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Phonon modes of diamond (100) surfaces from *ab initio* calculations

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We present a realistic theoretical study of the surface-phonon spectra of diamond (100) surfaces. Our results reproduce the major features of the vibrational spectra of clean and hydrogenated diamond (100)-(2×1) surfaces obtained from experiments. The reconstruction of the diamond (100)-(2×1) surface yields a rich spectrum of surface modes and we identify surface features involving excitations of the surface dimer. We detail connections between atomistic surface modes and peaks observed in surface probes measuring vibrational excitations.

Some of the most powerful techniques in surface science are probes designed to measure the dynamical properties of surfaces. These include inelastic neutral atom scattering, high-resolution electron-energy-loss spectroscopy (HREELS), and surface infrared absorption spectroscopy.[1] Using these experimental techniques, individual surface-phonon modes can be detected which provide unique information concerning the bonding, the structure, and the dynamics of the surface. With the recent interest in high-rate diamond-film synthesis, application of these experimental techniques has been redirected to the diamond surface itself.[2–4]

While the use of these surface vibration probes to study diamond surfaces is receiving increasing attention, there has been limited theoretical work on diamond surface vibrations. One attempt in this direction is the empirical tight-binding work of Davidson and Pickett on the surface hydrogen modes of flat (110), flat (111), and stepped (111) substrates of diamond.[5] Recent HREELS experiments confirmed the presence of several modes on diamond surfaces that have not been detected on the corresponding silicon surfaces.[3] The lack of theoretical calculations discourages interesting opportunities for further experimental investigations. Current analysis of the experimental surface vibrational spectra rely on information from gas phase hydrocarbon vibrational frequency data and scaled phonon frequencies for similarly reconstructed silicon surfaces.[2–4] Although these schemes are valuable in the interpretation of the experimental results, its application is limited since surface features which are intrinsic to diamond surfaces would not be included in this approach. Moreover, one cannot rely mainly on these schemes alone if one wants to address in detail subsurface excitations that could couple with the surface phonons.

A preferable approach to investigate surface vibrational properties is to apply *ab initio* force calculations based on density functional theory as implemented with the Harris local-density approximation functional, in the local basis method of Sankey and co-workers.[6] This first-principles technique offers reliable information about the interatomic force constants both in the bulk and at the surface. It has been successfully applied to structural, electronic, and vibrational studies of buckyballs, aluminum, amorphous systems, clusters, Si and C surfaces and yielded results in good agreement with available experimental data and self-consistent pseudopotential calculations.[7,8] Although more computationally intensive than semiempirical approaches, this technique does not involve fitting to experimental data and its transferability is demonstrated.[8] In this paper, we study the vibrational properties of clean and hydrogenated (100) diamond surfaces. Our motivation is to theoretically determine the surface-phonon spectra of the diamond surfaces for comparison with the accumulated experimental data for vibrational properties and to provide conclusive assignments of the different modes observed in various experiments. This work also provides a benchmark for future dynamical studies of surfaces in connection with growth. It is possible that specific phonon modes will play important roles in the adsorption of growth species on the diamond surface.

To study diamond surface-phonon modes, we start with the structure of clean and hydrogenated (100)-(2×1) diamond surfaces [C(100)-(2×1) and C(100)-(2×1)H, respectively], and obtain their minimum energy configurations. The surfaces are modeled using a 10-layer-thick slab with 8 C atoms per layer. The bottom layers of the slabs are terminated by H atoms. To model the C(100)-(2×1) surface, the (100) face is exposed and reconstructed into a (2×1) dimerized surface. This surface is terminated by H atoms to model the hydrogenated (100)-(2×1) diamond substrate. These slabs were relaxed with *ab initio* molecular dynamics,[6] from slabs relaxed initially with the Brenner potential.[9] All the atoms except the bottom C layer are allowed to relax. Two special $\vec{k}$ points were used to sample the electron Brillouin zone of the supercells[10]. The vibrational properties are obtained by construction and diagonalization of the dy-

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namical matrix $\phi^{ij}_{\alpha\beta}$ to obtain the vibrational eigenvalues and eigenvectors. $\phi^{ij}_{\alpha\beta}$ is obtained by displacing atom i from its equilibrium position by $\delta r = 0.03$ Å in the direction α and calculating the forces acting on atom j in the direction β. Here $\alpha = (x, y, z)$ and $i = 1, N$, where N is the total number of atoms. The computed density of states is insensitive to δr for 0.01 Å $\lesssim \delta r \lesssim$ 0.05 Å . Finite size artifacts and phonon Γ point Brillouin zone sampling excludes modes in the very low frequency ($\omega \lesssim 300$ cm^{-1}) part of the power spectrum. This region, however, is in general experimentally inaccessible to surface-phonon probes[11] and will not be of interest to us.

The relaxed equilibrium structures for the C(100)-(2×1) and C(100)-(2×1)H surfaces yielded rows of symmetric surface carbon dimers in agreement with previous experimental and theoretical work.[12] The calculated dimer bond lengths are 1.36 and 1.62 Å for the clean and hydrogenated surfaces, respectively. The tilt of surface H with respect to the surface normal in the hydrogenated phase is 24°. The rebonding of atoms on the surface, giving rise to the formation of surface C-C dimers, causes relaxations of atoms in the subsurface layers. We found reduction of the first interplanar spacing with respect to the bulk (24% and 5% contraction for the clean and hydrogenated surfaces, respectively). The buckling amplitudes (relative difference in the z coordinates of adjacent carbon atoms) on the third/fourth layer are 0.13/0.25 and 0.10/0.17 Å for C(100)-(2×1) and C(100)-(2×1)H, respectively.

The surface-phonon power spectra are shown in Fig. 1. These spectra are determined by broadening the eigenvalues of ϕ using a Lorentzian of width 40 cm^{-1}, to match the experimental resolution of the HREEL spectrometer employed in Ref. 3. The spectra shown for the C(100)-(2×1) surfaces are the projected vibrational density of states (VDOS) of the three topmost C layers of the slab used to model this surface, while the VDOS for the hydrogenated (100) surface also includes the surface H layer. By comparing the layer-resolved VDOS with corresponding bulk results, we found that the significant surface features were confined mainly to the upper layers we include. The predicted spectra for both the clean and hydrogenated (100) surfaces appear to have broadbands below ~ 1500 cm^{-1}. Compared to the C(100)-(2×1) case, the C(100)-(2×1)H spectrum has an additional band in the region 1300-1500 cm^{-1}, and a distinct peak centered at about 2730 cm^{-1}. The calculated spectra for the diamond (111) surfaces are also shown in Fig. 1 for comparison.[13] Notice that the gross features of the spectra for both surfaces [C(100)-(2×1) vs C(111)-(2×1) and C(100)-(2×1)H vs C(111)-(1×1)H] are qualitatively similar. The phonon modes of the (111) surfaces will be discussed in detail in a future publication.

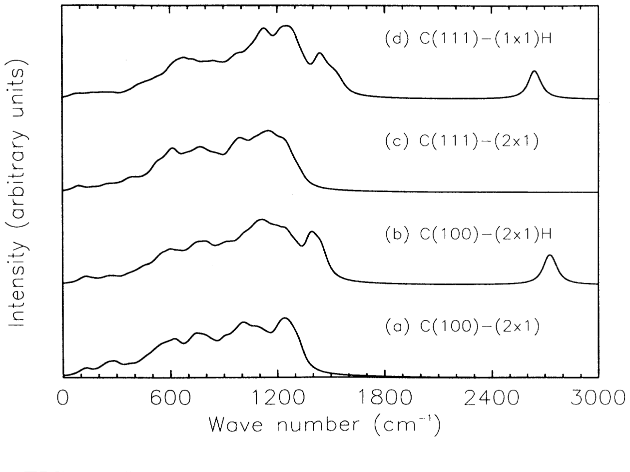

FIG. 1. Projected vibrational density of states of the diamond (100) and (111) surfaces; (a) clean (100)-(2×1), (b) hydrogenated (100)-(2×1), (c) clean (111)-(2×1), and (d) hydrogenated (111) surfaces.

We have identified phonon modes as various excitations of the surface dimers of the clean (100) surface. These modes involve rocking, swinging, twisting, bouncing, and stretching motions of the C-C dimer [Fig. 2(a)–

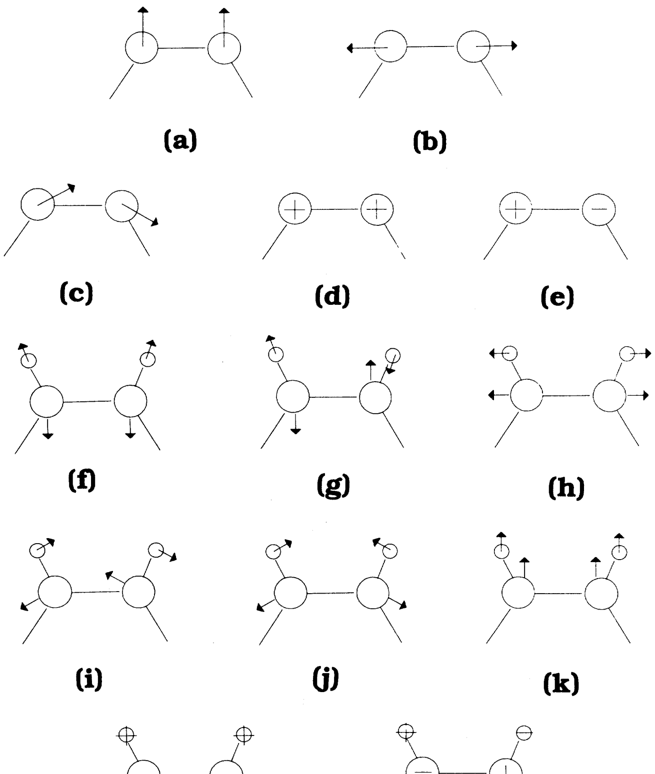

FIG. 2. Vibrations of a dimer on clean and hydrogenated (100) diamond surfaces. Big and small circles represent C and H atoms, respectively. Out of plane motion refers to vibrations perpendicular to the plane defined by the C-C or CH-CH chains. (a) Bouncing, (b) stretching, (c) rocking, (d) swinging (out of plane), (e) twisting (out of plane), (f) CH stretching (symmetric), (g) CH stretching (antisymmetric), (h) CH-CH stretching, (i) H rocking, (j) H scissoring, (k) CH-CH bouncing, (l) CH bend (out of plane).

2(e)] coupled with subsurface layer vibrations. Except for the C-C stretching vibrations, these can be considered as hindered translations (swinging and bouncing modes) and rotations (rocking and twisting modes) of the surface dimers. Notice that if these dimers were in the gas phase, the stretching vibration would be the sole mode available for this species. The highest frequency mode we find involves stretching of surface C-C dimers (Table I), which appears as a weak mode near 1489 cm^{-1} on the clean (100) surface-phonon spectrum and only enhances the tail near that frequency in Fig. 1. This value lies above the singly bonded C-C stretching frequency of ethane (995 cm^{-1}) and below the ethylene's doubly bonded C-C stretching frequency (1623 cm^{-1}). From the C(100)-(2×1) C-C dimer bond length (1.36 Å) and stretching frequency, the bond order of the dimer is roughly 1.5. This would indicate that the surface dimer bond is strained and the carbons belonging to the dimer pair may be susceptible to reaction with gas phase radical species. Except for the stretching motion, the vibrational motions of adjacent surface dimers couple, giving rise to a frequency splitting determined by the phase relationship of displacements of neighboring dimers. Table I lists surface-phonon modes where adjacent dimers undergo hindered vibrations in and out of phase. From the inspection of the eigenvectors, the in-phase motion of the adjacent dimers always lies at higher frequencies compared to the out of phase case, since the vibrations on the subsurface layer coupled with the in-phase motions are more pronounced in the first case. Notice that the surface features associated with bands at 604 and 1019 cm^{-1} which involve rocking motions strongly localized on the dimers and swinging of adjacent dimers 180° out of phase, respectively, are also reported on the Si(100)-(2×1) surface.[14] We did not find a feature similar to the high frequency subsurface bond distortion mode found on the Si surface resulting from the asymmetry of its dimers.[14] Since our calculations predict ground state diamond (100) surface whose dimers are not buckled, the difference in the surface dimer geometry may well be the reason why such mode is absent in the diamond (100) surface.

TABLE I. Examples of calculated frequencies and the corresponding surface vibrational features associated with dimers on the clean and hydrogenated (100) diamond surfaces. The phase refers to the motion of adjacent dimers.

Frequency (cm^{-1})	Feature	Fig. 2
	C(100)-(2×1)	
1489	dimer stretch	b
1235	dimer swing (in-phase)	d
1019	dimer swing (out of phase)	
1217	dimer rock (in-phase)	c
604	dimer rock (out of phase)	
1313	dimer twist (in-phase)	e
1272	dimer twist (out of phase)	
708	dimer bounce (in-phase)	a
503	dimer bounce (out of phase)	
	C(100)-(2×1)H	
2750, 2713	CH stretch (see text)	f, g
∼ 1000-1500	CH bend	l
∼ 900-980	CH-CH stretch	h
522, 648	dimer bounce	k
555	dimer bounce (out of phase)	

Lee and Apai used HREELS to study the phonon modes of diamond surfaces and their C(100)-(2×1) vibrational energy-loss spectrum consists of two distinct features at 700 and 1225 cm^{-1}, and a weak feature at 1015 cm^{-1}. These features are reproduced in our theoretical C(100)-(2×1) spectrum and estimated to fall in the energy regions of 440–900, 1160–1400, and 900–1160 cm^{-1}, respectively. It appears that their 700 and 1015 cm^{-1} bands correspond to our 604 (rocking of the surface dimer) and 1019 cm^{-1} (swinging of adjacent dimers 180° out of phase) features, respectively. This observation is in agreement with that of Lee and Apai whose interpretation is based on scaled Si(100)-(2×1) phonon frequencies. Instead of subsurface bond distortion found on similarly reconstructed Si (100) surfaces,[14] the in-phase swinging of the adjacent dimers coupled with subsurface excitation occurring at 1235 cm^{-1} (Table I) may be the mode corresponding to their 1225 cm^{-1} feature. Based on the character of its surface and subsurface excitations, this mode on the diamond surface can be dipole active[1] and may be accessible through HREELS experiments. Some of the difference observed between the Si(100) and C(100) modes imply different behavior in the lattice dynamics (arising from the more massive Si lattice), chemical differences, and the contrasting relaxation in the subsurface layers brought about by the difference in the surface feature of Si(100) and C(100) surfaces. Our clean diamond (100) spectrum appears to have more spectral features compared to the HREELS spectrum since the calculated VDOS are not constrained by possible instrumental energy resolution limitations (mimicked in our Fig. 1 by the *ad hoc* broadening used) and more importantly, by coupling selection rules of the diamond surface to the probes (i.e., in principle, we can "detect" all phonon modes except the ones in the low frequency region mentioned previously). The non-self-consistency of the charge densities we obtain, however, precludes us from carrying out a detailed determination of the dipole activity of the surface-phonon modes.

The C(100)-(2×1)H spectrum contains prominent phonon modes involving excitations of the H terminated surface dimers. These vibrations are coupled with phonons from the subsurface layers. The vibration of the hydrogens against the surface is a CH bond stretching mode [Figs. 2(f) and 2(g)]. The hindered rotations of the CH fragments belonging to the surface dimer have forms of CH bending character [Figs. 2(i), 2(j), and 2(l)]. Excitations in the form of translation of the CH center of mass [Figs. 2(h) and 2(k)] are analogous to the stretching and bouncing modes of the dimers of the clean (100) surface. Except for stretching vibrations, the other phonons are not modes of a gas phase CH fragment.

Table I summarizes the modes associated with the bands present in the C(100)-(2×1)H spectrum. One obvious difference between the spectra of the clean and hydrogenated surfaces is the presence of a distinct peak near

~ 2730 cm^{-1} on the spectrum of the latter. This high frequency vibrational mode in the hydrogenated (100) surface was also observed and discussed in the HREELS experiments of Aizawa *et al.*[4] Our predicted 2730 cm^{-1} peak is in good agreement with the sharp loss peak they measured at 2928 cm^{-1} which they ascribed to the CH (monohydride) stretching mode (we underestimate the experimental frequency by roughly 7%). Our feature near 2730 cm^{-1}, however, appears to be broader, suggesting the presence of more than one mode. From the inspection of the eigenvectors, we found symmetric and antisymmetric stretching accomplished by CH fragments belonging to the dimer pairs occurring at 2750 and 2713 cm^{-1}, respectively [Figs. 2(f) and 2(g)]. The presence of these two modes indicates that the stretch vibrations of CH groups belonging to each hydrogenated dimer are strongly coupled, producing a split of 37 cm^{-1} (~ 1.5%). Inspection of the equilibrated C(100)-(2×1) surface reveals that the tilt of the surface hydrogens to the [110] directions (perpendicular to the dimer row) can give rise to this coupling since the H bonded to adjacent dimers along the [110] directions are 0.1 Å closer together with respect to the 2.56 Å separation between the H on the dimer pairs. This antisymmetric mode, however, may give rise to dipole fields which counteract each other and could be the reason why it is not detected by HREELS measurements, together with a finite resolution.

High-resolution electron-energy-loss spectroscopy spectra in Ref. 4 also show a band in the region from 1000 cm^{-1} to 1450 cm^{-1} which the authors attributed to CH bending vibrations. This feature is reproduced in our theoretical C(100)-(2×1) spectrum. We predict a band between 1000 and 1500 cm^{-1} which we found to be dominated by CH bending modes coupled with the phonons of the subsurface layers. An interesting feature is the nearly pure "scissoring" motion accomplished by the hydrogens belonging to the dimer pair [Fig. 2(j)] at 1310 cm^{-1}. Analogous to the clean surface, the CH bending motions of dimers in different unit cells interact strongly. Examples are the rocking motions of the hydrogens belonging to the dimer pair occurring in phase and 180° out of phase with respect to adjacent dimers (1252 and 1336 cm^{-1}, respectively).

As for the clean surface, our C(100)-(2×1)H spectrum appears to have more spectral features compared with the measured loss spectrum.[4] The reason for such a difference is similar to that discussed above. We find features characterized by hindered normal translations (bouncing) of the dimer below ~ 650 cm^{-1} combined with lattice phonons. We have also identified several modes occurring between 900–980 cm^{-1} involving hydrogenated dimer bond stretches. Unlike the C-C stretching mode found on the clean surface, this excitation is strongly coupled with the vibrations of the lattice giving rise to splitting over a range of ~ 80 cm^{-1}. The softening of these modes may be partly attributed to the passivation of each surface C by hydrogen resulting in reduced bond order between the C-C dimer bond.

In summary, we study the vibrational properties of clean and hydrogenated (100) diamond surfaces employing first-principles molecular dynamics techniques. We have identified phonon modes on the clean (100) surface in the form of excitations of the surface dimers. The hydrogenated surface-phonon spectrum is dominated by modes associated with H terminated dimers vibrations.

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