Chapter 3. Semiconductor Surface Studies

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3.1 Introduction

Sponsor

Understanding the properties of surfaces of solids and the interactions of atoms and molecules with surfaces is extremely important from both a technological and academic point of view. The recent advent of ultrahigh vacuum technology has made microscopic studies of well-characterized surface systems possible. The way atoms move to reduce surface energy, the number of layers of atoms involved in this reduction, the electronic and vibrational states that result from this movement, and the final symmetry of the surface layer are all important in achieving a fundamental and microscopic understanding of the nature of clean surfaces, chemisorption processes, and the initial stages of interface formation.

The theoretical problems associated with surface systems are quite complex. We are currently, however, beginning to solve for the properties of these real surfaces systems (rather than for simple mathematical models). In particular, we continue to pursue our goal of calculating the total ground-state energy of a surface system from "first principles," to provide accurate theoretical predictions of surface geometries. In this program, we are concentrating our efforts on the areas of surface growth, surface reconstruction geometries, structural phase transitions, and chemisorption.

3.2 Thermal Amplitudes of Surface Atoms

The vibrational excitations of semiconductor surfaces provide a direct probe of the structural and bonding properties that result from their reconstruction. Moreover, studies of the vibrational properties of surfaces are necessary to understand the dynamical processes that occur on these surfaces (such as kinetics of adsorbates, diffusion and desorption, epitaxial growth, and possibly surface melting). The thermal fluctuations of the surface atoms are directly related to these phenomena. Furthermore, the analysis of a number of experimental probes requires a detailed knowledge of the vibrational amplitudes and correlations of the surface atoms. The Debye-Waller factors, which appear in the expressions for the intensity of radiation scattered from a surface, and the displacement-displacement correlations of the surface atoms enter into the interpretation of ion scattering and other experiments.

New developments in a number of experimental techniques for studying vibrational properties of surfaces have generated further interest, the need for realistic calculations, and better theoretical understanding. These include He-atom scattering, high-resolution electron-energy-loss spectroscopy, surface infrared spectroscopy, medium- and high-energy ion scattering, and surface extended x-ray-absorption fine-structure experiments. From a theoretical point of view, an underlying formalism for surfaces exists within the general framework of the theory of lattice dynamics, but we have made a few realistic calculations for specific surfaces.

In this work, we have made calculations of the atomic displacement-displacement correlation functions for atoms on the Si(111)

2 × 1 and Si(001) 2 × 1 surfaces. Both of these surfaces have been the subject of intense research for many years, and even though we have made considerable progress, several questions regarding their structure and basic excitations remain unresolved. Using a semi-empirical tight-binding theory for structural energies in Si, we investigate the thermal fluctuations of the atoms on these surfaces. Specifically, we determine the anisotropy of the vibrational amplitudes of the surface atoms between vibrations parallel and normal to the surface plane, their temperature dependence, and the interatomic vibrational correlations.

The Si(111) 2 × 1 surface is currenlty understood in terms of a π-bonding chain model. According to this model, the surface reconstructs by forming zigzag chains of surface atoms that run parallel to each other. The bonding along the chain is provided by the π interaction between the surface electrons. Figure 1 shows a side view of the Si(111) 2 × 1 surface. The chain model also helps us understand the unique vibrational properties observed on this surface. Its lattice dynamics are dominated by the chain geometry and the strong coupling between the electronic surface states and the structural degrees of freedom of the zigzag chains. In fact, the most salient features in the surface phonon spectrum are related to modes that have the same form and elementary vibrational excitations of the surface zigzag chains.

The appearance of a small-wavelength surface phonon with an unusually low energy is particularly relevant to the thermal fluctuations of the surface atoms. Indeed, one of the main reasons for this study is to investigate the thermal effects of this mode. This intrinsic vibration of the surface is dispersionless across the surface Brillouin zone, having an energy of $\hbar\omega = 10$ meV. Near the zone edge, it is located well below the acoustic continuum. Because of the low energy of this phonon and its lack of dispersion (leading to a large contribution to the phonon density of states at that energy), this mode is thermally populated with a large probability. Thus, one might expect that the vibrational amplitudes of the surface atoms on Si(111) 2 × 1 would be greatly enhanced.
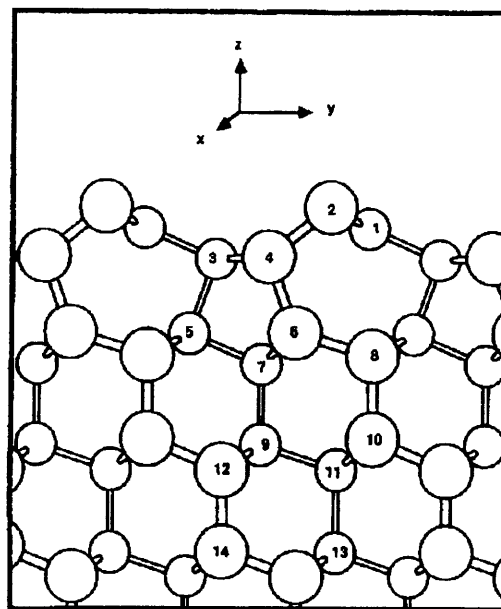

Figure 1. Side view of the π-bonded chain model of Si(111) 2 × 1. The two surface atoms, numbered 1 and 2, form zigzag chains that run parallel to the [112] direction (into the page); these chains are tilted with up (2) and down (1) atoms.

In contrast with the result for Si(111) 2 × 1, this low-energy small-wavelength surface phonon does not appear in the phonon spectrum of Si(001) 2 × 1. The basic building block in the reconstruction of Si(001) involves the formation of surface dimers between two neighboring surface atoms, halving the number of dangling bonds on the surface. Figure 2 shows a side view of the Si(001) 2 × 1 surface. The surface dimers do not remain symmetrical, tilting so that each dimer is formed by an up and down atom. With this model, we can understand the different periodicities observed on the surface [2 × 1, p(2 × 2) and c(4 × 2)] in terms of different ordered arrangements of the tilted surface dimers. We find that the normal modes of vibration of the higher-order reconstructions p(2 × 2) and c(4 × 2) are essentially the same as for the 2 × 1 reconstruction, since the surface phonons are essentially characterized by the vibrations of the nearly isolated surface dimers. Consequently, we concentrate only on the 2 × 1 reconstruction.
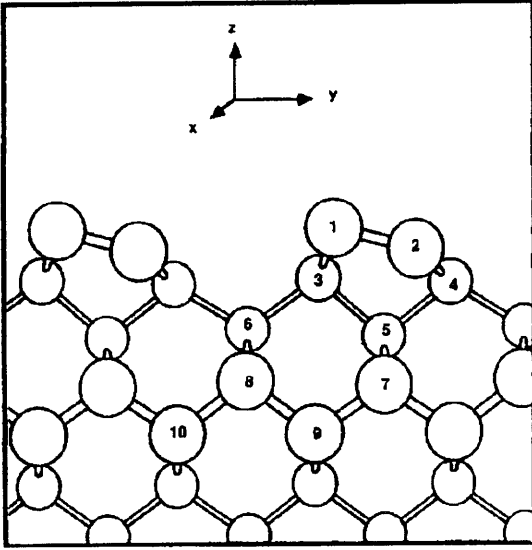
Figure 2. Side view of the tilted dimer model of Si(001)2 × 1.

In the harmonic approximation, the correlation function between the displacement u_{iv} of atom i along the direction μ (from its equilibrium position), and the displacement of atom u_{jv} of atom j along the direction v, can be expressed in terms of the phonons or normal modes of the system:

$$<u_{i\mu}u_{jv}> = \frac{h}{2N(M_iM_j)^{1/2}}$$

$$\times \sum_{q, \lambda} \frac{e_{i\mu}(q, \lambda)e_{jv}^*(q, \lambda)}{\omega_\lambda(q)}$$

$$\times e^{iq(R_i - R_j)}\{1 + 2n[\omega_\lambda(q)]\}, \qquad (1)$$

where the sum is over normal modes λ and wave vectors q in the Brillouin zone, $\omega_\lambda(q)$ e(q, λ) are the phonon frequencies and eigenvectors, respectively, R_i denotes the two-dimensional lattice vector of the surface unit cell where atom i is located, M_i is its mass, and N is the number of unit cells within the periodic boundary conditions used in the calculations. The temperature T enters through the Bose-Einstein distribution function n[ω].

The main difficulty in evaluating eq. (1) is that it requires the knowledge of the phonon energies and eigenvectors of the system over the entire Brillouin zone. Therefore, the calculation of vibrational correlation functions is usually limited to simple systems where the normal modes are determined by symmetry. Also, eq. (1) is usually approximated by low- and high-temperature expansions using models for the dispersion of phonon energies and the density of states, like the Debye model.

To make reliable predictions and to extract microscopic information from the thermal vibrational amplitudes of the system, eq. (1) must accurately represent the system's phonon energies and eigenvectors. For semiconductors surfaces, this representation is further complicated because their reconstruction leads to bonding configurations that can be quite different from the bulk; thus, dynamical properties cannot be simply described using force constants calculated for the bulk and transferred to the surface.

A realistic theory must be used to calculate phonon energies and eigenvectors for each particular reconstructed surface. In this work, we use a formalism based on a semi-empirical tight-binding theory for structural energies in semiconductors. To explain the model briefly, the total energy of the system is expressed in terms of the band-structure energy, an empirical potential energy of interionic interactions, and the Coulomb energy of on-site electronic repulsions. The band-structure energy is calculated using an sp³ tight binding representation of the valence electrons, and the interionic interactions are approximated with a sum of pairwise potentials. The on-site Coulomb repulsion term for the electrons is added to incorporate the effects of charge transfer. With this model, the dynamical matrix of a system can be calculated using perturbation theory, in which the bare ion-ion forces are renormalized by the electron polarizability; exponentially decaying interactomic forces are generated by the exchange of virtual electron-hole pairs between lattice distortions at different sites on the lattice. Because this approach incorporates the effects of reconstruction into the lattice dynamics of the surface, it successfully pro-

vides a description of the vibrational proper-
ties of Si surfaces.

The results of our calculations are presented
in figures 3 and 4. Here we notice that for
both Si(111) 2×1 and Si(001) 2×1, the
surface atoms have thermal vibrational ampli-
tudes that are larger along the direction per-
pendicular to the surface plane than parallel
to it. This is usually expected, since the
surface atoms have reduced coordination
normal to the surface. However, we find that
the degree of anisotropy between normal and
in-plane vibrations is very different for the
two surfaces. Indeed, for Si(111) 2×1 we
find that this anisotropy is quite large (1.8 in
the mean-squared amplitudes of vibration),
while on Si(001) 2×1 the fluctuations of
the surface atoms are nearly isotropic. Fur-
thermore, in the case of Si(111) 2×1, the
anisotropy increases rapidly with increasing
temperature, a feature we attribute to the
presence of a low-energy dispersionless
surface phonon. This large temperature
enhancement is not observed for the surface
atoms of Si(001) 2×1, which does not
support a similar low-energy surface phonon.
In comparing the atomic vibrational ampli-
tudes on the two surfaces, the most salient
feature is that, in the case of Si(111) 2×1,
the surface atoms have very large amplitudes
of vibrations normal to the surface. The dif-
ference in the vibrational amplitudes of
surface atoms on Si(111) 2×1 and Si(001)
2×1 shows that the specific microscopic
properties of the surface must be considered
in the calculation of the atomic vibrational
correlation functions.

Specifically, we predict the degree of
anisotropy between normal and in-plane
vibrations and the difference in vibrational
amplitudes between inequivalent surface
atoms. Experimental techniques exist that
can directly measure these variables.
Perhaps the most important contribution of
the calculations we have presented here is in
their use in the analysis of experiments. Our
calculated atomic vibrational amplitude and
correlation function results might greatly
reduce the uncertainties in the interpretation
of scattering experiments that probe the
structure of the surface; Debye-Waller factors
might also be easily calculated with the
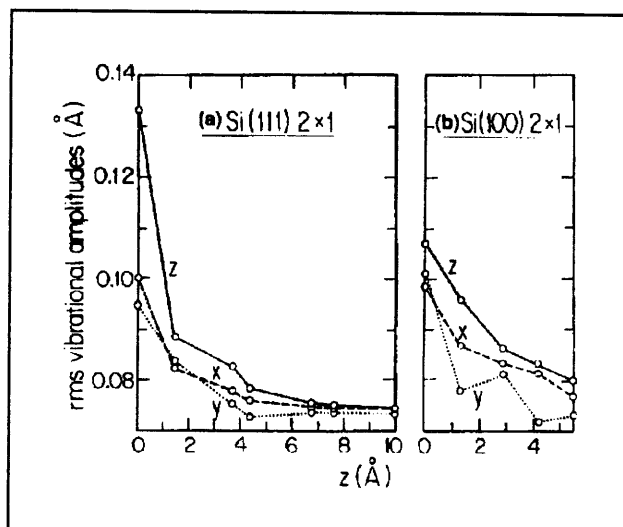information we have provided.

Figure 3. Atomic rms vibrational amplitudes at T=
270K as a function of penetration from the surface for
(a) Si(111) 2×1 and (b) Si(100) 2×1. The
Cartesian directions are defined in figures 1 and 2,
respectively.

3.3 Heteroepitaxial Growth

Heterostructures of semiconductors, ele-
mental or compound, have recently been the
subject of intense study as technologically
promising artificial materials. GaAs on Si is a
system of particular interest, not only from a
technological but also from a theoretical
point of view. Usually GaAs growth is initi-
ated on Si substrates oriented along the
(100) direction. The quality of the GaAs
overlayers is far from ideal with a very high
density of defects and dislocations present,
presumably due to lattice mismatch and
polarity differences. However, it is not known
to what degree other interface factors, such
as surface reactions or substrate morphology,
play an important role in growth inhibition or
initiation. These issues are at the core of
current growth models of GaAs on Si(100).

In this work, we investigate, from an ab initio
theoretical point of view, the possibility of
layered growth of GaAs on atomically flat
regions (terraces) of the Si surface. We shall
focus on the initial stages of growth by con-
sidering very low coverages (one to two
monolayers) where a number of important
issues can be isolated and addressed in
detail. For example, what is the structure of
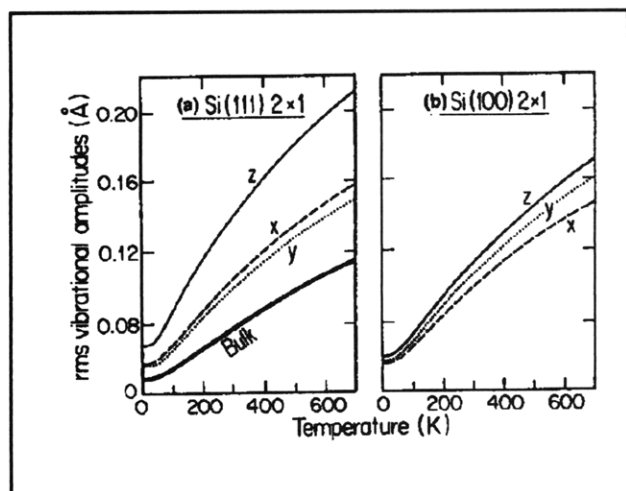the initial monolayers? Are the Ga and As

Figure 4. Atomic rms vibrational amplitudes of surface atoms on (a) Si(111) 2 × 1 (surface atom 2) and (b) Si(001) 2 × 1 (surface atom 1) as a function of temperature. The bold line is for a bulk atom.

atoms locally mixed or do they separate into domains of each species? Is the Si surface covered by Ga and As atoms to the largest possible extent at monolayers thickness or do these atoms form GaAs bilayer islands on part of the surface? What is the structure of the initial bilayer of GaAs? Does it resemble that of bulk GaAs with alternating places of Ga and As or does it have a novel structure?

To address the possibility of two-dimensional growth on Si terraces, we consider a slab of Si bounded by (100) surfaces on which we place Ga and As atoms. The issue of interest is the lowest-energy local structure and its effects on prospects for growth. There are two possibilities: the lowest-energy local structure may be the same as the structure of bulk GaAs, so that two-dimensional growth can proceed, or the structure may be different, in which case layered growth of zincblende GaAs will be inhibited. The easiest way to envision formation of the lowest-energy structure is to consider a Si surface covered by a monolayer of one species (corresponding to pre-deposition, for example, of Ga or As) and to introduce some amount of the opposite species. One must then consider the possible local atomic con-

figurations and identify the lowest-energy structure. In this sense, the exact relative abundance (chemical potential) of Ga and As atoms is not important, but the presence of both species is crucial.

Each surface layer of the slab is taken to be reconstructed, for simplicity, in the standard (2 × 1) dimer pattern (this choice will be justified below). The Ga and As atoms are placed on the slab in five different ways as shown in figures 5(a)–5(e). The total energies resulting from ab initio calculations allowing these geometries to fully relax, are presented in table 1.
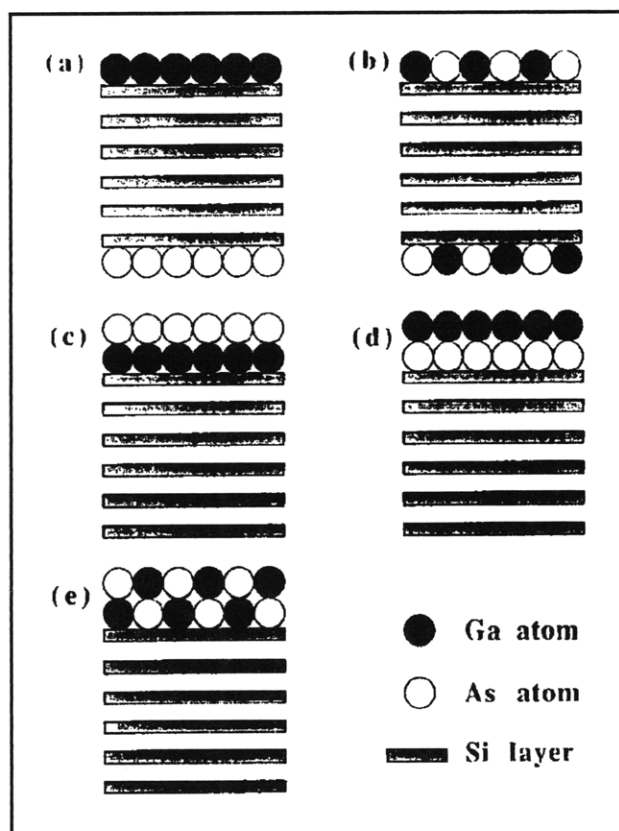

Figure 5. Schematic representation of overlayer arrangements. (a) Pure monolayer coverage, (Ga)[Si](As). (b) Mixed monolayer coverage, (GaAs)[Si](AsGa). (c) Bilayer coverage with pure layers and As-exposed surface, (As)(Ga)[Si]. (d) Same as (c) with Ga-exposed surface, (Ga)(As)[Si]. (e) Bilayer coverage with mixed layers, (GaAs)(AsGa) [Si].

Figure	Configuration	Relative Energy Difference
5(a)	(Ga)[Si](As)	0.8
5(b)	(GaAs)[Si](AsGa)	0.0
5(c)	(As)(Ga)[Si]	2.2
5(d)	(Ga)(As)[Si]	2.8
5(e)	(GaAs)(AsGa)[Si]	1.5

Table 1. Relative energy difference of the various overlayer configurations as depicted in figure 5 in eV/(2X1) SUC.

Based on the energies of the different configurations, a number of important conclusions can be drawn:

1. When the available amount of Ga and As atoms is less than a full monolayer, under equilibrium stoichiometric conditions, it wets the Si surface and formation of thicker GaAs islands is inhibited.

2. At monolayer coverage, the two species of atoms do not separate into pure Ga or pure As domains, but are locally mixed on the Si surface.

3. When GaAs is available in stoichiometric amounts sufficient for bilayer coverage, the equilibrium structure of the bilayers is not a succession of pure Ga and As layers as in bulk GaAs along the (100) direction. Rather, chemical and rehybrid-ization reactions are energetically very favorable, leading to a passivating mixed overlayer configuration. Once this mixed layer is formed, it could persist in a disordered phase even under non-stoichiometric conditions because of its considerable stability. The mixed layer resembles locally a wurtzite structure under large uniaxial stress. A structural barrier (requiring creation of extensive defects at large energy cost) is encountered in reverting from the mixed layer structure to the zincblende structure of bulk GaAs.

This conclusion has important implications: Since the mixed layers have very different structure from the thermodynamically stable zincblende phase of bulk GaAs, the growth of mixed layers on terraces will be undermined by any surface topology which could lead to nucleation of zincblende GaAs. Thus, nucleation centers of zincblende GaAs at specific surface topologies will prevail in the growth process. It is possible to grow bulk GaAs experimentally on vicinal Si(100) surfaces, that is, surfaces with large density of steps. It is likely that surface steps are precisely the topology that nucleates zincblende GaAs, and growth occurs directly on the steps. Indeed, experimental evidence appears to support this view. Search for a possible microscopic mechanism for the initiation of this kind of growth, which involves formation of zincblende GaAs seeds at double-layer steps on the Si surface, is currently in progress.