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Theoretical study of the electronic structure of a high-angle tilt grain boundary in Si

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We have constructed a model of a high-angle tilt boundary in Si and have examined its atomic and electronic structure. The 38.94° grain boundary studied contains fivefold and sevenfold rings of atoms in positions almost identical to those observed in high-resolution transmission electron microscopy. The grain boundary is continuous on a microscopic scale and does not contain any dangling bonds. The atomic positions on the two sides of the boundary are similar to those resulting from the joining of two crystals, aligned approximately in the directions of their respective [111] and [110] axes, along their common (221) surface. The two crystals have commensurate lattice sites on this surface. As a result, the grain boundary propagates on a macroscopic scale with no dislocations or strain due to lattice mismatch. We have performed energy-minimization calculations to determine the optimum atomic structure of the grain boundary. The calculated electronic structure for the optimized geometry has no defect states in the bulk band gap. The calculated surface energy per unit area of 0.02 eV/Å^2 for the grain boundary is appreciably lower than that obtained for any of the free surfaces of Si because of the absence of dangling bonds at the grain boundary. Static charge fluctuations of $-0.14|e|$ and $0.06|e|$ are found at the boundary.

I. INTRODUCTION

Grain boundaries are among extended intrinsic defects found in most metals and semiconductors. They form in regions where the surfaces of two small crystals of differing orientations meet. By using modern high-voltage, high-resolution electron microscopy it is possible to obtain direct-lattice images of such defects. There have been a number of applications of this method to the study of grain boundaries in semiconductors.[1–7] Grain boundaries which involve only a rotation about an axis in the plane of the boundary, called pure tilt grain boundaries, are especially suited to this technique. This is because viewed at the proper angle, such boundaries consist of parallel columns of atoms, a property which makes them much easier to image than twist grain boundaries.[6] Both high-angle[1–3] and low-angle[4] tilt grain boundaries have been examined in this way.

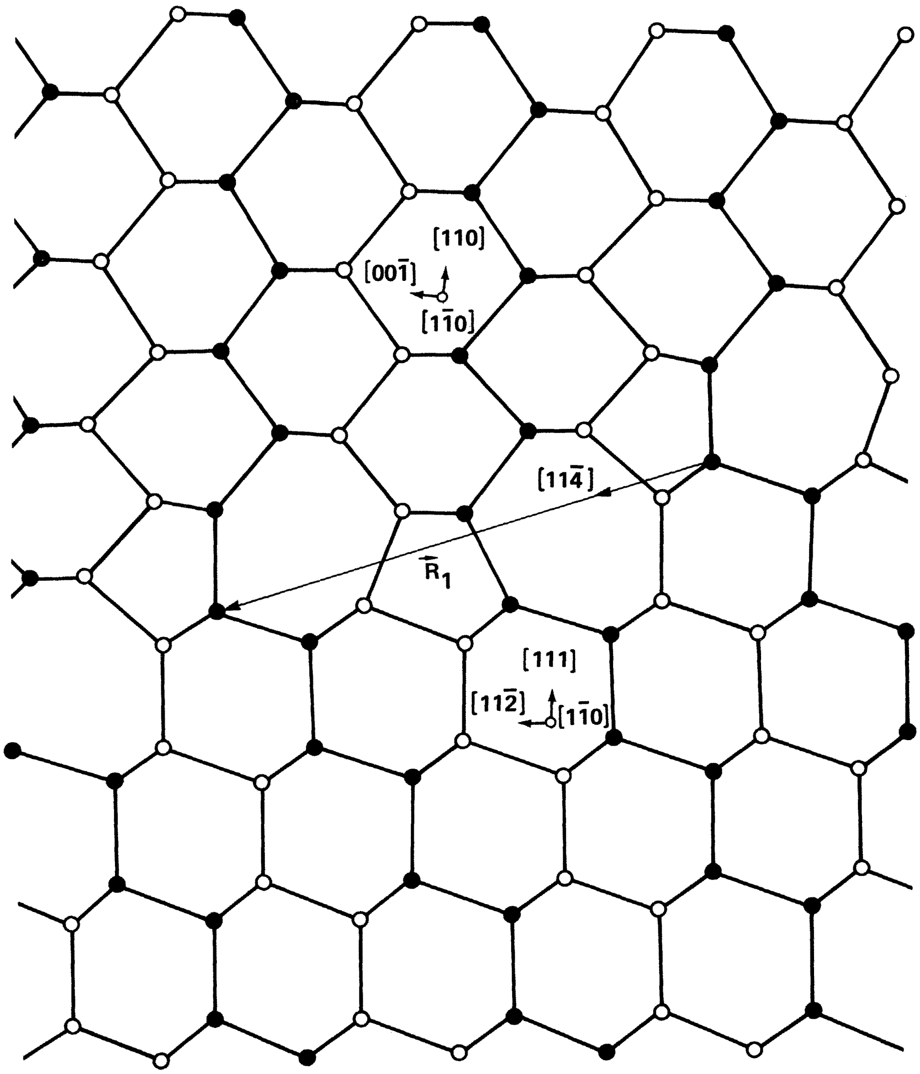
Krivanek, Isoda, and Kobayashi[1] examined a 39° tilt grain boundary using transmission electron microscopy. The image they obtained of a section of the boundary in Ge shows a complex structure with many twinning planes and alternating fivefold and sevenfold rings of atoms. The interesting feature of this grain boundary is that the rings are arranged in such a way as to eliminate all dangling bonds and to allow the boundary to be continuous.

In this paper we consider a grain boundary very similar to the one studied by Krivanek and co-workers.[1,2] The boundary can be regarded as the interface between a crystal oriented in the [111] direction and a second crystal oriented slightly off the [110] direction. The resulting grain boundary is continuous and periodic. It contains alternating fivefold and sevenfold rings of atoms arranged in the same pattern found in the electron microscopy study. In the following two sections we discuss (i) the relation of these fivefold and sevenfold rings to those in the Pandey π-bounded chain model[8] of the 2×1 reconstructed Si(111) surface, (ii) the atomic and electronic structure of the grain boundary, and (iii) its surface energy. We have also developed general conditions for lattice matching so that the boundary between two crystals can be continuous and periodic. These conditions cause the lattices to be commensurate, allowing the grain boundary to exist on a macroscopic scale with no strain from lattice mismatch. Periodic grain boundaries have been observed by electron diffraction and microscopy studies in some cases.[6]

II. 38.94° GRAIN BOUNDARY

A. Geometrical aspects

A side view of the grain boundary we have studied is shown in Fig. 1. The solid circles are in the plane of the page, and the open circles are in a parallel plane displaced by $\pm a_H/2$, where $a_H \simeq 3.85$ Å is the hexagonal lattice constant of the (111) surface of Si; $\vec{R}_1$ is a translation vector for the entire structure, i.e., the lower crystal, the upper crystal, and the boundary all have periodicity $\vec{R}_1$. Both crystals are also periodic in $\vec{R}_2=(1,-1,0)a_H/\sqrt{2}$, which is normal to the plane of Fig. 1. Since the grain boundary itself is also periodic in $\vec{R}_2$, the entire structure is periodic in $\vec{R}_1$ and $\vec{R}_2$. These two translation vectors define the (221) plane. The (111) planes of the two crystals are at an angle of 38.94° to each other; the boundary can be thought of, therefore, as a 38.94° tilt boundary. Alternatively, it can be viewed as a twin boundary, with the (221) plane being the twinning plane, since the two sides of the grain boundary across that plane are symmetrical. As can be clearly seen from Fig. 1, the grain boundary is very close to being an interface between a crystal oriented in the [111] direction and one oriented in the [110] direction, except that in this case the (110) surface normal is 3.68° off



38.94° TILT GRAIN BOUNDARY

FIG. 1. Side view of the 38.94° tilt grain boundary in Si is shown. Projection is on to a $(1\bar{1}0)$ plane. Atoms represented by open and closed circles are displaced from each other by $\pm a_H/2$ along the $[1\bar{1}0]$ direction normal to the plane of the drawing. Vectors $\vec{R}_1$ and $\vec{R}_2=(1,-1,0)a_H/\sqrt{2}$ are translation vectors of the entire structures, where a_H is the hexagonal lattice constant of the (111) surface. $\vec{R}_1$ is along the $[11\bar{4}]$ cubic axes of the two cystals forming the boundary. Translation vectors $\vec{R}_1$ and $\vec{R}_2$ lie in the (221) plane. Crystals on the two sides of the grain boundary are aligned along the [111] and 3.68° off of the [110] directions. (111) planes of the upper structure are rotated by 38.94° with respect to those of the lower one. Positions of the fivefold and sevenfold rings of atoms at the grain boundary are the same as those determined by high-resolution electron microscopy (Refs. 1 and 2).

the (111) surface normal.

A structure with a topology similar to this grain boundary is Pandey's π-bonded chain model[8] for the Si(111)-2×1 surface. This model contains alternating fivefold and sevenfold rings which produce a surface with zigzag chains similar to those on a (110) surface. A crystal in the (110) orientation, however, cannot actually grow on top of the Pandey surface because of lattice mismatch. The lattice vectors of the surface structure and the (110) crystal are commensurate along the cubic $[1\bar{1}0]$ direction; in the $[\bar{1}\bar{1}2]$ direction, however, the lattice vectors of the (110) and (111) surfaces differ by about 22%. This means that a crystal in the (110) orientation can grow continuously on top of the chain structure for only a very short segment. Otherwise, as the length of the interface is increased, the strains resulting from lattice mismatch become large and produce a dislocation. This problem can be overcome by allowing the grain boundary to propagate at an angle to the (111) surface, and by allowing the (110) surface to be tilted slightly in relation to the (111) surface as in Fig. 1.

TABLE I. Some lattice-matched grain boundaries that can be obtained by taking a crystal oriented along the [111] axis and rotating it by 180° along the lattice vector $\vec{R}_1$ are shown. Only the directions of the lattice vectors $\vec{R}_1$ and $\vec{R}_2$, with respect to the bulk cubic axes, are given.

$\vec{R}_1$ Axis of rotation	$\vec{R}_2$	Boundary plane	Rotation angle
$[\bar{1}\bar{1}4]$	$[\bar{1}10]$	(221)	38.94°
$[\bar{1}\bar{1}3]$	$[\bar{1}10]$	(332)	50.48°
$[\bar{1}\bar{1}1]$	$[\bar{1}10]$	(112)	31.59°
[132]	$[\bar{1}\bar{1}2]$	$(4\bar{2}1)$	−65.06°
[042]	$[\bar{1}\bar{1}2]$	$(5\bar{1}2)$	−31.01°
$[\bar{1}52]$	$[\bar{1}\bar{1}2]$	(201)	−7.93°

Both of these mechanisms are incorporated into the grain boundary model of Krivanek *et al.*[1] which was constructed on the basis of their high-resolution electron microscopy studies. Their grain boundary is nonperiodic but continuous and shows the way in which the fivefold and sevenfold rings of atoms eliminate all dangling bonds at the boundary. For our theoretical studies, we have determined a simple method to construct a grain boundary that is both continuous and periodic, but which retains the basic geometry of the model of Krivanek *et al.*[1] Several methods for generating periodic grain boundaries have been previously examined.[9–14]

The method referred to, basically consists of choosing a plane containing two lattice vectors normal to each other and forcing it to be a twinning plane. This is done by rotating the structure 180° around one of the lattice vectors in the chosen plane, and then joining the rotated and unrotated crystals along the plane. This results in a pure tilt boundary of angle

$$\alpha = 70.53^\circ - 2\theta \,, \tag{1}$$

where θ is the angle between the lattice vector serving as the axis of rotation and the (111) plane of the crystal. For example, for the configuration similar to that of Krivanek *et al.* a (111) crystal is rotated 180° about $\vec{R}_1$ in Fig. 1. Since $\vec{R}_1$ is at $\theta = 15.79^\circ$ relative to the (111) surface, this rotation produces a tilt boundary of $\alpha = 38.94^\circ$. Because (110) planes are at 35.26° relative to (111) planes in the ideal crystal, the top part of the grain bounary is aligned approximately along the [110] direction and is tilted by 3.68° away from the [111] direction of the lower crystal. This small tilt angle is clearly visible in Fig. 1.

The existence of a lattice vector normal to the axis of rotation is a necessary condition for the rotation to result in commensurate lattice sites. Lattice vectors $\vec{R}_1$, which are suitable candidates as rotation axes resulting in continuous periodic grain boundaries, are given by

$$\vec{R}_1 = \frac{m}{\sqrt{2}}(1,\bar{1},0) + \frac{n}{\sqrt{2}}(1,0,1) + \frac{p}{\sqrt{2}}(1,1,0) \,, \tag{2}$$

where m, n, and p are any positive or negative integers. Table I is a partial listing of such lattice vectors, their corresponding perpendicular lattice vectors $\vec{R}_2$, the plane in which they lie (i.e., the plane of the grain boundary), and the angle of rotation of the boundary. The particular grain boundary, which we have investigated results from the rotation about the first vector, is listed in Table I.

B. Optimization of structure

The atomic structure of the 38.94° grain boundary shown in Fig. 1 was optimized via tight-binding-based energy-minimization calculations.[15] The optimization was done in two stages. In the first stage a two dimensionally periodic slab with a (221) surface at each end was constructed. A (221) surface is easily created by "cleavage" of the structure shown in Fig. 1. This can be done by removing *all* atoms whose projections onto the plane of Fig. 1 fall on one side (or other) of a given line which is parallel to $\vec{R}_1$. An examination of Fig. 1 shows that this line can be picked in a way such that the surface atoms fall on fivefold and sevenfold rings.

In our calculations, we chose a 40-layer slab, periodic in only two dimensions, and constructed a (221) surface on each end of it in the manner described above. The two surfaces were made to have fivefold and sevenfold rings of atoms similar to those occuring in Fig. 1. The four dangling bonds (per unit cell) at each end were capped off by hydrogen. The optimal atomic configuration for the surface and substrate atoms was then determined by the minimization of the Hellmann-Feynman forces acting on the atoms.[16,17] This was done by moving each atom in the direction of the force acting on it. The absence of many layers of atoms above the fivefold and sevenfold rings of atoms in these calculations allowed a much faster optimization of the structure. At the end of this stage of calculations, the hydrogen atoms were removed and a grain boundary similar to that shown in Fig. 1 was constructed. The model used for these calculations was made to be periodic in three dimensions. The unit cell contained 10 layers each of (111) and (110) planes. Together with the boundaries,[18] each unit cell consisted of 146 atoms. The structure of the grain boundary was optimized again via the minimization of the Hellmann-Feynman forces. The resulting structure shown in Fig. 1 is found to have a very low energy. The difference in total energies ΔE_{tot} between a structure with this grain boundary and the perfect Si structure is calculated to be

$$\Delta E_{\text{tot}} = 0.85 \text{ eV} \,, \tag{3}$$

per boundary and per unit cell.[19] This translates into an energy per unit area of

$$\gamma = 0.02 \pm 0.002 \text{ eV/Å}^2 \,, \tag{4}$$

for the grain boundary which is appreciably smaller[17] than for any of the free surfaces of Si. For comparison, the surface energies of the ideal Si(111)-1×1 surface and of the π-bonded—chain model for the Si(111)-2×1 surface are calculated to be

$$\gamma_{1\times1} = 0.085 \pm 0.005 \tag{5}$$

and

$$\gamma_{2\times 1}=0.055\pm 0.005 \tag{6}$$

measured in eV/Å^2, respectively. Since cleavage leads to two surfaces, the values of γ in Eqs. (5) and (6) should be doubled for comparing the stability of the grain boundary relative to these surfaces.

III. ELECTRONIC STRUCTURE

The electronic states of the 38.94° grain boundary of Fig. 1 were calculated for eight points in the irreducible part of the Brillouin zone. No electronic states falling in the bulk fundamental band gap were found. The absence of any dangling bonds at the boundary, resulting from perfect lattice matching, is the most obvious explanation for the defect-free nature of the electronic states in the band-gap energy region. More surprisingly, the change in ring topology from sixfold to fivefold and sevenfold rings at the boundary and angular deviations as large as +29° (−20°) from the perfect tetahedral angle of 109.47°, do not lead to any band tailing.

The most sharply localized defect states associated with the boundary are calculated to be at 7.83 eV below the bulk valence-band maximum (VBM) in the region of the pseudogap in the bulk density of states of Si. It is well known that odd-membered rings of atoms give rise to such states in the pseudogap.[20] Many other resonances and localized states were found between 0.5 eV to 13 eV below the VBM.

The calculations reveal small deviations from charge neutrality at some boundary atoms. Most of the atoms are neutral to within $\pm 0.02e$, however, excess electronic charges as large as $0.14e$ and deficiencies as large as $0.06e$ occur on some atoms as a result of bond length and bond-angle variations. These values are consistent with experimental determinations[21] of static charge fluctuations of $0.11e$ (root-mean-square value) in amorphous Si from high-resolution Si 2*p* core-level spectroscopy. Our calculations show that the largest deviation from charge neutrality of $0.14e$ occurs at a boundary atom around which the bond angles are within 3° of 109.47°, but for which a bond-length shortening of 2.3% has occurred. The maximum bond-length variation from the ideal one is, in fact, −2.3%. Not all atoms with such a bond-length change are found, however, to have excess electrons on them. The bond-angle variations on most of these atoms tend to counterbalance the charge fluctuations resulting from bond-length variations.

IV. CONCLUSIONS

We have examined the structural and electronic properties of the high-angle 38.94° tilt grain boundary in Si. The atomic geometry of the boundary, consisting of fivefold and sevenfold rings of atoms first observed by high-resolution electron microscopy,[1,2] was optimized via total-energy—minimization calculations. The calculated electronic structure of the boundary has no defect states with an energy falling in the fundamental band gap of crystalline Si. This results from the absence of any dangling bonds at the grain boundary studied. Static charge fluctuations as large as $0.14e$, consistent with experimentally determined values[20] for amorphous Si, are found. A simple method for producing continuous grain boundaries is described.

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[18] Each unit cell contains two grain boundaries which are alternately separated by approximately 10 layers of (111) or (110) atoms. The whole structure can be made to have inversion symmetry. This was used to make the two grain boundaries identical to each other. As a result, the electronic states for wave vectors along the two principal lattice vectors occur as doublets in the calculations.

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