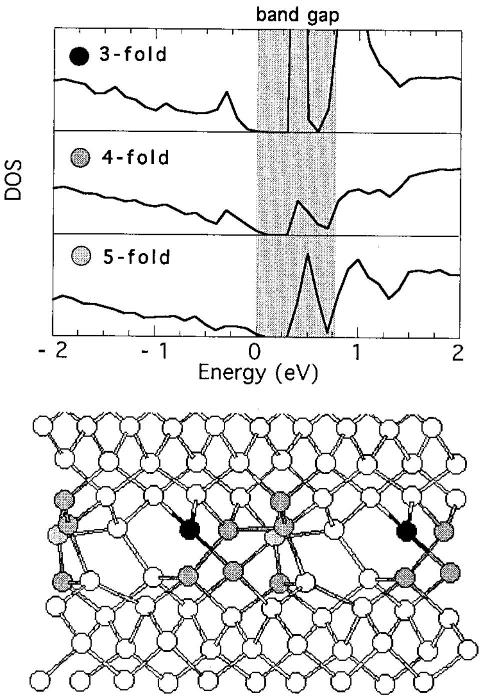

FIG. 3. Upper panel: electron DOS for representative threefold, fourfold, and fivefold coordinated atoms in the grain-boundary region; the shaded region indicates the crystalline-Si band gap. Lower panel: equilibrium structure of the Σ5 grain boundary, with the atoms displaying localized gap or edge states highlighted (black, threefold; dark gray, fourfold; light gray, fivefold coordinated atoms).

A detailed analysis of the correlation between the localization index and the local atomic structure reveals that localized gap states in the electronic structure arise from coordination defects in the disordered atomic structure of the GB. This correlation can be seen rather nicely already in the Σ5 GB. Figure 3 shows the equilibrium configuration of this GB, in which all the atoms satisfying the localization criterion $L_{n,i} \geqslant 0.15$ are highlighted. All of the threefold and fivefold, and some of the fourfold coordinated atoms in the GB structure are found to display localized states; the local DOS's for three such atoms (one for each coordination state) are also shown in Fig. 3. From this analysis it appears that deep gap states are mostly localized at coordination defects, with very high values of the localization index (up to $L_{n,i} \sim 0.38$). Shallow band-edge states turn out to be localized (with only minor exceptions represented by fourfold coordinated atoms in odd-membered rings) either at such defects or at their nearest neighbors, with somewhat more distributed values of $L_{n,i}$.

The nature of the gap states becomes apparent when analyzing the local bonding around coordination defects in terms of its *s*- and *p*-orbital components. The distribution of the band-structure energy (i.e., the sum of the single-particle energies for the occupied states), $U_{\rm BS}$, has large variations around the coordination defects. Such variations, $\Delta U_{\rm BS}$, can be traced back to a change in the degree of s-p mixing, by calculating for each atom i the s-p mixing parameter,[10] $M_i = N_{ip}/N_{is}$, with $N_{ip}=\Sigma_{n,\alpha}|c_{n,i\alpha}|^2$, $\alpha = p_x, p_y, p_z$, and $N_{is} = \Sigma_n |c_{n,i\alpha=s}|^2$. Perfect sp^3 hybridization would result in $M_i = 3$ (but even in the perfect crystal, for which we obtain $M_i = 1.684$, bonds are never formed from complete sp^3 hybrids), while $M_i = 1$ is the value for a free Si atom with its valence electrons evenly distributed in unhybridized $3s$ and $3p$ orbitals. In general, we find a good linear correlation between $\Delta U_{\rm BS}$ and M_i. The largest variations for both $\Delta U_{\rm BS}$ and M_i are observed for the threefold defect, with $\Delta U_{\rm BS} = 3.05$ eV and $M_i = 1.35$; such a value of M_i reflects a drastic change towards a s^2p^2-like hybridization,[10] the dangling electron tending to form states with a large s-orbital component. All the fivefold defects also have sizable variations of the hybridization character, $M_i \sim 1.5$, and $\Delta U_{\rm BS} = 0.8-1.4$ eV. Also, those fourfold coordinated atoms that are neighbors to two coordination defects display variations of M_i in the same range combined with very large values of $\Delta U_{\rm BS}$. Clearly, such large changes in the s-p hybridization character around coordination defects are responsible for the appearance of gap states at energies that are extraneous to tetrahedrally bonded Si.

The main conclusion of our study is that gap states in *pure* polycrystalline Si can originate from coordination defects present in the amorphouslike structure of the high-energy GB's. It is noteworthy that a similar correlation between coordination defects and localized gap states had previously been found in a detailed theoretical study of a-Si.[22] Despite this, the connection between the localization behavior of coordination defects in a-Si and localized gap states in polycrystalline Si has gone practically unnoticed. This is even more surprising, considering that an amorphouslike behavior of GB's had been repeatedly suggested in the analysis of various experimental results.[3,4,23] Although impurities may also play an important role, the above results demonstrate that gap states in polycrystalline Si, arising from coordination defects existing *in thermodynamic equilibrium*, are an intrinsic feature of the universal, disordered structure of the high-energy GB's.

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