Chapter 3. Semiconductor Surface Studies

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Understanding the properties of surfaces of solids and the interactions of atoms and molecules with surfaces has been of extreme importance both from technological and academic points 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 the energy of the surface, 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 of utmost importance in arriving at a fundamental and microscopic understanding of the nature of clean surfaces, chemisorption processes, and the initial stages of interface formation. Actually, one of the most difficult and fundamental problems in surface studies, both from the experimental and theoretical points of view, is simply the determination of the precise positions of the atoms on a surface. Currently, there are many surface geometries, even for elemental surfaces, that remain extremely controversial.

The theoretical problems associated with these systems are quite complex. We are, however, currently in the forefront of being able to solve for the properties of real surface systems (rather than simple mathematical models). In particular, we are continuing our goal of calculating the total ground-state energy of a surface system from "first principles" so that we may be able to provide accurate theoretical predictions of surface geometries. Our efforts in this program have concentrated in the areas of surface growth, surface reconstruction geometries, structural phase transitions, and chemisorption.

3.1 Ground State Geometries of Surfaces

Using "first principles" total energy calculations, it is possible to determine on a microscopic scale how atoms behave when they are on the surface of a solid. This is a fundamental problem that has plagued both theorists and experimentalists for decades. The difficulty lies with the very strong interactions that may exist between the surface atoms and the host atoms constituting the rest of the solid. These interactions can strongly disturb the original idealized atomic arrangement at the surface, changing the nature of the bonding and even the original stoichiometry.

At short length-scales the atomic reorientations on the surface typically lead to what is known as "reconstruction." At long length-scales, it has always been assumed that there exists a perfect state of the surface that is otherwise atomically smooth and uniform. This implies that the intrinsic ground-state of a facetted surface of a crystal, which in general includes a reconstruction, is otherwise atomically smooth and uniform.

To test this hypothesis we have combined quantum total energy calculations which can describe accurately the microscopic properties of the surface at very short length scales with continuum mechanical calculations which can describe collective phenomena at very long length-scales.

The results of our theoretical analysis lead to the following exciting prediction: *surfaces of crystals which reconstruct with broken*

orientational symmetry and exhibit an aniso-tropic intrinsic stress tensor are unstable to a spontaneous formation of elastic stress domains. Thus, the ground-state of such a surface is not uniform and will form an ordered array of domains of reconstructions in different orientations.

Recently an experiment was performed by F. Men, W. Packard, and M. Webb, *Bull. Am. Phys. Soc.* 33:472 (1988), on Si(100) that we believe provides evidence for our predic-tion. Their results are shown in the top panel of figure 1. They observe that upon annealing, the fraction of one type of domain grows at the expense of the other when an external strain is applied to the surface. The domains for which the applied compression is along the dimers are the ones that grow, in agreement with our calculations or the surface stress tensor. When the external strain is released, however, the surface returns to its "initial" configuration of equal domain populations. This surprising result is consistent with our idea of spontaneous for-mation of stress domains, where the ground-state of the surface corresponds to a domain configuration. Comparison of the exper-imental intensities of domain populations with the theoretical curves (top and lower panels in figure 2, respectively) suggests that the experimental surface is only in quasi-equilibrium. This is presumably because of local surface miscuts or kinematic consider-ations which allow for only local equilibration. Indeed, the difference in the data between positive and negative applied strains is indicative of kinematic constraints.

With our calculated value of the stress anisotropy, F_o, and our fitting the exper-imental data to determine the strain constant ε_o = 0.03%, we can predict the characteristic size of the domains, *l*. We obtain a value for *l* between 300 and 1000 Å. The uncertainty comes from the fit of ε_o, from the choice of bulk elastic constants, and from the uncer-tainty in F_o. This length scale is consistent with the experiment of Men, Packard, and Webb, which puts a lower bound for *l* of approximately 500 Å.

We are currently investigating this system in more detail to understand the effects of dif-ferent types of steps, defects and miscuts on the final geometry.

All ab-initio theoretical calculations on surface systems have been at zero temper-ature. It is now becoming possible, however, to begin studying the statistical mechanics and temperature related phase transitions of surfaces of solids. This is a completely new and unexplored area. As an example, the myriad of surface reconstructions that may exist on clean semiconductor surfaces at dif-ferent temperatures is an extremely inter-esting and fundamental problem that needs to be investigated. Modern studies of phase transitions utilize a powerful theoretical tool which is the renormalization group scheme. The scheme is based on scaling ideas, and has as input simple spin Hamiltonians which model the degrees of freedom of the system. Until now there has been no way of calcu-lating what these Hamiltonian parameters should be for real surfaces of solids. The total energy calculations described above, however, should provide precisely the kind of information needed. The exciting possibility
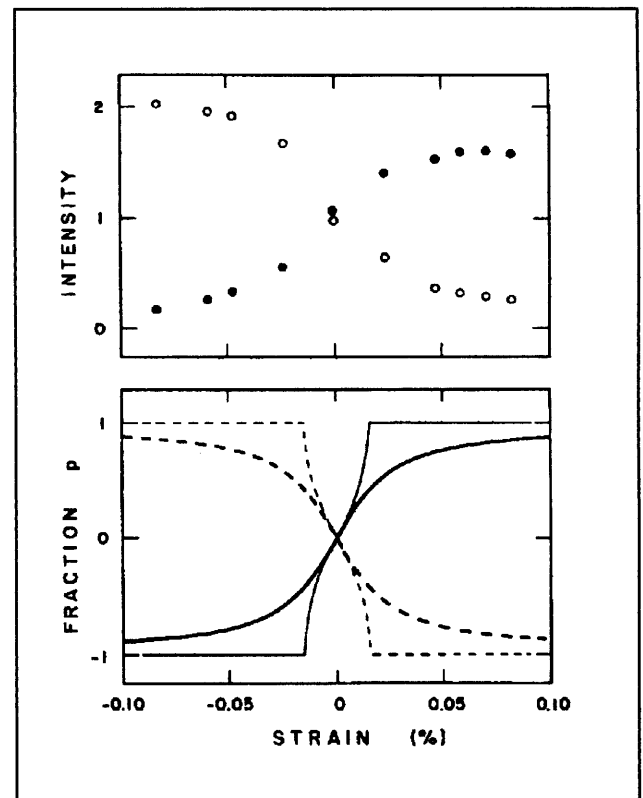
Figure 1. Top: Experimental intensity of (1x2) (open circles) and (2x1) (filled circles) domains on the Si(001) surface as a function of applied external strain. Bottom: Theory for ε_o = 0.03%. The thick (thin) lines correspond to quasi (global) equilibrium.
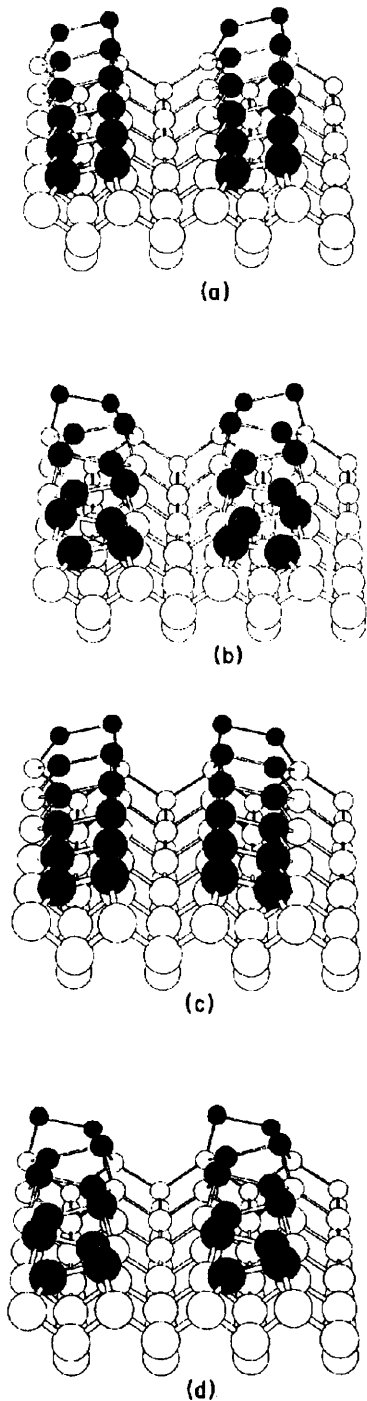
Figure 2. Perspective view of dimer models of the Ge(100) surface. The solid atoms are the surface layer. (a) Buckled (2x1) symmetry configuration. (b) Centered (4x2) symmetry configuration. (c) Primitive (4x1) symmetry configuration. (d) Primitive (2x2) symmetry configuration.

then arises of coupling the results of microscopic studies of surface systems (at zero temperature) with simple spin Hamiltonians and the renormalization group approach to study phase transitions at finite temperatures from "first principles."

In the past, using a simple-empirical total energy approach, we succeeded in developing such a scheme and have applied it to the Si(100) surface, resolving important questions regarding the structure of the Si(100) surface. We are now investigating the possible phase transitions that may occur on the Ge(100) surface. This system, however, cannot be described accurately by a semi-empirical approach so that we are forced to use the more powerful and much more complex ab-initio total energy methods.

To perform these studies we have been developing a new scheme for relaxing a system with many degrees of freedom to its lowest energy configuration. The scheme is based on a molecular dynamics approach to calculating quantum mechanical total energies and resembles a simulated quench.

Using this approach we have calculated the total energy of four members of the (2x1) family of buckled dimer reconstructions. These are illustrated in figure 2. The total energies are given in table 1.

Table 1. Total energy of (2x1) family symmetry configurations.	
System	Total energy (eV/dimer)
b (2 X 1)	0.000
p (4 X 1)	0.035
c (4 X 2)	− 0.066
p (2 X 2)	− 0.069

We expected p(2x2) and c(4x2) to be close in energy because of our previous tight-binding work in Si. We find that c(4x2) is lower in energy than b(2x1) because the alternation of up and down dimers along the dimer rows allows the second-layer atoms to relax. To keep bond distances close to the bulk value, the atoms in the second layer want to move towards the up dimer atom to which they are bonded and away from the down dimer atom. This motion is energetically favorable only when the "up" and "down" dimers alternate along the dimer

rows as in the p(2x2) and c(4x2) recon-structions. When the second-layer atoms are either bonded to two "up" or two "down" dimer atoms, they cannot move towards or away from a dimer without further stretching or compressing an already stretched or com-pressed bond, as the case may be. If this were the sole mechanism differentiating the energies of the various dimer reconstructions, p(2x2) would be degenerate with c(4x2) and p(4x1) would be degenerate with b(2x1). Since p(4x1) is significantly higher in energy than b(2x1), this is strong evidence that an additional mechanism is at work.

The magnitudes of the displacements of the atoms are extremely similar between p(2x2) and c(4x2) dimers. In fact, if one takes the position of the two independent dimers in the p(2x2) geometry and maps them into the other two dimers according to c(4x2) rules, one gets an identical energy with the original minimum energy c(4x2). In contrast to pre-vious work, there was negligible breaking of the reflection symmetry of the (010) plane. This symmetry breaking did not affect the total energy and probably arose from difficul-ties in performing those calculations. We find a dimer tilt of 14 degrees for all four minimum-energy configurations.

To predict a phase-transition temperature one maps the dimer problem to a two-dimensional Ising-spin-problem:

$$-H = V \sum_{i,j} s_{i,j}\, s_{i,j+1} + H \sum_{i} s_{i,j}\, s_{i+1,j}$$

$$+ D \sum_{i,j} s_{i,j}\, s_{i+1,j+1} + U \sum_{i,j} s_{i,j}\, s_{i,j+2}$$

$$+ F \sum_{i,j} s_{i,j}\, s_{i,j+1}\, s_{i+1,j}\, s_{i+1,j+1}$$

This Hamiltonian includes all interactions up to two surface-atom spacings as shown in figure 3. The T=0 values of V, H, and D are derived from the total-energy differences of the four configurations and are given in table 2.
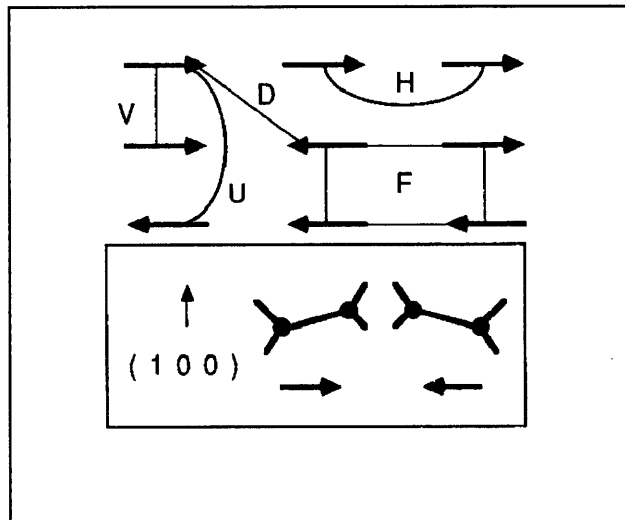

Figure 3. Effective couplings between adjacent dimers.

Table 2. Effective coupling constants between adjacent dimers.	
Coupling constant	E (meV)
V	− 43
H	10
D	4

As can be seen by the relative magnitude of V to H and D, the strongest coupling between dimers is along the rows. The terms involving U and F interactions contribute equally to the total energies for all four sym-metries and are initially set equal to zero. A position-space renormalization-group-theory calculation is performed with a finite cluster of four cells of five sites each and the flows occur in the parameter space of V, H, D, and F. These values of the parameters lead to a phase-transition temperature of 380 ± 100 K.

These calculations also predict that the crit-ical exponents associated with diffraction spot intensities and widths should be in the Ising universality class.

3.2 Hydrogenation

The interaction of atomic hydrogen with cleaned semiconductor surfaces has been extensively studied for over a decade. Hydrogen atoms appear to saturate surface dangling bonds resulting in a nearly ideal, bulk-terminated plane of exposed surface atoms. It is interesting that in cases where the surface does not have the geometry and

periodicity of the bulk-terminated plane, the interaction of hydrogen with surface atoms is strong enough to unreconstruct the complicated reconstruction patterns. This process takes place for example on the (2x1) Si(111) surface, which exhibits a low-energy 9=bonded-chain reconstruction. Upon hydrogenation this chain of Si atoms with (2x1) periodicity reverts to the (1x1) pattern of the bulk-terminated plane. Similar phenomena have been observed on the Ge(111) surface. Theoretically, this process is not very well understood and a realistic, first-principles study with adequate accuracy to define precise low energy positions of atoms, corresponding total energies, and vibrational excitations above the ground-state has been completely lacking.

Presently, we have undertaken precisely such a study. Using ab-initio quantum mechanical total energy calculations, we find that the atomic positions of the hydrogenated Si and Ge(111) surfaces differ significantly from those of an ideal bulk terminated plane. In particular, the Si-H and Ge-H bonds are found to be considerably larger than the sum of covalent radii. The substrate relaxations are small and their physical origin can be explained in terms of electronic charge transfer, which eliminates the surface dipole moment by shifting charge from the hydrogen bond to the back-bonds.

To determine vibrational excitations we need to investigate the change in total energy with various configuration coordinates. There are three vibrational modes that are of interest to study. Two are easily identified in terms of simple atomic motions and involve hydrogen atoms moving relative to the substrate. The large difference in mass between H, Si and Ge effectively decouples the motion of H from collective modes of the lattice. These are the stretching (ωHstretch) and bending (ωHwag) modes of the Si-H and Ge-H bonds. The third mode (ω1) involves a vibration of the upper bilayer of the system. The calculated total energies and corresponding fitted curves to quadratic polynomials are shown in figures 4 through 6. Higher order polynomial fits give frequencies that differ by less than 1 percent from the quadratic-fit values for all cases considered. The nearly perfect harmonic character
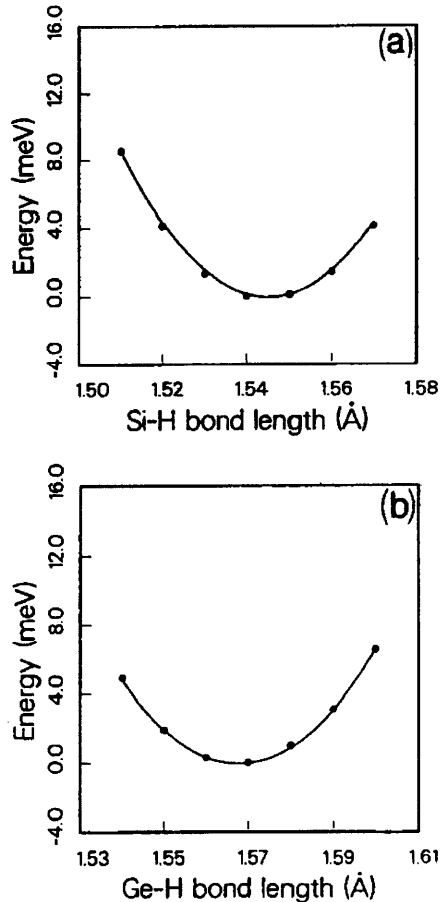
Figure 4. Calculated total energies and quadratic polynomial fits for the hydrogen bond stretching mode in (a) Si(111):H and (b) Ge(111):H. Energies are given in meV per (1x1) surface unit cell, with respect to the fully relaxed configuration.
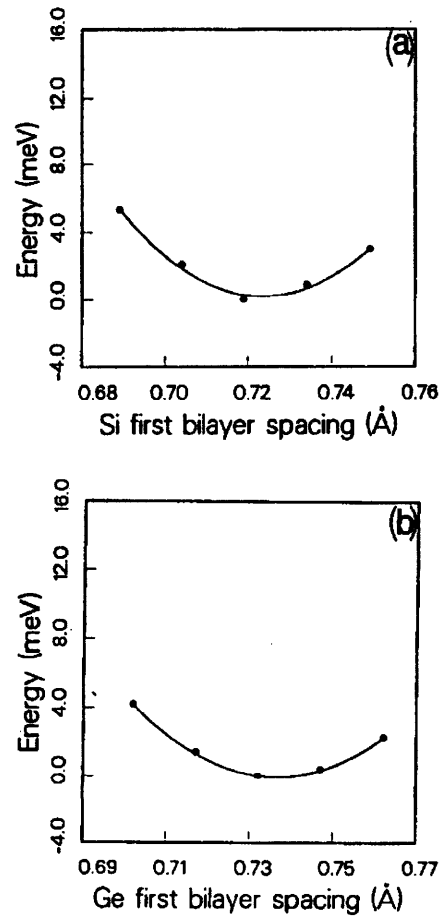
of the energy curves is a reflection of the high degree of convergence of the calculations, which gives the energy differences with a relative accuracy of 10-4 eV.

The frequencies for the three modes (ωHstretch, ωHwag, and ω1) and the experimental values are collected in table 3. There is no experimental measurement for ω1 because it lies in the region of other vibrational modes of the crystal and couples strongly to them. There is, however, a similar vibrational mode in the amorphous materials for which experimental measurements exist. Vibrational frequencies associated with H motion in amorphous hydrogenated Si and Ge have also been determined experimentally; their values are included in table 3.
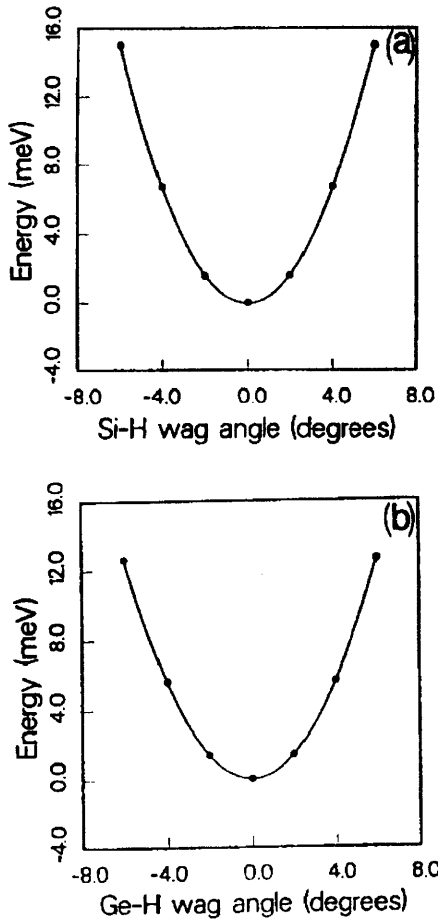
Figure 5. Same as in figure 4 for the hydrogen bond wagging (bending) mode.

Figure 6. Same as in figure 4 for the top layer vibration mode.

The calculated values for ωHstretch and ωHwag are in excellent agreement with the experimentally determined frequencies. By contrast, the calculated values for ω1 differ by approximately 35 percent from the experimental ones. Given the good agreement we can obtain between theory and experiment for the hydrogen-related vibrations, we conclude that the discrepancy in the values of ω1 is not related to some theoretical shortcoming. In particular, the systematic errors in the hydrogen relaxations and the surface
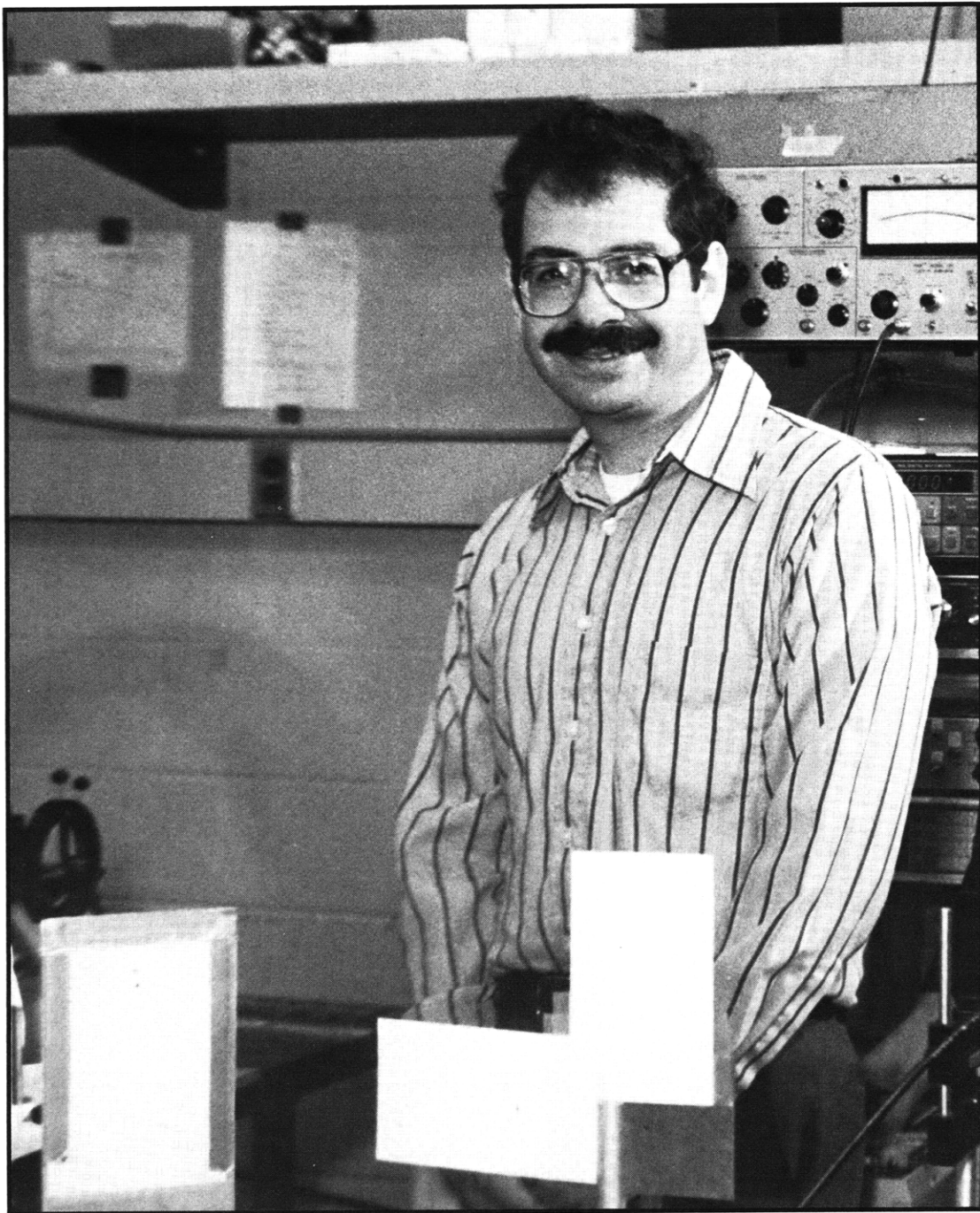
layer relaxations are the same and the expected accuracy for the ω1 mode is therefore 5-10 percent. The large discrepancy in ω1 indicates a significant difference between the motion of atoms in the hydrogenated surfaces and in microvoids of the amorphous material. The comparison predicts that internal surfaces (microvoids) in the amorphous network are locally much softer than the corresponding crystalline surface configuration.

Table 3. Comparison of calculated vibrational frequencies with experiment and with corresponding values in amorphous materials. Frequencies are in meV. The corresponding wave number in cm^{-1} is also given after each frequency in brackets. $\omega_H^{stretch}$ is the stretching mode of the hydrogen bond, ω_H^{wag} is the wagging mode of the same bond, and ω_1 the frequency for vibration of the top layer of hydrgenated atoms.

	Si			Ge		
	Theory	Expt.[a]	αSi:H[b]	Theory	Expt.[a]	αSi:H[b]
$\omega_H^{stretch}$	245 (1978)	257 (2085)	248 (2000)	231 (1860)	245 (1975)	235 (1895)
ω_H^{wag}	71 (569)	77 (630)	79 (640)	63 (505)	66 (530)	70 (565)
ω_1	35 (283)		26 (210)	20 (162)		15 (120)

Note: [a]From: Frozheim et al., Phys. Rev. B 27:2278 (1983); Richter et al., J. Non-crystalline Solids 59-60:181 (1983). [b]From: Papagno et al., Phys. Rev. 34:7188 (1986); Shen at al., Phys. Rev. B 22:2913 (1980).

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