Semiempirical approach for calculating surface stress: Application to As/Si(001)2 × 1

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A semiempirical approach for calculating the bulk and surface stress is developed and presented in this work. It is based on the tight-binding method with Chadi’s total energy model. A strained system is treated as a perturbation of an unstrained system; the corresponding stress can be calculated by the resolvent Green function method. This approach is applied to an arsenic terminated Si(001)2 × 1 surface.

I. INTRODUCTION

It is well known that the surface stress plays an important role in determining the surface reconstruction and is a significant factor in understanding various phenomena of surface physics, especially in the process of heteroepitaxial growth.1–6 It is shown1–3 that an external stress imposed on a heteroepitaxial film can drive a transition from one kind of surface reconstruction to the other. Theoretical studies on surface stresses can be divided into two categories. One is based on empirical interatomic potentials,7,8 The other is based on the first-principles calculation in the framework of the local-density approximation and ab initio pseudo-potentials.2,4,9,10 Meade and Vanderbilt4,9 performed surface stress calculations for adsorption of III, IV, and V group elements such as B, Al, Ga, and As on Si(111) and Ge(111) surfaces. It was found by their calculations that there are stress calculations for adsorption of III, IV, and V group elements such as B, Al, Ga, and As on Si(111) and Ge(111) surfaces. It was found by their calculations that there are stress calculations for adsorption of III, IV, and V group elements such as B, Al, Ga, and As on Si(111) and Ge(111) surfaces. It was found by their calculations that there are...
the atom \( l \). Thus, the stress contributed by the repulsive energy, \( \sigma_{ij}^{\text{rep}} \), can be easily expressed analytically,

\[
\sigma_{ij}^{\text{rep}} = \frac{1}{2} \sum_{l'} \left( U_1 + 2U_2 \left[ \frac{|\mathbf{R}' - \mathbf{R}|}{d_0} - 1 \right] \right) \times \frac{(R'_i - R'_{i'}) [R'_j - R'_{j'}]}{d_0|R' - R'|}.
\]  

(2)

The calculation of the stress contributed by the band-structure energy, \( \sigma_{ij}^{\text{bs}} \), is not trivial and will be described in the following paragraph.

Since a strained system can be treated as a perturbation of an unstrained system, it is appropriate to use the Green function method. If the Hamiltonian, the Green function, and the density of state of the unstrained system are described by \( \hat{H}^0 \), \( \hat{G}^0(E) \), and \( N^0(E) \), respectively, for the strained system they can be represented by \( \hat{H} = \hat{H}^0 + \delta \mathbf{H} \), \( \hat{G}(E) \), and \( N(E) \), respectively, where \( \Delta \mathbf{H} \) is the perturbation. The stress corresponding to the strain, \( \epsilon_{ij} \), contributed by the band-structure energy can be expressed with the help of Green function as

\[
\sigma_{ij}^{\text{bs}} = \frac{\partial}{\partial \epsilon_{ij}} \int_{E_F}^{E_F} E \{ N(E) - N^0(E) \} dE
\]

\[
= \frac{1}{\pi} \frac{\partial}{\partial \epsilon_{ij}} \int_{E_F}^{E_F} \text{Im} \{ \text{Tr} \left[ 1 - \hat{G}^0(E) \Delta \mathbf{H} \right] \} dE
\]

\[
= -\frac{1}{\pi} \frac{\partial}{\partial \epsilon_{ij}} \int_{E_F}^{E_F} \text{Im} \{ \hat{G}(E) \frac{\partial \Delta \mathbf{H}}{\partial \epsilon_{ij}} \} dE,
\]

(3)

where the change of Fermi energy with strain has been neglected, since an infinite-small strain characterized by \( \epsilon \) does not create a localized state deep in the energy gap.\(^{17,18}\) In the framework of the empirical tight-binding method and under the assumption that atomic orbitals are independent of the strain, the derivatives of \( \Delta \mathbf{H} \) with respect to the strain tensor, \( \epsilon_{ij} \), can be expressed by the product of the atomic position \( \mathbf{R} \) and the derivatives of \( \mathbf{H} \) with respect to \( \mathbf{R} \). To first order, a symmetric strain tensor \( \epsilon_{ij} \) transforms \( R_i \) into \( R_i + \sum_j \epsilon_{ij} R_j \), thus we have \( \partial R_i / \partial \epsilon_{ij} = R_j \). In addition, \( \partial \Delta \mathbf{H} / \partial \epsilon_{ij} = \partial \mathbf{H} / \partial \epsilon_{ij} \). Note the elements of matrix \( \mathbf{H} \) are the function of \( \mathbf{R}' - \mathbf{R}'' \) and all \( \mathbf{R}' - \mathbf{R}' \) are the function of strain tensor \( \epsilon_{ij} \), where \( l \) runs over all atoms in unit cell and \( l' \) over all first and second neighbors of the \( l \) atom. Therefore, when the derivative of matrix \( \mathbf{H} \) with respect to \( \epsilon \) is transformed to that with respect to \( \mathbf{R}' = \mathbf{R}' - \mathbf{R}' \), the sum over \( l \) and \( l' \) is needed:

\[
\frac{\partial \Delta \mathbf{H}}{\partial \epsilon_{ij}} = \sum_{l'} \frac{\partial \mathbf{H}}{\partial R_i} \frac{\partial R_{i'}}{\partial \epsilon_{ij}} \bigg|_{\mathbf{R}' = \mathbf{R}'} = \sum_{l'} \frac{\partial \mathbf{H}}{\partial R_i} R_{i'} \bigg|_{\mathbf{R}' = \mathbf{R}'}
\]

(4)

The derivatives of \( \mathbf{H} \) with respect to the atomic positions can be also analytically expressed for the tight-binding Hamiltonian. From the above expressions we can derive the sum over \( l' \) and define the stress for the \( \mathbf{R}' \) layer contributed by the band structure as

\[
s_{ij}^{\text{by}}(\mathbf{R}') = -\frac{1}{\pi} \int_{E_F}^{E_F} \text{Im} \{ \text{Tr} \left[ \hat{G}(E) \sum_i \frac{\partial \mathbf{H}}{\partial R_i} R_{i'} \bigg|_{\mathbf{R}' = \mathbf{R}'} \right] \} dE
\]

as well as that contributed by the repulsive energy,

\[
s_{ij}^{\text{rep}}(\mathbf{R}') = \frac{1}{2} \sum_{l'} \left[ U_1 + 2U_2 \left[ \frac{|\mathbf{R}' - \mathbf{R}|}{d_0} - 1 \right] \right] \times \frac{(R'_i - R'_{i'}) [R'_j - R'_{j'}]}{d_0|R' - R'|},
\]

(6)

thus the total surface stress is now given by

\[
\sigma_{ij} = \sum_l s_{ij}^{\text{by}}(\mathbf{R}') + \sum_l s_{ij}^{\text{rep}}(\mathbf{R}').
\]

The interaction parameters of Si as well as parameters between Si and As were determined by fitting its band structures to our \textit{ab initio} calculation results. The SiAs solid was modeled in a zinc-blende structure, and the lattice constant was obtained by the minimization of total energy. The \textit{ab initio} calculations were performed by the \textit{ab initio} molecular-dynamics package of the Car-Parrinello-like scheme,\(^{19}\) \textit{phi96md},\(^{20}\) based on the framework of local-density-functional theory (LDFT). The Ceperley and Alder exchange-correlation form\(^{21}\) parametrized by Perdew and Zunger\(^{22}\) and the fully separable \textit{ab initio} pseudopotentials\(^{23}\) for Si and As were used. In the present work, the empirical tight-binding parameters up to the second-nearest neighbors are taken into account. In this way, the valence bands and the lowest conduction band along the high symmetry axis in the Brillouin zone were reproduced within 0.2 eV. The \( d^{-2} \) scaling was used for parameters. The potential parameters, \( U_1 \) and \( U_2 \), were obtained by fitting the curves of total energy versus bulk volume to the corresponding \textit{ab initio} results, which were also obtained by the \textit{phi96md} package.\(^{20}\) All the tight-binding parameters and the potential parameters are listed in Table I. The justification of this procedure to determine the parameters is described and discussed in detail in Refs. 24 and 25. We use the parameters of Si-As for Si and As atoms on the interface layers. The charge transfer between layers has also been taken into account by the self-consistent semi-empirical tight-binding method.\(^{17,18}\) Since the net charge induced by the charge transfer is treated in this method as the charge uniformly distributed on the layer, it will not change the above stress expression. For details, please refer to Ref. 18.

III. RESULTS AND DISCUSSIONS

It is well known that the clean Si(001) can form the buckled \( p(2 \times 2) \) or \( c(4 \times 2) \) reconstruction (see, e.g., Refs. 26 and 27), however it was also shown that the adsorption of the group V elements such as As (or Sb) on Si(001) can form domains of \( 2 \times 1 \) or \( 1 \times 2 \) reconstruction,\(^{28,29}\) with a twofold degeneracy. In this structure, the adsorption of As on Si(001) will change the reconstruction of the clean surface from the buckled \( p(2 \times 2) \) or \( c(4 \times 2) \) to the \( 2 \times 1 \) or \( 1 \times 2 \). It can be interpreted that As atoms after breaking Si-Si dimers and filling the dangling bonds of Si(001) can form the \( 1 \times 2 \)
TABLE I. The interaction (V) and on-site energy (E) parameters for Si as well as for Si-As in eV. Here the superscripts a and c refer to anion and cation, 1 and 2 to first and second neighbors, respectively, and the subscripts s and p correspond to s and p orbital.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Si-As</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a)</td>
<td>(-3.885)</td>
<td>(-3.455)</td>
</tr>
<tr>
<td>(E_p)</td>
<td>(0.384)</td>
<td>(0.814)</td>
</tr>
<tr>
<td>(E_s)</td>
<td>(-10.900)</td>
<td>(-2.649)</td>
</tr>
<tr>
<td>(V_{i\sigma}^{p})</td>
<td>(-1.988)</td>
<td>(-1.296)</td>
</tr>
<tr>
<td>(V_{i\sigma}^{s})</td>
<td>(1.983)</td>
<td>(2.269)</td>
</tr>
<tr>
<td>(V_{pp}^{\sigma})</td>
<td>(2.363)</td>
<td>(2.347)</td>
</tr>
<tr>
<td>(V_{pp}^{\pi})</td>
<td>(-0.676)</td>
<td>(-0.603)</td>
</tr>
<tr>
<td>(V_{ss}^{\sigma})</td>
<td>(0.000)</td>
<td>(-0.017)</td>
</tr>
<tr>
<td>(V_{ss}^{\pi})</td>
<td>(-0.008)</td>
<td>(-0.056)</td>
</tr>
<tr>
<td>(a_0) (Å)</td>
<td>(5.388)</td>
<td>(5.585)</td>
</tr>
<tr>
<td>(U_1)</td>
<td>(-15.512)</td>
<td>(-11.633)</td>
</tr>
<tr>
<td>(U_2)</td>
<td>(50.672)</td>
<td>(43.811)</td>
</tr>
</tbody>
</table>

A side view of the \(2 \times 1\) reconstruction of the equilibrium geometry of one monolayer of arsenic on a Si(001) semi-infinite substrate is determined. Only the relaxation of the top six surface layers has been taken into account, since it can also be found that further relaxation has no numerically significant effects both on the structures and stresses. Calculations for various numbers of relaxed layers, i.e., the top eight and ten surface layers, have been performed, and the variation of the total energy and the stress is smaller than 0.03 eV and 0.01 eV/(1 \(\times 1\) cell), respectively. For the \(2 \times 1\) reconstruction, the integrations were calculated using eight special \(k\) points in the irreducible part of the surface Brillouin zone. The bulk Green’s function has been calculated by summing over 100 \(k\) points (in the direction perpendicular to the surface).\textsuperscript{13}

A side view of the \(2 \times 1\) structure of the semi-infinite surface is shown in Fig. 1. The semi-infinite geometry is treated by the Green function method.\textsuperscript{13} The optimal structure of As on the Si(001) semi-infinite surface is determined by limiting the Hellmann-Feynman force on each relaxed atom to be smaller than 10^{-4} eV/Å. This optimizing procedure has been described in detail in our previous work,\textsuperscript{7,18} in which the charge transfer between layers has also been taken into account by the self-consistent semiempirical tight-binding method.

In the \(2 \times 1\) reconstruction, the optimal procedure within the numerical exactness by using several different original geometries all leads to the same result with As atoms forming the same symmetric dimer geometries, without a significant tilted angle. Each surface As atom is thus threefold coordinated and bonded to two atoms in the subsurface, which is fourfold coordinated. In Table II the obtained results for As on the Si(001)\(2 \times 1\) semi-infinite surface are listed in summary. The As-As dimer bond length is found to be 2.47 Å, comparing well with the results of \textit{ab initio} calculations by Krüger and Pollmann,\textsuperscript{30} 2.52 Å, as well as by Uhrberg \textit{et al.},\textsuperscript{28} 2.55 Å. The backbond length between the As atom and the subsurface Si atom is found to be 2.42 Å, which is in good agreement with the results of 2.42 Å by Krüger and Pollmann\textsuperscript{30} and 2.44 Å by Uhrberg\textsuperscript{28} This means that the present tight-binding model can be used to describe the As/Si(001)\(2 \times 1\) system.

As in other models in the literature, each As atom is bonded to its partner As atom to form a symmetric dimer. Each As atom of the dimer is bonded to two Si atoms in the second layer and thus pulls the Si atoms to move towards the direction of the dimer bond. Due to the symmetry restriction, the forces on the atoms in the third and fourth layer lead to displacements of 0.35 Å and 0.27 Å between the up atom.

TABLE II. Structural parameters for As on Si(001) \(2 \times 1\) semi-infinite surface, in Å. \(\Delta x\) and \(\Delta z\) represent the atomic displacements relative to the corresponding position of an ideal Si.

<table>
<thead>
<tr>
<th>Layer</th>
<th>(\Delta x)</th>
<th>(\Delta z)</th>
<th>(\Delta x')</th>
<th>(\Delta z')</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.67</td>
<td>0.02</td>
<td>-0.67</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.19</td>
<td>-0.03</td>
<td>-0.19</td>
<td>-0.03</td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>0.17</td>
<td>0.00</td>
<td>-0.18</td>
</tr>
<tr>
<td>4</td>
<td>0.00</td>
<td>0.13</td>
<td>0.00</td>
<td>-0.14</td>
</tr>
<tr>
<td>5</td>
<td>0.07</td>
<td>0.00</td>
<td>-0.07</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>0.03</td>
<td>0.00</td>
<td>-0.03</td>
<td>0.00</td>
</tr>
</tbody>
</table>
TABLE III. Surface stress for As on Si(001) 2×1 semi-infinite surface in eV/(1×1 cell). The symbols $\parallel$ and \perp refer to directions parallel and perpendicular to the dimer bonds. $\bar{\sigma}=(\sigma_\parallel + \sigma_\perp)/2$, $\Delta\sigma=\sigma_\parallel - \sigma_\perp$.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_\parallel$</th>
<th>$\sigma_\perp$</th>
<th>$\bar{\sigma}$</th>
<th>$\Delta\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>2.1</td>
<td>2.0</td>
<td>2.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ref. 31</td>
<td>2.41</td>
<td>2.35</td>
<td>2.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Ref. 11</td>
<td>3.1</td>
<td>2.9</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Ref. 16</td>
<td></td>
<td></td>
<td>2.57</td>
<td></td>
</tr>
</tbody>
</table>

and the down atom in the direction perpendicular to the surface, as shown in Table II. Due to the restoring forces, a displacement of about 0.07 Å remains in the fifth layer beneath the surface, as shown in Table II.

With the optimal structures calculated by the above mentioned method, the surface stress for As/Si(001) 2×1 has been calculated using Eq. (7). As expected, the As/Si(001) 2×1 was shown to be under tensile stress. The stresses of 2.1 eV/(1×1 cell) along the dimer direction and 2.0 eV/(1×1 cell) perpendicular to the dimer direction were obtained. The anisotropy of surface stress is 0.1 eV/(1×1 cell). This result is listed in Table III together with theoretical and experimental results by other authors.

In order to understand the relationship between the structure and the stress, we calculate the planar stress by using Eq. (5) and Eq. (6). In Fig. 2 the planar stress parallel (circles) and perpendicular (squares) to the dimer bonds is plotted as a function of the atomic layer beneath the surface. The marked points are calculated values. A straight line connecting the calculated points serves as a guide to the eye. The dashed lines represent the sum of the total planar stress to the corresponding layer [Eq. (7)], and also the circles and squares representing the planar stresses parallel and perpendicular to the dimer bond, respectively. It is clearly shown that the sum of the planar stress approaches constant values of 2.1 and 2.0 eV/(1×1 cell) with the atomic layers for stress parallel and perpendicular to the dimer bond, respectively. The planar stress contributed by the As atomic layer has an anisotropy of 0.1 eV/(1×1 cell). The sum up to three surface layers has shown that the anisotropy of stress does not change, which means that the contribution of Si atomic layers to the planar stress has compensated each other.

The planar stress parallel to the dimer bond shows an almost linear decrease from the first layer to the fourth layer, which indicates that the influence of the strain induced by the formation of the As dimer bond in that direction decreases with the increase of the distance beneath the surface and approaches zero at about the fourth layer beneath the surface. But there still exist significant relaxations beneath the fourth layer, as shown in Table II.

The component of the planar stress for the second layer perpendicular to the dimer bonds is almost the same as that for the first layer, which is about 0.9 eV/(1×1 cell). It can be understood by checking the displacements of atoms. Due to the formation of the As-As dimer bond, the As atom pulls its neighboring atoms in the second layer toward itself. The displacements of atoms in the second layer are about 0.19 Å, which leads to a 0.6 eV/(1×1 cell) tensile planar stress parallel to the dimer bond. Meanwhile, it should push the neighboring second-layer atoms in the direction perpendicular to the dimer bond. However, due to the symmetric restriction, the second-layer atoms cannot move in that direction, thus it results in a tensile planar stress. Due to the restriction of the symmetry, the atoms in the third layer relax up and down, thus the distance between the two neighboring atoms increases, which means that it will result in a tensile stress, about 0.4 eV/(1×1 cell) in the direction parallel to the dimer bond. On the other hand, there exist almost no changes in the direction perpendicular to the dimer bond, which means that the planar stress in that direction is small, as shown in Fig. 2.

**IV. CONCLUSIONS**

Based on the semiempirical self-consistent tight-binding method and Chadi’s short-range force-constant model, an approach for calculating the bulk and surface stress was presented in this work. By applying this approach to study the system of As adsorption on the Si(001) substrate, it was shown that this approach could describe quite well the surface stress with its relative simplicity in the computation. Furthermore, the planar stress could also be easily obtained.

It was shown that the main contribution of surface stress of As/Si(001) comes from the top three layers, for both directions parallel and perpendicular to the dimer bond, although the significant relaxations can be found up to the sixth layer. By analyzing the planar stress, it was found that in the 2×1 reconstruction the contributions of the Si atomic layers to the surface stress anisotropy compensate each other, whereas the contribution of the As atomic layer to the surface stress anisotropy was the same as the total surface stress anisotropy.
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