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Nanoindentation of silicon surfaces: Molecular-dynamics simulations of atomic force microscopy

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We investigate the atomic-scale details of atomic force microscopy through a quasistatic molecular dynamics simulation together with a density-functional-based tight-binding method. The changes in the AFM tip shape, the size of the tip-sample contact area, as well as the microscopic hardness and Young's moduli of silicon {111},{110},{100} surfaces are studied. Furthermore, the effects of hydrogen termination of the surface and of subsurface vacancies on hardness and Young's modulus are discussed.

I. INTRODUCTION

Atomic force microscopy (AFM) has become a standard tool in experimental surface physics, revealing atomic scale structures of surfaces. Manipulation of single atoms by an AFM tip has also been successful.¹ Experimental work has been carried out to obtain information of macroscopic quantities, such as hardness, Young's modulus, and shear modulus of surfaces. These quantities can be estimated from the force curves obtained from the AFM experiments.^{2,3}

Calculations have been made to clarify the changes in the electronic and atomic structure during nanoindentation, i.e. the pushing of the AFM tip into the surface and pulling it back to its original position. Results regarding the tip-surface interactions have been reported for Al{001}, Au{100} and Si{111} surfaces.⁴⁻⁶ In the work by Ciraci *et al.* atom transfer and force components in scanning force microscopy were investigated using *ab initio* methods.⁴ In the second work (Ref. 5) effective medium theory was used to study the role of thermally activated processes in the tip-surface contact formation. The third work *ab initio* calculations by Pérez *et al.* are similar to this work and are discussed in more detail below.⁶ These three studies show that an AFM (or a scanning tunneling microscope [STM]) tip can extract atoms from the surface and cause plastic deformation of the substrate. It was found that the changes in the electron distribution precede the changes in the atomic configuration.

Shluger *et al.* have studied the non-contact-mode of AFM on ionic LiF, NaCl, and MgO surfaces using an embedded-cluster Hartree-Fock method.⁷ They found that the tip causes surface deformation, which may even result in neck formation between the tip and surface. The energy barriers for the diffusion events on the surface are shown to be reduced due to the tip in the vicinity of the surface. Furthermore, electron tunneling from the tip to the surface was observed.⁷

Classical simulations have focused on the AFM force curves (i.e., the force acting on the AFM tip as a function of the indentation depth) and on explaining the atomic response of the surface during the AFM measurement. Furthermore, these simulations gave insight into surface friction properties and revealed the stick-slip type of tip motion during horizontal-scanning AFM, for example on the MoS₂{0001}

surface.⁸ The contact area between the tip and the surface has been approximated within continuum mechanics by Lantz *et al.* for various systems, with good results for metal-tip metal-substrate systems.⁹

The influence of a metal (Ni) tip shape on the metal (Cu{110}) surface has been evaluated by Buldum *et al.*¹⁰ They found that the tip shape affects both the type of jump that the tip makes to the contact and the localization of surface deformation. They discovered a connective neck formation between the sample and the tip in some cases.

In this paper, we give an overall picture of the AFM measurement on Si{111}(2×1) Pandey chain, Si{100}(2×1) and Si{110} surfaces, using density-functional based tight-binding (DFTB) potentials.¹¹ AFM simulations for some Si surfaces have been performed recently, and it is interesting to compare the earlier results with our DFTB calculations when there is overlap in the investigated properties. It should be noted that our simulations were performed as quasistatic molecular dynamics in 0 K. Therefore, we have neglected the time-dependent effects such as interstitial and vacancy diffusion.

AFM simulations have been performed for Si{111}(2×1) Pandey chain surfaces with the density-functional theory⁶ (DFT) and recently for the (5×5) reconstructed Si{111} using DFT extended with van der Waals contributions for the tip-surface interactions.¹² A detailed description of the atomic processes, for instance interstitial formation and plastic deformation of the surface, is given in Ref. 6. Therefore we have compared our results to theirs, and further extended the investigations to a wider range of structures.

The organization of the paper is as follows. In Sec. II, we describe the density-functional based tight-binding method as well the simulation geometries. The nanoindentation simulations are described in Sec. III. The results are given in Sec. IV. Finally, a discussion and conclusions follow in Secs. V and VI.

II. THEORETICAL METHOD AND THE MODEL SYSTEMS

The density-functional based tight-binding method (DFTB) derives its name from its use of self-consistent

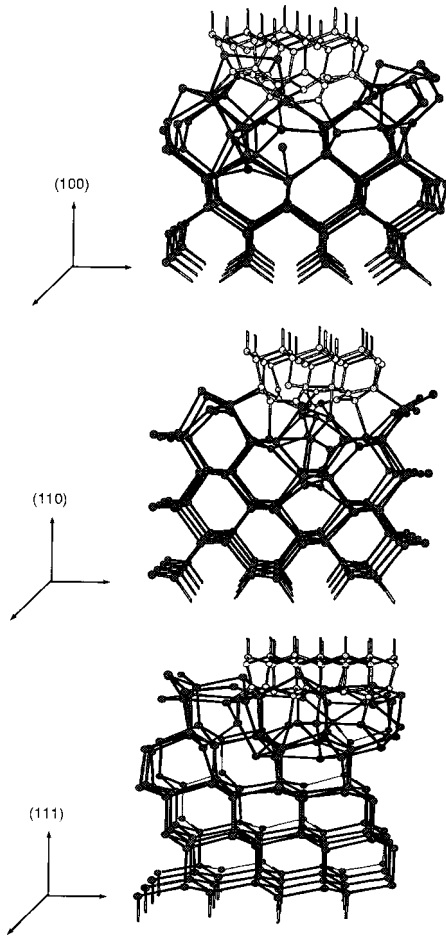


FIG. 1. The flat tip indenting different surfaces. Si surfaces from top: $\{100\}$, $\{110\}$, $\{111\}$. The formation of an amorphous layer near the tip and a region with interstitials below the amorphous layer is observed.

density-functional calculations of single and contracted pseudoatoms. This is done in order to construct transferable tight-binding (TB) potentials for a non-self consistent solution of the Kohn-Sham equations for the many body case. It differs from conventional tight-binding techniques because there is a systematic way of deriving these potentials, independent of the atom type involved. This is thus not a “parametrization” as is usually meant when discussing TB approaches. The excellent review article written by Goringe *et al.* summarizes the general theoretical basis of the tight-binding method and the current progress in the theory.¹¹ For an in-depth description of the DFTB, the reader is recommended to consult Ref. 13. The detailed description of the application of DFTB for silicon is given in Ref. 14.

In this paper, we examine three silicon surfaces. The $\text{Si}\{100\}(2 \times 1)$ surface consists of eight layers of silicon at-

TABLE I. Dimensions of the sample surfaces.

Surface	$x(\text{\AA})$	$y(\text{\AA})$	$z(\text{\AA})$
$\{100\}$	15.35	15.35	9.6
$\{110\}$	15.35	16.28	9.8
$\{111\}$	13.30	15.35	13.7

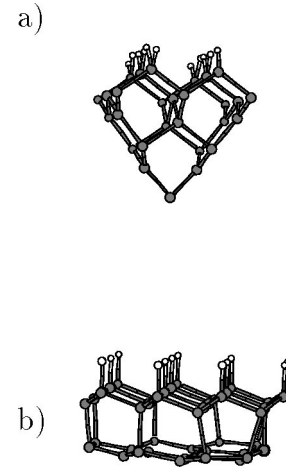


FIG. 2. The sharp and flat tips. The sharp tip (a) has totally 40 atoms, 28 C and 12 pseudo H to saturate dangling bonds. The flat tip (b) consists of 55 atoms (43 C, 12 pseudo-H). The tips are generated by cutting a piece of diamond in the $\{111\}$ direction, saturating the upper surface with pseudo-H and thereafter conjugate gradient relaxing.

oms with in total 160 atoms in the unit cell. The $\text{Si}\{111\}(2 \times 1)$ buckled Pandey chain surface has 176 atoms in five double layers, and the $\text{Si}\{110\}$ surface includes 168 atoms in six Si layers. All silicon atoms are allowed to move freely, except for the fixed bottom layer. The dangling bonds at the bottom of the surface are saturated with immobile hydrogen atoms. The surfaces during AFM measurements are depicted in Fig. 1. The dimensions of the super-cells in x - y (surface plane), and the slab height in z (surface normal) directions are given in the Table I.

Both a sharp and a flat diamond tip are used in this paper. The sharp tip has in total 40 atoms: 28 carbon atoms and 12 pseudohydrogens to saturate the dangling bonds. The distance in the surface normal direction of the undisturbed sharp tip from the apex to the uppermost carbon layer is 4.4 \AA . The flat tip consists of 55 atoms of which 43 are carbons and 12 pseudohydrogens. The distance from the lowest to the uppermost carbon layer is ~ 2.4 \AA . These tips are made by cutting a piece of unreconstructed diamond $\{111\}$ surface and conjugate gradient (CG) relaxing the piece in order to find a minimum energy configuration. The tips are shown in Fig. 2.

The effect of surface hydrogen on the AFM experiment is investigated with a hydrogen terminated $\{100\}:\text{H}2 \times 1$ surface. The influence of a single subsurface vacancy on the film properties is studied for the $\{100\}$ and $\{111\}$ surfaces.

III. SIMULATION DETAILS

In all simulations a push-pull (loading-unloading) AFM cycle is performed. The tip is pushed to an indentation depth of 0.7–3.2 \AA and then pulled upwards.

The indentation depth is measured as the distance between the uppermost fixed carbon layer of the tip and the topmost atomic layer on the surface, minus the height of the undisturbed tip, i.e., the indentation depth $z=0$ corresponds a situation where the undisturbed tip just touches the undisturbed surface. This depth is well defined even if the tip is deformed. The simulations with the flat tip are performed

using the depths of 0.7–0.5 Å. The low depth range is used to gain information not distorted by the effects resulting from the finite sizes of the unit cells in the z direction. The maximum depth for the sharp tip is selected so that the fixed atoms on the top of the tip remain above the surface.

The simulations are performed using constant-volume conditions in the lateral plane. The tip (flat or sharp) is positioned so that the initial minimum distance in z direction between the surface and tip atoms is 2.5–3.1 Å. It is pushed into the surface with steps of 0.1 a.u. (0.0529 Å). After each step, the system is conjugate gradient (CG) relaxed (corresponding to zero temperature) with two exceptional groups of atoms. First, the atoms at the bottom layer of the surface are kept fixed in order to prevent an all-atom movement of the supercell. Also the pseudo-H's bonded to the bottom layer are kept fixed. Secondly, the two topmost layers of C atoms and the pseudo-H's of the AFM-tip are kept fixed in the surface normal direction in order to apply force to the system. The force acting on the AFM tip is calculated by summing the z -components of forces acting on the individual tip atoms,

$$F_z = \sum_{tip} F_{z_i}. \quad (1)$$

This force is well defined because the number of C and pseudo-H atoms on the tip remains constant in every simulation.

In order to make the tip more stable, the topmost two C layers and the pseudo-H's are fixed relative to each other in the x - y plane. This is accomplished by calculating the z component of the torque and the forces in the x - y plane on the fixed tip atoms and then redistributing them as uniform acceleration and rotation on the x - y plane. The torque is calculated as

$$\vec{\tau}_{fix} = \sum_{fix} (\vec{r}_i - \vec{r}_{cm_{fix}}) \times \vec{F}_i \quad (2)$$

and the fixed atoms are rotated according to

$$\vec{F}_{rot_i} = \vec{\tau}_{fix} \times \frac{\vec{r}_i - \vec{r}_{cm_{fix}}}{\sum_{fix} (\vec{r}_j - \vec{r}_{cm_{fix}})^2}. \quad (3)$$

The contact area between the tip and the surface is estimated by calculating the number of bonds between the tip and the surface. An estimated area of 5.51 Å² per bond is used. This is the area per dangling bond in the unreconstructed diamond {111} surface.

IV. RESULTS

A. Tip shape and contact area

1. General features

Apart from the case of the hydrogen-terminated surface, a small attraction between the surface and the tip is noticed during the preloading phase, i.e., before the tip-surface contact has been established. The attraction vanishes with the hydrogen-terminated surface because of the surface dipole (the surface hydrogen atoms are positively charged). After

TABLE II. Transferred atoms and maximum total contact area for the deepest indentations (Å²). The contact areas in the table are the maximum values over all indentation depths.

Tip, Surface	Atoms transferred	Contact area
Sharp tip, {100}	8	50
Sharp tip, {110}	8	77
Sharp tip, {111}	4	66
Sharp tip, {100}, vacancy	6	61
Sharp tip, {100}:H	0	39
Flat tip, {100}		50
Flat tip, {110}		88
Flat tip, {111}	2	72
Flat tip, {100}, vacancy		28
Flat tip, {111}, vacancy		72

the unloading phase, there is a strong attraction of few eV/Å because of the bonds which have formed between the tip and the sample.

In most simulations the tip is deformed during the simulation. With the sharp tip the deformation is most severe on the {110} and {111} surfaces. The number of Si atoms sticking to the tip after the simulation sequence is shown in the Table II. As a general trend one can observe that a surface with energy-lowering reconstruction ({111}) is more resistant against the abstraction of surface atoms.

The deformation process of the surface begins when the tip approaches the contact regime. The outermost tip and surface atoms start to form bonds, and they are slightly attracted towards each other. As the tip further approaches the surface, this attraction turns to repulsion when the atoms are forced closer to each other, with a typical interatomic Si-C distance of order 2 Å. The surface atoms forming bonds with the tip are homogeneously forced downwards deeper into the surface and the sample is further deformed. With the sharp tip and perfect surface, the deformation of the surface is restricted to the few uppermost atom layers on the surface.

Interstitials are detected with flat tip on all three surfaces. The geometries of interstitials in bulk silicon are discussed in Ref. 15. The ⟨110⟩ dumbbell interstitial is also described in Refs. 16 and 17. When interstitials start to form in our simulations, the uppermost Si layers are typically in an amorphous state, and the pressure from these layers induces the interstitial formation in lower atomic layers. Since the crystal environment above these interstitials is amorphous, these interstitials have unusual geometries, which cannot be classified as any of the bulk interstitials presented in Ref. 15.

The surface remains locally deformed after the indentation process, mainly because of the Si atoms transferred to the tip. The maximum total contact area ranges from 39 to 77 Å² with the sharp tip on the perfect Si surfaces. It increases slightly with the flat tip, apart from the vacancy case (see Table II). The {100} surface has smaller values for the contact area than the other surfaces because of the resistant (2×1) reconstruction. The contact area typically increases strongly during the loading phase from near zero value to its maximum value in a short distance. The contact area as a function of indentation depth for the clean surfaces probed with the flat tip is shown in Fig. 3. The increase is nearly

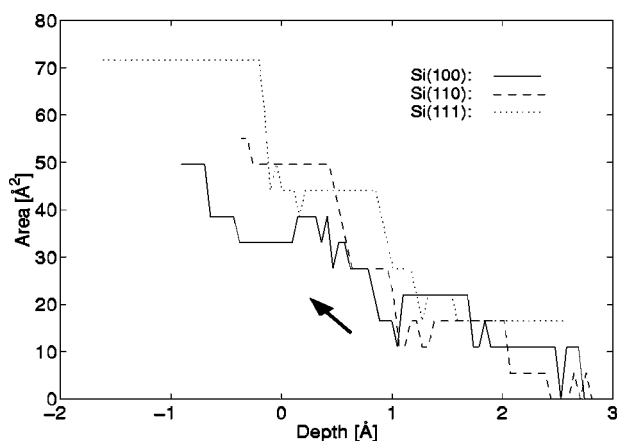


FIG. 3. Development of contact area (\AA^2) vs indentation depth (\AA) for the flat tip indenting Si{100} (solid line), {110} (dashed line) and {111} (dotted line).

monotonous, as the small jumps in the curve are likely to result from the method used in the evaluation of contact area.

2. {111}, {100}, {110}, and (100:H) surfaces

Both Pandey chains on the {111} surface in our simulation cell reconstruct to the regular diamond-structure under the pressure from the flat tip. This is understandable because the AFM tip acts as a source of bonds for the under-coordinated surface atoms. Similar reconstruction of Pandey chains occurs also on the {111} surface with the sharp tip. In this case only the atoms in the Pandey chain under the tip undergo the “phase transition” to the diamond structure. During the Pandey chain destruction, the energy release for the reconstruction of one 7 ring of the Pandey chain to a regular 6 ring of unreconstructed surface is of the order of 1 eV. The simultaneous change in the bonding of the tip atoms with the surface atoms contributes significantly to this energy.

The interstitial formation on the {111} surface is not clear. With the flat tip, four atoms in the second topmost double layer are pushed downwards from their original position towards interstitial positions. These atoms move deeper into the substrate by more than 0.6 \AA . Two of them move more distinctly, one to a $\langle 110 \rangle$ dumbbell-like position, while the other moves to an interstitial position beneath the {111} layer (Fig. 1). However, there is no clear jump to the interstitial position, and it seems that the interstitials do not fully form. The dumbbell-like interstitial has different bond ordering than the usual $\langle 110 \rangle$ dumbbell, and the bond lengths have differences when compared to *ab initio* calculations.¹⁷ With the sharp tip, only two surface atoms migrate downward, and the migration is much weaker than with the flat tip. When compared to Ref. 6, the behavior of the sharp tip in the {111} surface has a similar feature of the upward flow of some surface Si atoms along the tip sides.

On the {110} surface with the flat tip, the formation of three dumbbell-type interstitials starts to take place for indentation depths of 0.6 \AA . The interstitials are formed in the third atom layer below the surface. Because the surface directly above the interstitials is in an amorphous state, and the three interstitials are next to each other in a {110} chain, they cannot be clearly identified as {110} dumbbell interstitials.

No interstitials are formed with the sharp tip on the {110} surface.

On the {100} surface with the flat tip, one Si atom is forced near the hexagonal interstitial position between the fifth and sixth layer. There is no clear jump to the interstitial position, and this interstitial vanishes as the deformation of the surface proceeds. Also some dumbbell-type interstitials start to form, but this behavior is obscured due to the amorphization of the surface.

In the simulations for hydrogen-terminated Si{100}, the tip first goes on top of the dimer chain between hydrogen atoms. This behavior is due to hydrogen atoms, which screen the energy minima between the dimer rows. The tip pushes one of the H atoms into the surface and starts to move between the dimer chains. Eventually, the H atom moves to an interstitial position in a third Si layer.

The sharp tip finds an energy minimum between the surface atom chains in the simulations on clean {100} and {110} surfaces. On the {111} surface, the tip does not go between the Pandey chains. Instead, the Pandey chains are reconstructed in the previously discussed manner.

3. {100} and {111} surfaces with a subsurface vacancy

The influence of a subsurface vacancy on the hardness is studied with the {100} surface with a single vacancy in the sixth silicon layer from the surface, and with the {111} surface with a vacancy in the fourth double layer. The point group of the relaxed vacancy is close to D_{2d} , i.e., the nearest neighbors of the vacancy have two short distances of 2.9 \AA and four nearly equal bond lengths (two 3.3 \AA and two 3.4 \AA). In the {111} surface with a vacancy there are two shorter distances of 3.2 and 3.3 \AA with four longer distances of 3.5 \AA . In the case of the {100} surface with a subsurface vacancy, the sharp tip does not go to the intermediate position between the dimer chains in the {100} plane, but remains near the top of the dimer row. This has an effect of slightly increasing the contact area. The surface is less deformed than in the case of plain {100} surface.

On the {111} surface, the vacancy which is initially positioned in the fourth double layer, localizes in two neighboring lattice positions under the pressure from the tip. This occurs for the indentation depth of 0.8 \AA . The energy gain associated with the vacancy splitting is 1.2 eV. In the vacancy splitting, the atom above the vacancy moves downwards in the $\langle 111 \rangle$ direction to the halfway point between its original position and the empty lattice site. This behavior is similar to that of a tin-vacancy complex in silicon.¹⁸ The migration to the mid-vacancy position can be interpreted as a stress relief mechanism in both cases. The transported atom forms bonds with the other neighboring atoms of the empty tetrahedral position. The atom shifts downwards below the halfway position as the pressure from the tip increases. Finally, when the unloading is started, the atom does not return to its original position. Two bonds with its initial neighbors break, and the atom stays closer to the original vacancy site in the fourth double layer. This behavior is explained by the greater deformation of the next upper double layer, which reduces the binding energy of the atoms there, so that it is energetically preferable for the atom to form bonds with the atoms in the lower double layer.

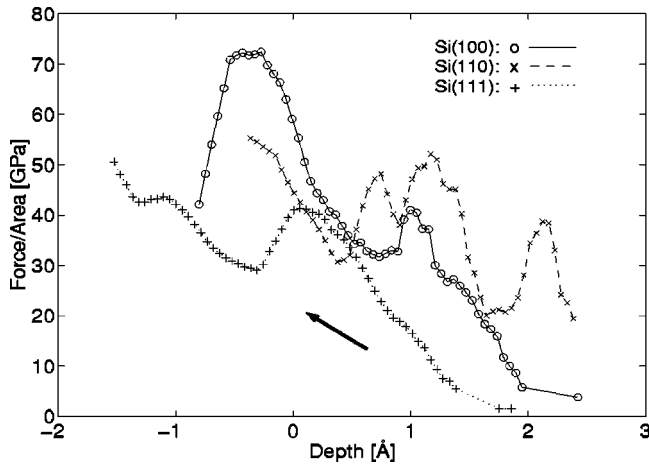


FIG. 4. Development of force/area (GPa) vs indentation depth (\AA) for the flat tip indenting Si $\{100\}$ (solid line), $\{110\}$ (dashed line) and $\{111\}$ (dotted line).

The reconstruction of the $\{111\}$ surface occurs also with the vacancy. The energy gain is about the same as for the perfect surface.

B. Hardness and Young's modulus

The hardness of the substrate is calculated as

$$H = \frac{F_{max}}{A_{projected}}, \quad (4)$$

where F_{max} is the maximum value of the repulsive force measured during the loading, and $A_{projected}$ is the corresponding projected contact area. For the geometry of a sharp tip,

$$A_{projected} = 0.558 * A. \quad (5)$$

The coefficient between the projected and the total contact area A is derived from simple geometrical considerations by projecting the total area of the undeformed tip facing the surface onto a plane. With the flat tip, the projected area is considered equal to the total contact area. The $F/A_{projected}$ ratios of the surfaces probed with the flat tip are presented in Fig. 4. The points in the curve are calculated by computing $F/A_{projected}$ and then averaging over five neighboring depths. This is done in order to smooth out the fluctuations in

TABLE III. Hardness in different simulations.

Tip, Surface	Depth (\AA)	Hardness (GPa)
Sharp tip, $\{100\}$	-1.8	52
Sharp tip, $\{100\}$, vacancy	-1.8	28
Sharp tip, $\{110\}$	-1.8	47
Sharp tip, $\{111\}$	-1.8	89
Sharp tip, $\{100\}$:H	-1.8	43
Flat tip, $\{100\}$	-0.9	57
Flat tip, $\{100\}$, vacancy	0.7	43
Flat tip, $\{110\}$	0.4	36
Flat tip, $\{111\}$	-0.4	30
Flat tip, $\{111\}$, vacancy	-0.4	28

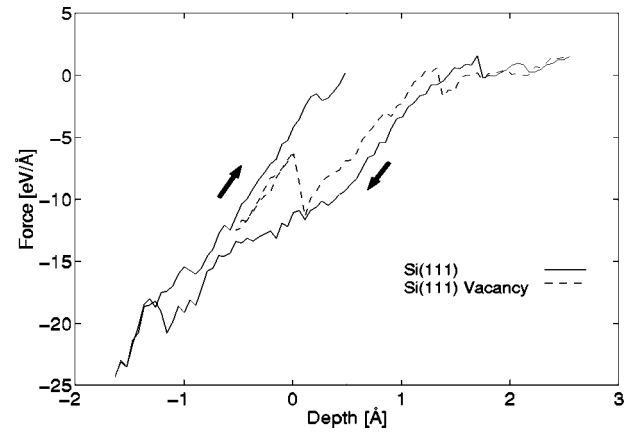


FIG. 5. The depth (\AA) dependence of force ($\text{eV}/\text{\AA}$) on the clean $\{111\}$ (solid line) and $\{111\}$ surface with a vacancy (dashed) when indenting with the flat tip. The lower portions of the curves display the loading and the upper portion the unloading phase. Around the zero depth the figure displays the less steep region in the plain surface curve and the peak of the force in the vacancy curve.

the force. The depths with attractive values of force or zero contact area are rejected in the averaging, since they would give unacceptable values for the $F/A_{projected}$.

As discussed above, the subsurface vacancy affects the penetration position of the AFM tip on the xy plane. The energetically favored penetration position on the $\{100\}$ surface with a vacancy is such that the contact area increases compared to ideal $\{100\}$ surface, thus decreases the hardness measured at low indentation depths. (See Table III.)

The reconstruction of the Pandey chain structure on the $\{111\}$ surface during the indentation of the flat tip has an effect of decreasing the steepness of the loading curve by about 60%, due to the fact that there is no more surface reconstruction which would require extra energy input to be converted to a plain diamond structure. During the less steep region, the force against the tip stems from the bond shortening of the bulk structure. Finally, the interstitial formation and the finite size of the sample start to take effect, and the loading curve steepens again. In the vacancy case, the final reconstruction of the second Pandey chain happens approximately at the same depth as the final reconstruction of the remaining 7-atom rings beneath the tip. During this process, there is a strong jump in the loading curve, and the resisting force decreases by 55% (Fig. 5). Otherwise the steepness of the loading curve is not significantly affected, when compared to the simulation without the vacancy. During the jump, the increase in the number of 6-atom rings on the surface layer is more than three times greater than in the corresponding reconstructions in the undefected surface. In the tip-surface interface region, there are rings containing Si and C atoms. The number of carbon atoms taking part in the 6-atom and 5-atom rings is generally greater in the vacancy case during the jump.

During the unloading phase, the bonds between the surface and the tip atoms cause an attractive force between the tip and the sample ($z > 0$ region).

The Young's modulus is calculated using the theory of Hertzian contact

TABLE IV. Estimates for Young's modulus (GPa) observed in the indentation. There are two values for some of the flat tip indentations from two maximum depths.

Tip, Surface	Depth (Å)	Young's modulus
Sharp tip, {100}	-2.3	397
Sharp tip, {100}, vacancy	-1.8	325
Sharp tip, {110}	-2.2	296
Sharp tip, {111}	-3.2	334
Sharp tip, {100}:H	-2.0	220
Flat tip, {100}	0.7/-0.9	382/193
Flat tip, {100}, vacancy	0.7	252
Flat tip, {110}	0.3	323
Flat tip, {111}	-0.4/-1.6	260/414
Flat tip, {111}, vacancy	-0.5	219

$$E_{sub}^* = \frac{\sqrt{\pi}S}{2\beta\sqrt{A}}, \quad (6)$$

where S is the unloading stiffness, i.e., slope of the unloading curve, measured at the very beginning of the unloading phase.² β is a coefficient depending on the tip geometry and E_{sub}^* is the reduced modulus corresponding to the elastic response of both the tip and the surface.² The value of $\beta = 1.012$ is used for the sharp tip because of its pyramid geometry. For the flat tip, $\beta = 1$ is considered most suitable since its geometry after the relaxation is near circular.¹⁹ The macroscopic Young's modulus E_{sub} is then derived from

$$\frac{(1 - \nu_{sub}^2)}{E_{sub}} = \frac{1}{E_{sub}^*} - \frac{(1 - \nu_{tip}^2)}{E_{tip}}, \quad (7)$$

where E_{tip} , ν_{tip} and ν_{sub} are the Young's modulus of the tip, the Poisson ratio of the tip and the Poisson ratio of the surface, respectively. Their numerical values are taken from experimental results: $E_{tip} = E_{diamond} = 1050$ GPa, $\nu_{tip} = \nu_{diamond} = 0.10$, $\nu_{sub} = \nu_{silicon} = 0.28$.²⁰ The derivation of Young's modulus assumes that all deformations are reversible, i.e., elastic. For more detailed discussion of Hertzian theory of normal contact, see Ref. 21. The calculated values

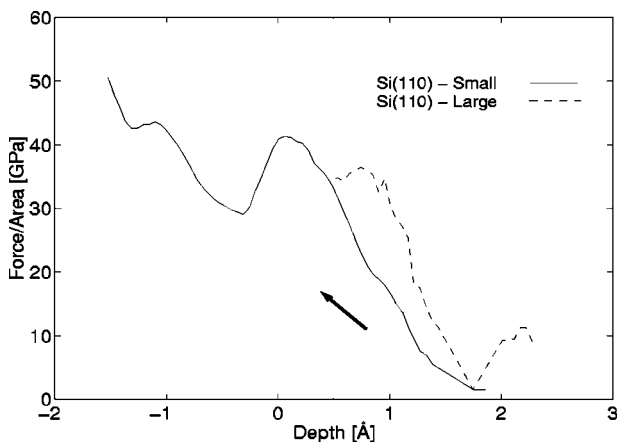


FIG. 6. Development of force/area (GPa) vs indentation depth (Å) for the flat tip indenting small (solid line) and large (dashed line) {110} surface.

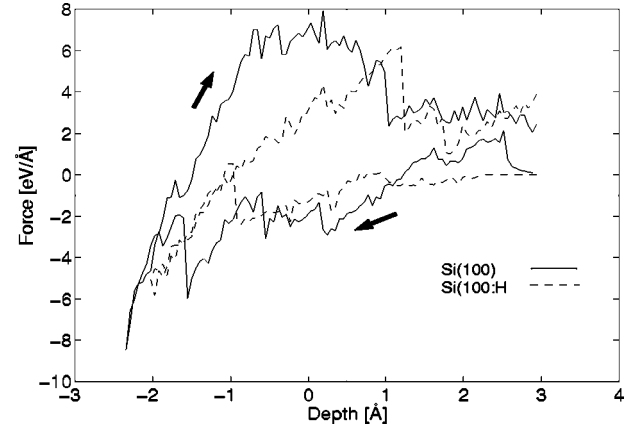


FIG. 7. The depth (Å) dependence of force (eV/Å) on the clean (solid line) and hydrogenated {100} (dashed line) surfaces when indenting with the sharp tip. The lower portion of the curve displays the loading and the upper portion the unloading phase. The arrows also indicate the direction of tip movement.

for the Young's modulus for different surfaces are shown in Table IV. We will discuss these results in the following section.

The maximum value of torque [Eq. (2)] on the fixed atoms of the tip is of order 7×10^{-18} Nm. The torque typically oscillates around the zero value in an irregular fashion.

The influence of the finite size effect on hardness is tested making a low-depth simulation with a bigger supercell of the {110} surface in the x - y plane ($19.184 \text{ Å} \times 21.705 \text{ Å}$) with the flat tip. The evolution of the F/A ratio is depicted in Fig. 6. The first maximum in the ratio is $\sim 15\%$ smaller with the bigger supercell. However, the unloading stiffness S is for both sizes of the simulation cell near 13 eV/Å^2 . This gives an implication that the unloading stiffness is a robust quantity, which can be used to characterize the surfaces.

V. DISCUSSION

In all simulations there is adhesion between the tip and the surface. The small attraction at the beginning of the loading phase can be interpreted as a jump to a tip-surface contact. The strong attractive force between the tip and the surface at the end of the unloading phase stems from the bonds formed between the tip and the surface atoms (Figs. 7 and 5).

The indentation processes in all simulations are nonelastic. This can be seen from the hysteresis-like behavior of loading and unloading curves or by visually inspecting the surfaces and the tips after the indentation (Figs. 7 and 5). These processes are not elasto-plastic in the classical sense, since adhesion between the surfaces due to the bond formation and a transfer of the surface atoms to the tip are taking place.

The sharp tip deforms easily because of the large number of dangling bonds on the tip and on the surface, causing the tip and the surface atoms to react strongly with each other. The flat tip is more resistant against deformations, because of the smaller number of dangling bonds. The deformation of tips is consistent with the experimental results of destruction of diamond tips on contact-mode probing of Si surfaces.²²

The depth dependence of the F/A ratio in Fig. 4 has a maximum around the depth of -0.6 - 0.2 Å . On the {100}

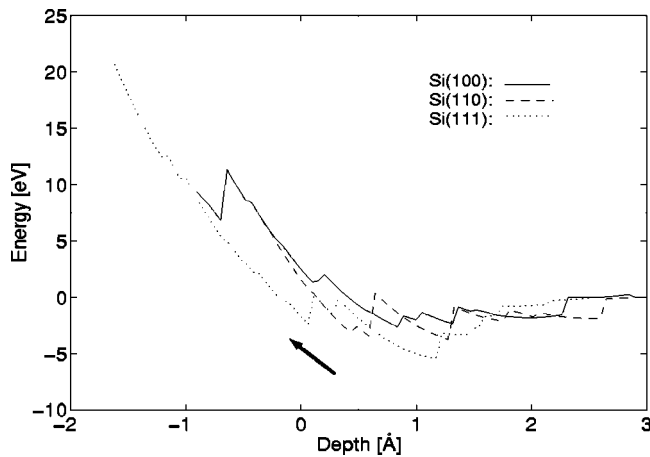


FIG. 8. Development of energy (eV) vs indentation depth (\AA) for the flat tip indenting Si{100} (solid line), {110} (dashed line) and {111} (dotted).

surface with the flat tip, the sudden decrease in energy is associated with the interstitial formation in the subsurface region. In this transformation, over-coordinated atoms recover their sp^3 bonding, and one hexagonal-like interstitial is formed.

The F/A ratio has on average the lowest value on the {111} surface probed with the flat tip. The force on the tip has almost always a smaller value during the loading on the {111} when compared to {100} and {110} surfaces at the same depths. This can partly stem from the Pandey chain reconstruction, which causes a downward movement among the topmost surface atoms and effectively lowers the sample surface. On the other hand, there is no clear local maximum in the F/A ratio with the {111} surface. This indicates that there is no large energy barrier associated with the Pandey chain \rightarrow diamond reconstruction. The newly-formed diamond structure is more resistant against interstitial formation compared to the {100} and {110} surfaces. This surface has no sudden drops in the energy curve (Fig. 8) as in the {100} case.

The extracted values of Young's modulus for the surface are in average 70–220% higher than the experimental bulk value of 130 GPa.²⁰ However, using the DFTB for the computation of the Young's modulus by compressing bulk silicon gives a value of 137 GPa. We believe that the difference compared to the experimental values and our results can be understood as follows. In the real experiment the indentation depth is much greater than in our simulations. In the simulations one is still in the nearly elastic region, while we believe that in the experiments one has local amorphization and massive interstitial formation. As seen in Fig. 4, the slope of the force curve still steepens for the deeper indentation depths, indicating nearly plastic behavior. So in our simulation we are not deep enough to gain a depth-independent response from the surface. Furthermore, the reconstruction effects on the surface may also steepen the unloading curve and thus yield higher estimates for Young's modulus.

The simulation temperature of zero may also affect the extracted forces. In higher temperature it is less likely for the system to get trapped into some local energy minimum, thus the force on the tip may decrease. The experimental nanoindentation measurement has a duration of several minutes.

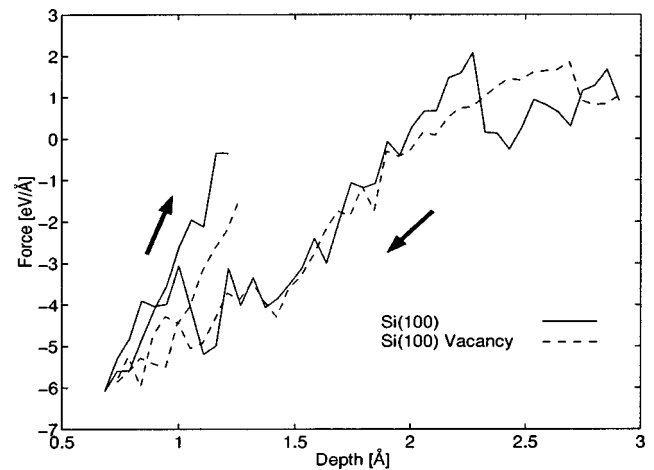


FIG. 9. The depth (\AA) dependence of force ($\text{eV}/\text{\AA}$) on the {100} surface with and without the vacancy when indenting with the flat tip. The solid curve displays the clean and the dashed curve the vacancy case.

Since the migration of self interstitials in Si has low energy barriers (<1 eV),^{16,23} the surface can relax during the experiment at room temperature by interstitial diffusion. This will lead to lower values of the forces. Long time-scale room-temperature molecular-dynamic, simulations which would take the diffusion of defects into account, are unattainable by our simulation methods.

The subsurface vacancy decreases Young's modulus as expected (see Table IV). However, the simulated values for Young's modulus with the vacancy and the sharp tip are very sensitive to the xy position of the tip during the indentation. The vacancy affects the shape of the tip-surface energy landscape and thus the penetration position of the tip on the xy plane. With reconstructions on the surface this leads to different contact areas and thus to different values for Young's modulus (Table II and Fig. 9). When using the flat tip, the xy position dependence is not strong. The simulation with the vacancy with the {100} surface using the sharp tip gives $\sim 18\%$ smaller value of Young's modulus and 54% smaller value for the hardness than the simulation with the surface without the vacancy. Interestingly the sudden drop in the force curve (Fig. 5) is associated with ring formation processes in the surface reconstruction, not near the vacancy itself (as discussed in Sec. IV A.3). One should note that the migration energy barriers for Si vacancy are low (~ 0.7 eV).²³ Thus the vacancies are highly mobile at room temperature conditions. As mentioned above, the experimental nanoindentation measurement has a long duration. Therefore, it is unlikely that the effect of single subsurface vacancy can be seen in a room-temperature AFM measurement.

For the hydrogenated surface {100}: $H(2 \times 1)$, because of the small tip size, only a small fraction of the tip-C atoms are able to make bonds with the Si atoms on the surface. We obtain, however, a decrease in hardness and Young's modulus (Tables III and IV). The minimum energy pathway between the dimer rows is blocked due to hydrogen on the surface, so the values with the flat tip would probably decrease less.

VI. CONCLUSIONS

We have performed DFTB quasi-static simulations of AFM processes on Si surfaces in order to study the shape of the contact area, hardness and Young's modulus.

The contact area is found to depend on the indentation depth in a way that could imply a jump from non-contact to contact mode. This is implicated by a sudden increase in contact area under a short distance, and by a presence of a small attractive force during the preloading phase.

We have shown that a simulated AFM measurement can be used to identify the atomic rearrangements during the indentation. AFM can detect impurities on the surfaces and defects beneath the surface, at least at zero-temperature conditions. We find that subsurface vacancies or hydrogen coverage of the surface decrease the hardness and Young's modulus. The numerical values for hardness and Young's modulus depend strongly on the tip shape and the indentation depth. Experimentally, instead of measuring Young's modulus, which requires *a priori* knowledge of the Poisson ratio of the surface and tip, a simple $\Delta F/\Delta z$ ratio at the beginning of the unloading phase would better reflect the elastic response of the surface. Our results do not support the use of Eq. (6) in determining Young's modulus of the surface. A

phase transition triggered by an AFM tip has been found on $\{111\}$ surface. The Pandey chains are transformed into a regular diamond structure under the pressure of the tip.

Finally, we make a speculative proposition for the tip-surface interactions during an AFM measurement. It is speculative because in the simulations the tip penetrated maximally only few Å into the surface. However, our suggestion is as follows: (i) The tip experiences an attractive force near the surface, basically due to the unsaturated bonds on the surface and in the tip. (ii) The surface reconstruction is destroyed because the AFM tip atoms act as a source of new bonds, and also the pressure from the tip destroys the surface reconstruction. (iii) The bonds below the top surface layers are globally shortened. (iv) Interstitials and vacancies are formed in the subsurface layers. (v) Amorphization takes place in the vicinity of the tip. One may therefore infer the elastic response by examining the force curves in the region (iii).

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