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Transferable tight-binding model for hydrogen–silicon interactions

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Abstract. We present a novel empirical tight-binding model of the hydrogen–silicon system suitable for realistic molecular-dynamics simulations. The hydrogen–silicon and hydrogen–hydrogen interactions are constructed to reproduce the electronic levels and vibrational frequencies of silane (SiH_4) and hydrogen molecules, respectively. The potential functions are rescaled with an exponential factor in addition to the simple inverse square law. This smooths the potential change at some appropriate cut-off distances, which is a prerequisite condition in realistic molecular-dynamics simulations. The application of this model to other molecules and surfaces yields excellent agreement with the experimental results, proving the good transferability of our model.

1. Introduction

The hydrogen–silicon (H–Si) system has been intensively studied not only for its importance in device technology but also for its many interesting physical phenomena from the theoretical aspects. The hydrogen is generally known to passivate the surfaces and the dangling bonds in hydrogenated amorphous silicon. The hydrogen thus changes the electrical and optical properties [1]. The hydrogen atom plays a crucial role in the polycrystalline silicon growth at low temperature [2]. The hydrogen atom is also known to act as a surfactant to supress the Ge atom segregation in Si–Ge epitaxial growth [3]. Despite the fact of their abundant appearance in many H–Si systems, the physical mechanism underlying these phenomena is still far from being completely understood. Part of the reason is the lack of a realistic theoretical model to describe such complex systems.

First-principles approaches within the local-density approximation have been successfully applied to hydrogen in bulk Si and Si surfaces [4–6]. The accurate molecular-dynamics (MD) simulations with the local-density approximation by Car and Parrinello (CP) have made progress for further understanding of hydrogenated amorphous Si [7, 8]. However, this method is limited to a small number of atoms ($\leqslant$ 100 atoms) and the computational cost is still high for some dynamical properties. Classical potentials have been proposed in hydrogenated amorphous Si [9, 10]. Even though the computational cost is low in this approach, the reliability cannot be guaranteed.

A few empirical tight-binding (TB) models have been proposed [11, 12]. Since the TB scheme uses the valence electrons only in the electronic-structure calculations where the overlap integrals are empirically fitted to the first-principles calculations or experiments, both accuracy and efficiency are achieved. Although the TB model of Min *et al* [12] takes account

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of the anharmonic effect by implementing the universal binding-energy curve in the fitting procedure, the simple inverse-scaling law of the distance still causes undesirable effects in describing particularly the hydrogen dynamics and absorption and desorption process. A model with smooth potential cut-off is generally required in a typical MD simulation.

Goodwin, Skinner and Pettifor (GSP) [13] have proposed a transferable TB total-energy scheme by introducing an exponential factor into the distance scaling in the silicon system. This has been successfully applied to many complex systems [14, 15]. In this paper we propose a new TB model for the H–Si system by introducing an exponential factor into the distance scaling similar to GSP scheme such that the potential cut-off is smoothed so as to apply for a more complex system. We expect that this model is transferable to many complex systems such as hydrogen dynamics in hydrogenated amorphous Si and the absorption–desorption reaction in the chemical-vapour-deposition process or at hydrogenated Si surfaces.

2. Fitting procedure for H–Si and H–H interactions

The total energy in an empirical TB scheme can be written as

$$E_{tot} = \sum_{n,k} \varepsilon_{n,k} + U. \qquad (1)$$

Here the first term represents the band-structure energy which can be constructed from the TB Hamiltonian H_{TB} and the second term is the repulsive ion–ion interactions. The diagonal term of H_{TB} is equal to the atomic energy levels and the off-diagonal elements are constructed via the Slater and Koster empirical TB scheme [16].

For the H–Si system, there are three types of interacting parameter, Si–Si, H–Si, and H–H. For Si–Si pairs, we choose the GSP total-energy scheme. The elements of the H_{TB} matrix are determined by

$$V_\alpha^{Si-Si}(r/r_0) = V_\alpha^{Si-Si}(1)(r_0/r)^n \exp\left\{n\left(-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right)\right\} \qquad (2)$$

where the $V_\alpha^{Si-Si}(1)$ are the overlap integrals at equilibrium distance r_0. These are listed in table 1. The repulsive interaction term has a similar form

$$U^{Si-Si}(r/r_0) = U^{Si-Si}(1)(r_0/r)^m \exp\left\{m\left(-\left(\frac{r}{r_c}\right)^{m_c} + \left(\frac{r_0}{r_c}\right)^{m_c}\right)\right\}. \qquad (3)$$

The total energy from this model reproduces well the universal binding-energy curves of various phases generated by the first-principles calculations [17]. The main idea of this scheme is to improve the transferability by introducing an exponential factor into the distance scaling, in contrast with the previous inverse square law of Chadi [18].

For the H–Si system, we adopt a similar scheme to the GSP. The respective parameters are also shown in table 1. In this system, the energy levels and the vibrational frequencies of silane (SiH_4) are used for the fittings. The significance of this formulation is that the potential change is smooth at the cut-off distance, which is required in realistic MD simulations, and the quantitative accuracy is improved. Figure 1 shows the total-energy curve of the H–Si interaction. One can see that both the band-structure energy and the repulsive potential energy smoothly approach zero at cut-off 2.186 Å and the total energy shows an equilibrium at 1.48 Å with the binding energy 3.73 eV, as compared to the experimental value 3.355 eV. For the H–H system, the energy levels and the stretching frequency of the H_2 molecule are used for the fittings. These are listed in table 1. Figure 2

Table 1. The TB potential parameters of the H–Si system.

	Si–Si	H–Si	H–H
$V_{ss\sigma}(1)$ (eV)	−1.82	−3.5535	−7.59
$V_{sp\sigma}(1)$ (eV)	1.96	5.088	
$V_{pp\sigma}(1)$ (eV)	3.06		
$V_{pp\pi}(1)$ (eV)	−0.87		
r_0 (Å)	2.35	1.48	0.742
r_c (Å)	3.67	2.186	1.6
n	2	1.9877	2.18
n_c	6.48	13.269	14.0
m	4.54	2.255	4.215
m_c	6.48	13.269	14.0
$U(1)$ (eV)	3.5481	3.01	3.5
E_s(Si) (eV)	−13.08		
E_p(Si) (eV)	−4.785		
E_s(H) (eV)	−8.34		

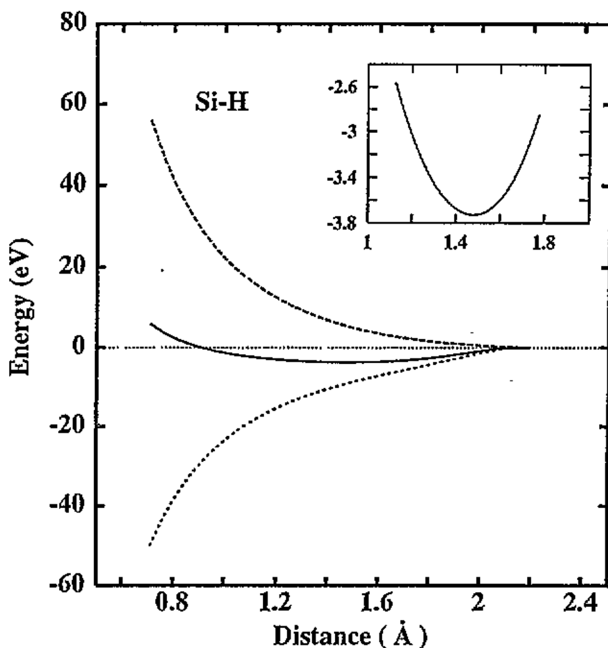

Figure 1. The total-energy curves of the H–Si interaction. The band-structure potential energy, repulsive potential energy (dashed lines) and total energy (solid line) are smooth at the cut-off distance 2.186 Å. The inset shows a well defined equilibrium at 1.48 Å with binding energy 3.73 eV.

shows the total-energy curve of the H–H interaction. The band-structure energy which is determined only with $ss\sigma$ electrons and the repulsive potential energy smoothly approach zero at cut-off 1.6 Å. The total energy shows an equilibrium at 0.742 Å with the binding energy 4.44 eV, as compared to the experimental value 4.45 eV.

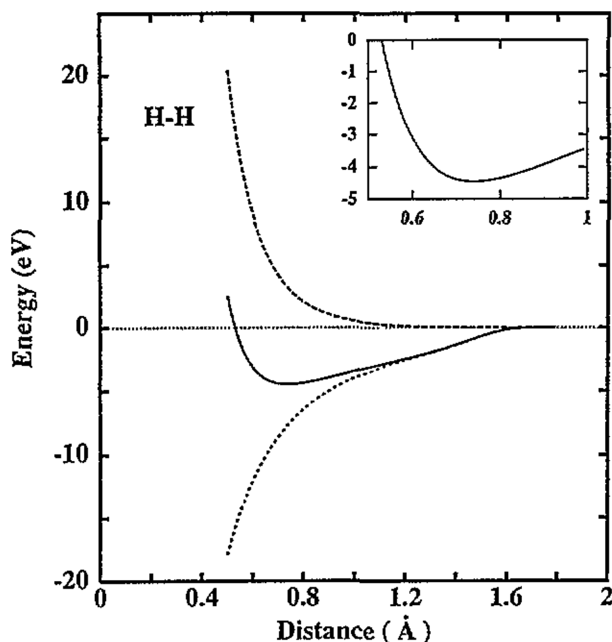

Figure 2. The total-energy curves of the H–H interaction. The band-structure potential energy, repulsive potential energy (dashed lines) and total energy (solid line) are smooth at the cut-off distance 1.6 Å. The inset shows a well defined equilibrium at 0.742 Å with binding energy 4.44 eV.

3. Results and discussion

Table 2 shows the calculated energy levels and the typical vibrational frequencies of the SiH_4 molecule from our model. In order to calculate the vibrational spectra, we performed the MD simulations. Once the velocity–velocity autocorrelation function is calculated, the Fourier transformations are taken to get the vibrational spectra. We run MD with a microcanonical ensemble at room temperature for 25 picoseconds which will give a resolution of 0.001 meV. We do not require the model to reproduce the energy levels of the antibonding states. The energy levels of the antibonding states are not well described with a minimal basis set in the TB scheme. In the H–Si system, the antibonding states are far away from the Fermi level and do not strongly affect the bonding character of the system. This restriction is similar to Min *et al*'s procedure [12]. Although our bonding states are somewhat sacrificed compared to Min *et al*'s model, we improved the asymmetric bending frequency from 103 to 108 meV where the bending frequencies are solely determined from the change of $V_{sp\sigma}$(H–Si). The difference of $V_{ss\sigma}$ and $V_{sp\sigma}$ determines the accuracy of the asymmetric bending mode. Our $V_{sp\sigma}$(H–Si) value is a little larger than Min *et al*'s value.

We now check our model with a different molecule in order to see the transferability. The fully relaxed Si_2H_6 molecule is shown in figure 3. Since the electronegativity of the Si atom is a little larger than that of the H atom, charge is transferred to the Si atom, producing the contraction of the Si–Si bond from 2.35 to 2.31 Å. The H–Si bond length lengthens to 1.49 from 1.48 Å. The bond angle between H atoms is 107° and the bond angle between Si and H atoms is 111.8°, as compared to the tetrahedral angle 109.5°. These values are in good agreement with electron-diffraction experimental results [20]. The calculated energy levels are in better agreement with experiments than Min *et al*'s results. We note that the bending

Table 2. The energy levels and the vibrational frequencies of the SiH_4 molecule.

Level/modes	Present TB/TBMD	Min *et al* [12]	Experiment[a]
Eigenvalues			
a_1^- (eV)	−3.34	−2.84	−4.1
t_2^- (eV)	−0.53	−1.93	−5.4
t_2^+ (eV)	−12.60	−12.71	−12.7
a_1^+ (eV)	−18.08	−18.23	−18.23
Frequencies			
Symmetric bending (meV)	121	122	121
Asymmetric bending (meV)	108	103	113
Symmetric stretching (meV)	276	276	270
Asymmetric stretching (meV)	284		271.7

[a] [12] and references therein.

modes are in excellent agreement with experiments which are important in identifying the various hydrogen-bonding species in many real systems. Since we calculate the vibrational frequencies from MD simulation, we get higher values in the stretching frequencies than the frozen-phonon calculations, which was observed in previous work [12]. Furthermore, the highest stretching frequency of SiH_4 is used in the fittings. This will overestimate the stretching frequencies of other species of similar molecules. We emphasize that the bending modes are well reproduced to be comparable with experimental results. The stretching frequency of the Si–Si bond is 52 meV. The fact that the energy levels, molecular structure and vibrational frequencies are decribed well in the Si_2H_6 molecule proves the transferability of our model.

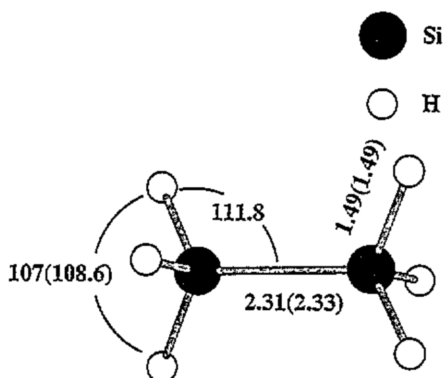

Figure 3. The fully relaxed disilane molecule. The angles between atoms deviate from the tetrahedral angle 109.5°. The values in parentheses are from experiments [19]. Lengths are in units of Å.

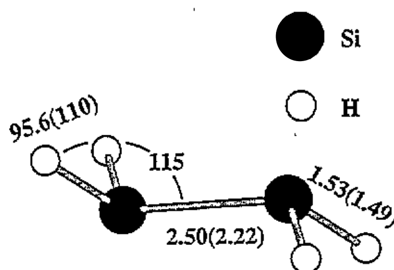

Figure 4. The fully relaxed disilene molecule of non-planar form. The hydrogen bond length becomes longer compared to that of the SiH_4 molecule. The Si–Si bond length becomes longer than the Si crystalline bond length. The values in parentheses are from GVB calculations [20]. Bond lengths are in units of Å.

We further apply this model to the disilene Si_2H_4 molecule. Figure 4 shows the fully relaxed geometry from the steepest-descent relaxation. The Si–Si distance of this non-planar form is 2.50 Å which is larger than that of the generalized-valence-bond (GVB) calculation [20] but another calculation shows this value as 2.52 Å [21]. The stretching frequency of

Table 3. The energy levels and the vibrational frequencies of the Si_2H_6 molecule with the fully relaxed geometry.

Level/modes	Present TB/TBMD	Min *et al* [12]	Experiment[a]
Eigenvalues			
a_g (eV)	−10.49	−11.07	−10.7
e_g (eV)	−12.15	−12.28	−12.1
e_u (eV)	−12.79	−13.23	−13.3
a_u (eV)	−16.74	−16.65	−17.3
a_g (eV)	−18.50	−18.71	
Frequencies			
Symmetric bending (A_1) (meV)	113	75	112
Asymmetric bending (E) (meV)	105		105
Twist (meV)	67	55	62
Wagging (meV)	88		78
Symmetric stretching (meV)	272	276	265
Asymmetric stretching (meV)	281		

[a] [12] and references therein.

Table 4. The relaxations of surface layers of monohydride and trihydride surfaces. 'Ideal' means bulk structures and H–Si bonds in the SiH_4 molecule. 'Clean' and 'H' mean the clean surface and the H-terminated surface, respectively. The notations are from figure 5. All units are in Å.

		Monohydride				Trihydride		
		Ideal	*Relaxed*			*Ideal*	*Relaxed*	
			Present TB	Min *et al* [12]	KJ [6]		Present TB	Kim [23]
Clean	d_{12}	0.78	0.76	0.76	0.57	2.35	2.31	2.35
	d_{23}	2.35	2.38	2.4		0.78	0.79	0.85
H	d_H	1.48	1.51	1.50	1.54	1.48	1.50	1.41
	d_{12}	0.78	0.78	0.81	0.72	2.35	2.34	2.35
	d_{23}	2.35	2.35	2.37	2.32	0.78	0.78	0.81

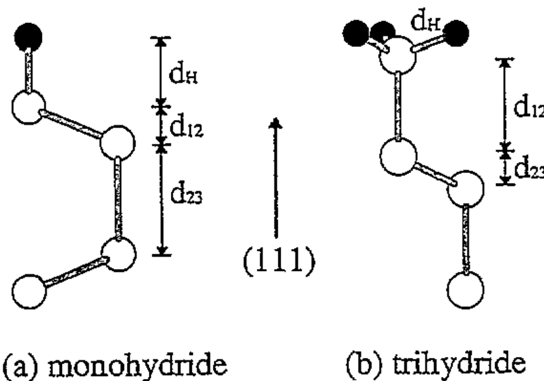

Figure 5. Slab geometry of hydrogenated Si(111) surface: (a) monohydride, (b) trihydride.

the Si–Si bond is 42.5 meV which is less than that of the Si_2H_6 molecule, as expected from the larger bond lengths between Si atoms. The respective bond lengths and bond

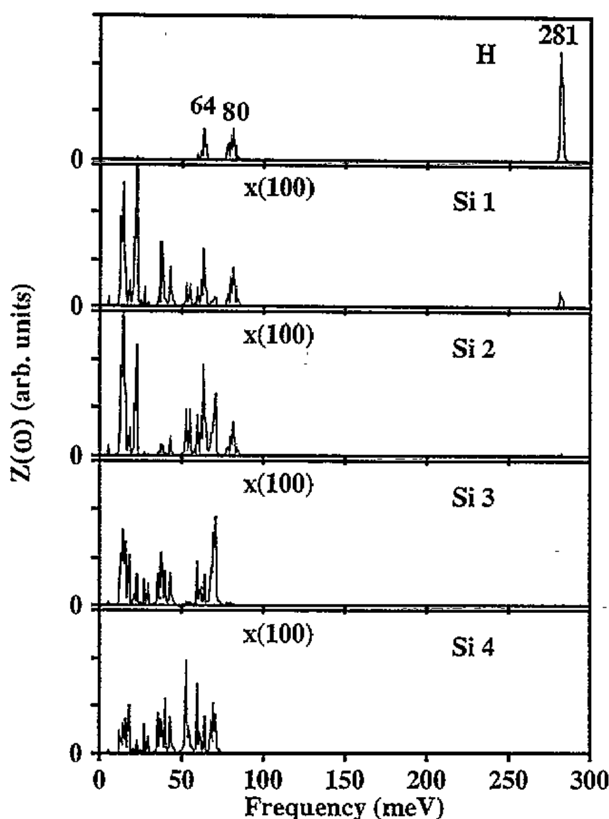

Figure 6. Local phonon spectra of the monohydride surface. H indicates the top hydrogen layer and Si 1 the first surface Si layer.

angles are shown in figure 4. The out-of-plane angle in this form is 24°, as compared to 18° from the GVB calculations. We note that the planar form is a degenerate state of this non-planar form, in contrast with the previous GVB calculation that the energy of the non-planar form is 65 meV lower than that of the planar one. We expect that there exists a potential barrier between these two forms. Both the non-planar and planar forms are singlet states. The bonding states are −17.28, −15.95, −12.04, −11.56, −10.54, and −7.83 eV. The symmetric bending frequency of the Si_2H_4 molecule is 113 meV, as compared to 110 meV from the experiment [22]. These calculations also prove the good transferability of our model.

We now apply this model to the hydrogenated Si(111) surface. The hydrogenated Si(111) surface sustains an ideal (1×1) structure. We construct a supercell of 72 atoms $(3\times4\times6$ layers). The periodic boundary conditions are applied along the x and y directions with the top and bottom layers saturated by hydrogens so as to form an ideal (1×1) structure. The equilibrium structures are obtained by the steepest-descent method. For a trihydride surface, we added two more layers on both ends where the terminated layers are saturated by three hydrogens per silicon atom, having a supercell of 96 Si atoms. Table 4 shows the calculated values of the relaxations of different layers. The top two Si layers are allowed to relax. The first layer for a clean Si(111) surface shows contraction whereas the second layer expands to compensate the contraction of the first layer. With H absorption, these relaxations are recovered to an ideal configuration and the hydrogen bond length becomes

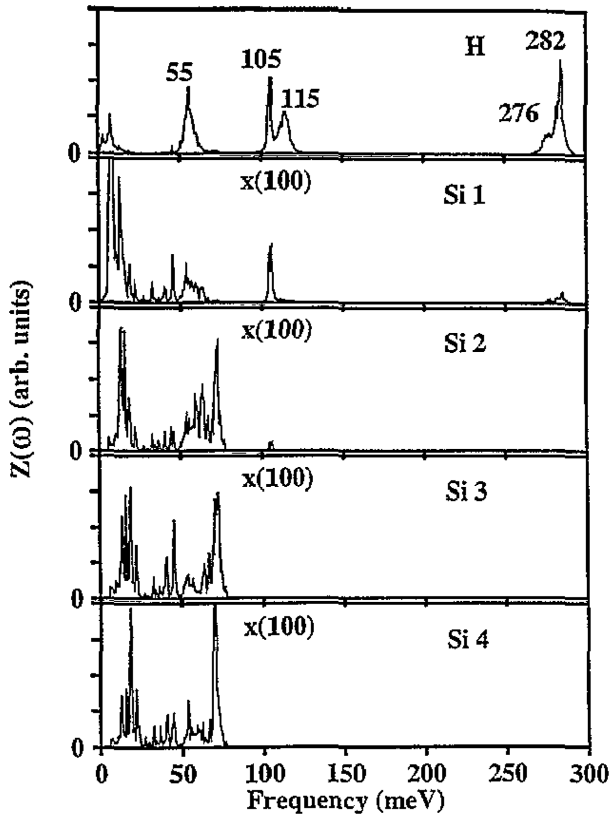

Figure 7. Local phonon spectra of the trihydride surface. H indicates the top hydrogen layer and Si 1 the first surface Si layer.

longer than the fitted value 1.48 Å. The vibrational frequencies of hydrogens on this surface can be obtained from MD simulations. In MD all the atoms are allowed to move. The average temperature is about 300 K. We calculate the vibrational spectra from the Fourier transform of the velocity–velocity autocorrelation function. In this case, specific atoms can be chosen in the calculation so that the local vibrational spectrum can be obtained. We show in figure 6 the local vibrational spectra of a monohydride surface. The resolution of these spectra is about 1 meV. The top H surface shows clearly the bending mode at 80 meV and the stretching at 281 meV. The extra mode at 64 meV is also observed from the experiment. We see that this mode is bulk related, which can be clearly seen from the consecutive Si layer spectra. This was also identified from the previous work [12].

We further calculate the vibrational spectra of the trihydride surface. Figure 7 shows the local vibrational spectra of the trihydride surface. The top hydrogen layer shows several hydrogen-related peaks. It is clear that the peaks at 276 and 281 meV are the symmetric and asymmetric stretching frequencies, respectively. Although the peaks at 105 and and 115 meV can be identified to be asymmetric and symmetric bending frequencies, respectively, it is not clear where the peak at 55 meV originates from. In order to clarify this, we replaced the H atoms by deuterium atoms. All the hydrogen-related peaks should be scaled down by a factor of $\sqrt{2}$ by the replacement of deuterium atoms. Shown in figure 8 are the vibrational spectra of the deuterated surface. As expected, the stretching and bending modes are scaled down by a factor of approximately $\sqrt{2}$ although the asymmetric bending

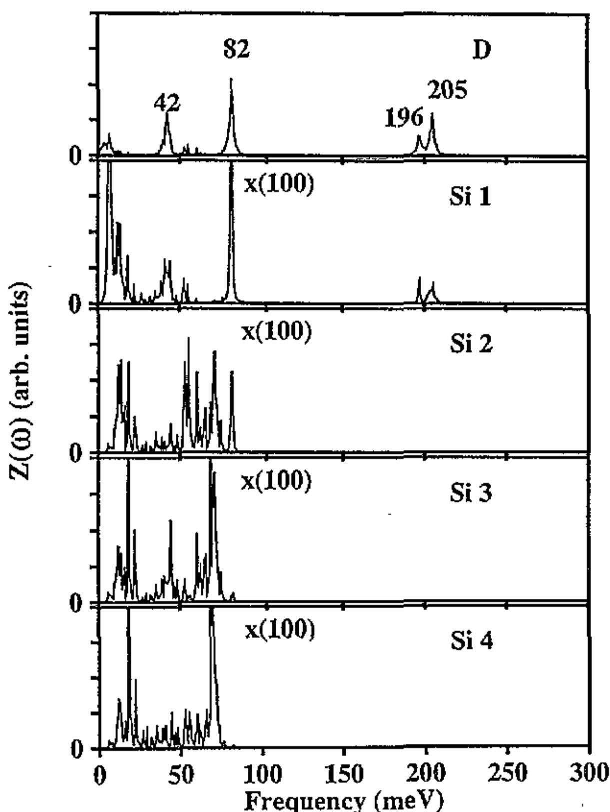

Figure 8. Local phonon spectra of the trideuteride surface. D indicates the top deuterium layer and Si 1 the first surface Si layer.

mode is not clearly seen. This peak may be visible if we run MD long enough so that good statistical time averages can be taken. We note that the peak at 55 meV is scaled down to 42 meV. Therefore, this peak is clearly a hydrogen-related peak. We speculate that this peak is a twist mode (67 meV) in the Si_2H_6 molecule. Because the bulk peaks are involved near this frequency, the peak position can be shifted by the mode interactions. In fact, the TO(Γ) is 70 meV in the bulk Si crystal. This bulk mode may couple to the twist mode, shifting the frequencies from 67 to 55 meV, although the coupling may not be strong because they are not completely in in-plane polarization.

4. Conclusion

We have constructed a transferable TB scheme for the H–Si system. The overlap integrals of H–Si and H–H interactions are empirically fitted to the SiH_4 and H_2 energy levels and vibrational frequencies for Si–H and H–H interactions, respectively. The application of this method to other molecules, Si_2H_6 and Si_2H_4, and the hydrogenated Si(111) surface shows the good transferability of our model. We expect that this model can be applied to more realistic MD simulations.

Acknowledgment

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References

[1] See, for instance,
Joannopoulos J D and Lucovsky G (ed) 1984 *The Physics of Hydrogenated Amorphous Silicon II* (New York: Springer)
[2] Otobe M and Oda S 1992 *Japan. J. Appl. Phys.* **31** L1443, L1388
[3] Tsu R, Xiao H Z, Kim Y W, Hasan M A, Birndaun H K, Green J E, Lin D S and Chiang T C 1994 *J. Appl. Phys.* **75** 240
[4] Chang K J and Chadi D J 1989 *Phys. Rev. Lett.* **60** 1422; 1989 *Phys. Rev.* B **40** 11 644
[5] Van der Walle C G, Bar-Yam Y and Pantelides S T 1988 *Phys. Rev. Lett.* **60** 2761
[6] Kaxiras E and Joannopoulos J D 1988 *Phys. Rev.* B **37** 8842
[7] Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471
[8] Buda F, Chiarotti G L, Car R and Parrinello M 1989 *Phys. Rev. Lett.* **63** 294
[9] Guttman L 1981 *Phys. Rev.* B **23** 1866
[10] Mousseau N and Lewis J 1990 *Phys. Rev.* B **41** 3702
[11] Allan D C and Mele E J 1984 *Phys. Rev. Lett.* **53** 826
[12] Min B J, Lee Y H, Wang C Z, Chan C T and Ho K M 1992 *Phys. Rev.* B **45** 6839, **46** 9677
[13] Goodwin L, Skinner A J and Pettifor D G 1989 *Europhys. Lett.* **9** 1701
[14] Wang C Z, Chan C T and Ho K M 1989 *Phys. Rev. Lett.* **66** 189
[15] Song E G, Kim E and Lee Y H 1993 *Phys. Rev.* B **48** 1486
Kim E and Lee Y H 1994 *Phys. Rev.* B **49** 1743
Lee I H, Chang K J and Lee Y H 1994 *J. Phys.: Condens. Matter* **6** 741
[16] Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
[17] Yin M T and Cohen M L 1982 *Phys. Rev.* B **26** 5668
[18] Chadi D J 1978 *Phys. Rev. Lett.* **41** 1062; 1984 *Phys. Rev.* B **29** 785; 1988 *Phys. Rev. Lett.* **59** 1691
[19] Beagley B, Conrad A R, Freeman J M, Monaghan J J, Norton B G and Holywell G C 1972 *J. Mol. Struct.* **11** 371
[20] Horowitz D and Goddard W A 1988 *J. Mol. Struct.* **163** 207
[21] Dubois I, Herzberg G and Verma R D 1967 *J. Chem. Phys.* **47** 4262
[22] Lucovsky G, Nemanich R J and Knights J C 1979 *Phys. Rev.* B **19** 2064
[23] Kim E and Lee Y H, unpublished