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Empirical interatomic potential for Si-H interactions

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An empirical many-body interatomic potential has been developed to describe Si-H interactions. The potential was fitted to various gas-phase silicon hydride species and interstitial sites of atomic hydrogen in bulk silicon, and gives a reasonable description of hydrogen-terminated silicon surfaces. The potential is computationally efficient and may be used, with caution, for molecular-dynamics investigations of Si-H interactions on hydrogen-terminated silicon surfaces and hydrogenated amorphous silicon.

The chemistry of hydrogen and silicon has received increased attention because hydrogen is an important component in several device-processing steps such as chemical-vapor deposition (CVD), reactive ion etching, wet chemical cleaning, lithography, and annealing ambients such as forming gas. Hydrogen plays an important role in the overall CVD growth mechanism from precursors such as silane and disilane. Hydrogen in bulk silicon can passivate dopants and deep-level defects. Hydrogen passivation of the silicon surface prevents oxidation and chemisorption of impurities over long periods of time. Hydrogen termination of silicon surfaces prior to epitaxy in ultrahigh vacuum has become increasingly popular due to the relatively low desorption temperature of the passivation layer. Epitaxial silicon layers have been deposited on hydrogen-terminated surfaces.[1–3] A low-temperature Ar^+-ion beam-induced (2×1) reconstruction from an initially dihydride-terminated Si(001) surface has also been observed.[4] Many of these processes occur on a time scale and crystal size scale which is beyond the scope of a first-principles approach, but which can be described with empirical force constants. Silicon has been described previously by empirical potentials,[5,6] and hydrogen interactions with diamond surfaces have been investigated.[7] We have developed an empirical Si-H potential for molecular-dynamics simulations of the hydrogen-terminated silicon surfaces and various gas-surface interactions.

Before proceeding to develop a potential, it is pertinent to ask whether a classical description of the silicon-hydrogen system is reasonable. A look at the various bonding configurations of silicon and hydrogen provides a good start. The Si-H bonding in gas-phase molecules and radicals is varied. Saturated molecules such as SiH_4 and Si_2H_6 contain sp^3-type bonds, whereas p-type bonds are found in SiH and SiH_2. The molecule Si_2H_4 exhibits π bonding. Hydrogen adsorption on a silicon surface can result in different reconstructions depending on coverage. The hydrogen atoms on the surface are quite localized even at low coverages. Scanning-tunneling-microscope images at low coverages reveal the location of hydrogen atoms[8] (or more precisely, the unpaired electron opposite the hydrogen atom). This is in contrast to some metals where a delocalized state of the proton has been observed at low coverages.[9] The properties of hydrogen in bulk silicon depend on its charge state.[10] An important position is the bond-centered site of atomic hydrogen where it is bonded to two silicon atoms.[11] It is clear from this brief description that some aspects, such as the dependence on charge state, do not allow for a simple solution within a classical adiabatic framework. Other aspects such as the different types of Si-H bonds and the multiple bonding of hydrogen in the bond-centered site can be modeled, particularly by making a special case for them. Finally, the strongly localized bonding of hydrogen on silicon surfaces and the directional bonds on both the surface and in molecules are features which readily permit a classical description. It is clear from the above that this range of silicon-hydrogen interactions provides a formidable challenge.

Empirical expressions for the Si-H potential have been developed previously.[12,13] However, these potentials were not tested over a sufficiently wide range of configurations to determine their usefulness and limitations. A classical potential with an expression similar to the one described here was reported recently.[14] An earlier version of the potential described here can be found in Ref. 15. Several interatomic potentials have been developed to model silicon-silicon interactions.[5,6] The strong directional bonding in silicon is described by a many-body term attached to a Morse-type potential. The Si potential in Ref. 5 gives a good description of the different allotropes of silicon and the Si(001) surface. This has been extended to germanium and carbon,[16] and has also been used to describe the C-H interactions in hydrocarbons.[7] We have chosen this form to model the Si-H interactions. The total potential energy is written as a sum over pairs[17]

$$V=\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}\Phi_{ij}\ , \tag{1}$$

$$\Phi_{ij}=\{AF_1(N)\exp(-\lambda_1 r_{ij}) -B_0F_2(N)\exp(-\lambda_2 r_{ij})(1+\zeta_{ij}^{\eta})^{-\delta}\}f_c(r_{ij})\ , \tag{2}$$

$$\zeta_{ij}=\sum_{k\neq i,j} f_c(r_{ik})[c+d\{H(N)-\cos\theta_{jik}\}^2] \times\exp[\alpha\{(r_{ij}-R_{ij}^{(e)})-(r_{ik}-R_{ik}^{(e)})\}^{\beta}]\ . \tag{3}$$

The valency of hydrogen is set by the parameters α, β,

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and H in the many-body part of the potential. A high value of α and $\beta=1$ gives a monovalent nature to hydrogen while $\alpha=0$ and $H=-1$ in the presence of two Si atoms describes the bond-centered site in bulk Si. Here F_1, F_2, and H are functions of the coordination N of the ith Si atom. To obtain a continuous function for the coordination, we write[7]

$$N_{\mathrm{H}}^{i=(\mathrm{Si})}=\sum_{j=(\mathrm{H})} f_c(r_{ij}),\quad N_{\mathrm{Si}}^{i=(\mathrm{Si})}=\sum_{j=(\mathrm{Si})} f_c(r_{ij})$$

and

$$N=N_{\mathrm{H}}^{i=(\mathrm{Si})}+N_{\mathrm{Si}}^{i=(\mathrm{Si})}\ , \tag{4}$$

$$f_c(r_{ij})=\begin{cases} 1\ , & r_{ij}<R-D \\ \frac{1}{2}-\frac{9}{16}\sin\left[\pi\frac{r_{ij}-R}{2\mathrm{D}}\right]-\frac{1}{16}\sin\left[3\pi\frac{r_{ij}-R}{2\mathrm{D}}\right]\ , & R-D<r_{ij}<R+D \\ 0\ , & r_{ij}>R+D\ . \end{cases} \tag{5}$$

For nonintegral values of N, the values of F_1, F_2, and H are determined by cubic spline fits. The cutoff function $f_c(r_{ij})$ terminates the potential at first-nearest-neighbor interactions. This function with two sinusoidal terms gives a smoother termination of the potential because at the cutoff points $r=R-D$ and $R+D$ it possesses a continuous third derivative. This leads to better energy and momentum conservation at minimal computational expense, since at any given time the fraction of atom pairs within the cutoff region is quite low.

For Si-Si and H-H interactions, the potentials of Refs. 5 and 7 (potential I) were used, respectively. A combination of the three potentials is used to determine the potential energy and forces for the different triples such as Si-Si-H, H-Si-H, etc., as shown in Fig. 1. One could, in principle, derive a separate set of coefficients for each of the triples. It was found that a single Si-H potential gives a reasonable description in most situations, the exception being the Si-H-Si triple. The values of η and δ depend only on the atoms i and j. The values of α, β, $H(N)$ (or h), c, and d are those of the potential indicated between atoms i and k in Fig. 1.

Numerical values for the parameters were obtained by fitting the potential to the various silicon hydride molecules and interstitial hydrogen sites in bulk silicon. The Si-H bond energy of 3.42 eV for silane was obtained from the heat of formation at 0 K,[18] the values of 4.63 eV for Si cohesive energy[19] and 2.375 eV for hydrogen,[18] neglecting the zero-point energy correction. The Si-H bond length for silane was taken[20] as 1.476 Å. The parameters were also adjusted to give a reasonable fit to the stretch and bend modes of various silicon hydride molecules. The value of δ was taken to be the same as that of the H-H potential.[7] The potential was cut off at 2.00 Å. The parameters of the Si-H potential along with the Si-Si (Ref. 5) and H-H (Ref. 7) potentials are listed in Table I. The interstitial sites of atomic hydrogen in bulk Si were used to determine the values of the parameters in column IIb of Table I. It is noted that the parameters in the potential were not systematically optimized.

The predicted bond lengths, angles, and some vibrational wave numbers for the $\mathrm{Si}_m\mathrm{H}_n$ molecules and radicals are shown in Table II. The properties of the Si_2 dimer and the H_2 molecule are also included. The geometry and vibrational properties of most molecules are fairly well reproduced. The bond length in disilane is 0.07 Å higher than the experimental value of 2.33 Å. Due to the neglect of long-range interactions, the potential does not distinguish between eclipsed and staggered forms of disilane. The experimental value for the rota-

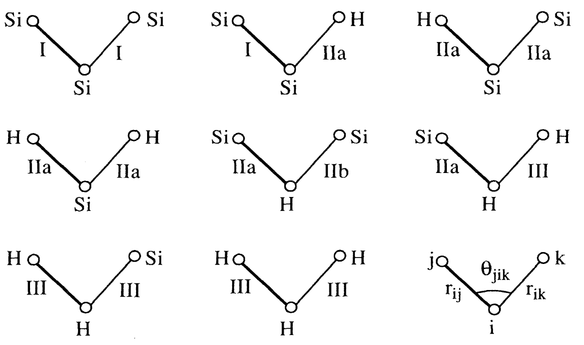

FIG. 1. The combination of the potentials used for different triples. I is the Si-Si potential, IIa and IIb are parts of the Si-H potential, and III is the H-H potential.

TABLE I. The parameters used in the Si-H interatomic potential along with the Si-Si and H-H potentials. The symbol h is used for H (N) in columns I and IIb.

Parameter	Si-Si I (Ref. 5)	Si-H IIa	 IIb	H-H III (Ref. 7)
A (eV)	1830.8	323.54		80.07
B_0 (eV)	471.18	84.18		31.38
λ_1 (Å^{-1})	2.4799	2.9595		4.2075
λ_2 (Å^{-1})	1.7322	1.6158		1.7956
α (Å^{-1} or Å^{-3})	5.1975	4.00	0.00	3.00
β	3	3		1
$R^{(e)}$ (Å)	2.35	1.475		0.74
c		0.0216	0.70	4.00
d	0.160	0.27	1.00	
h	−0.598 26		−1.00	
R (Å)	2.85	1.85	1.85	1.40
D (Å)	0.15	0.15	0.15	0.30
η	0.787 34	1.00		1.00
δ	0.635	0.804 69		0.804 69
$F_1(1)$		1.005		
$F_1(2)$		1.109		
$F_1(3)$		0.953		
$F_1(n), n\geq 4$		1.000		
$F_2(1)$		0.930		
$F_2(2)$		1.035		
$F_2(3)$		0.934		
$F_2(n), n\geq 4$		1.000		
$H(1)$		−0.040		
$H(2)$		−0.040		
$H(3)$		−0.276		
$H(n), n\geq 4$		−0.470		

TABLE II. Properties of some Si_mH_n molecules. Vibrational wave numbers in cm^{-1}. The bond energy of H_2 includes the zero-point energy. The asterisk ($*$) indicates a theoretically calculated value. The dagger ($\dagger$) indicates properties that were fitted to the Si-H potential.

	Si-H potential	Expt./ theory	Ref.		Si-H potential	Expt./ theory	Ref.
SiH_4				SiH			
$a_{Si\text{-}H}$	1.475 Å	1.48 Å	18†	$a_{Si\text{-}H}$	1.51 Å	1.51 Å	20*†
$E_{Si\text{-}H}$	3.42 eV	3.42 eV	18†	$E_{Si\text{-}H}$	3.10 eV	3.14 eV	21†
$\theta_{H\text{-}Si\text{-}H}$	109.5°	109.5°	18†	ν_1	2034	2042	21
ν_1	2100	2186	21				
ν_2	985	972	21	SiH_2			
ν_3	2151	2189	21†	$a_{Si\text{-}H}$	1.51 Å	1.51 Å	20*†
ν_4	913	913	21†	$E_{Si\text{-}H}$	3.42 eV	3.49 eV	18†
				$\theta_{H\text{-}Si\text{-}H}$	92.3°	92.1°	26†
Si_2H_6				A_1 sym stretch	2136	2032	26
$a_{Si\text{-}H}$	1.48 Å	1.49 Å	22	A_1 bend	878	1004	26
$a_{Si\text{-}Si}$	2.40 Å	2.33 Å	22				
$\theta_{H\text{-}Si\text{-}Si}$	109.4°	110.3°	22	SiH_3			
A_{1g} Si-H stretch	2110	2163	23	$a_{Si\text{-}H}$	1.48 Å	1.48 Å	20*†
A_{1g} SiH_3 bend	894	920	23	$E_{Si\text{-}H}$	3.21 eV	3.25 eV	18†
A_{1g} Si-Si stretch	387	432	23	$\theta_{H\text{-}Si\text{-}H}$	106°	110.5°	27
A_{1u} torsion	0	91	20*	Inv. barrier	0.21 eV	0.23 eV	27†
E_g Si-H stretch	2150	2155	23	ν_1	2051	1955	26
ΔH_f^0	0.96 eV	1.00 eV	18†				
				H_2			
Si_2H_4				$a_{H\text{-}H}$	0.74 Å	0.74 Å	18
$a_{Si\text{-}H}$	1.48 Å	1.48 Å	20*	$E_{H\text{-}H}$	4.75 eV	4.75 eV	18
$a_{Si\text{-}Si}$	2.36 Å	2.17 Å	20*	ν_1	4400	4400	28
$\theta_{H\text{-}Si\text{-}Si}$	106.0°	118.9°	20*				
$\theta_{H\text{-}Si\text{-}H}$	106.0°	112.8°	20*	SiH_3SiH			
				$a_{Si\text{-}Si}$	2.37 Å	2.39 Å	20*
Si_2				$a_{Si\text{-}H}(1)$	1.48 Å	1.48 Å	20*
$a_{Si\text{-}Si}$	2.30 Å	2.24 Å	24*	$a_{Si\text{-}H}(2)$	1.51 Å	1.51 Å	20*
$E_{Si\text{-}Si}$	2.66 eV	3.13 eV	18	$\theta_{H\text{-}Si\text{-}Si}(1)$	109.5°	114.2°	20*
ν_1	469	518	25	$\theta_{H\text{-}Si\text{-}Si}(2)$	92.3°	89.1°	20*

tion barrier is about 0.05 eV.[23] The predicted wave number of the torsion mode therefore vanishes; for this wave number a small value of 91 cm^{-1} has been estimated.[20] The energy differences for the decomposition reactions of disilane are listed in Table III. The values for the Si_2H_4 and SiH_3SiH decomposition reactions deviate by about 0.7 and 0.4 eV, respectively. There is reasonable agreement between the values calculated from the potential and the experimental/theoretical estimated values for the other reactions. It is noted that these are the energy differences between the products and disilane but not the activation energies for the reactions. The Si-Si bond length in disilene is also larger than the experimental value. The inadequate description of the π bonding in this molecule accounts for this large difference. The bond angle and the inversion barrier in SiH_3 are 106° and 0.21 eV, respectively. The corresponding experimental values are 110.5° and 0.23 eV, respectively.[27] There are no metastable structures for the SiH_2 and SiH_3 molecules. Most of the vibrational wave numbers are within 15% of the experimental values.

Hydrogen termination of the silicon surface results in different reconstructions depending on coverage. A clean Si(001) surface exhibits a (2×1) reconstruction with the dimer bond along the $\langle 110\rangle$ direction. The Si-Si interatomic potential gives a dimer bond length of 2.37 Å. The structures of hydrogen-terminated Si(001) surfaces as described by the potential are shown in Fig. 2. For a hydrogen coverage of one monolayer (ML), the surface retains a (2×1) reconstruction with hydrogen atoms terminating the dangling bonds of silicon. The Si-Si dimer length increases to 2.43 Å. A similar lengthening of the

TABLE III. The energy differences ΔH for disilane decomposition. The asterisk ($*$) indicates a theoretically estimated value.

Reaction	Potential	Literature	Reference
$Si_2H_6 \rightarrow 2SiH_3$	3.27 eV	3.21 eV	18
$Si_2H_6 \rightarrow Si_2H_5 + H$	3.73 eV	3.78 eV	18
$Si_2H_6 \rightarrow Si_2H_4 + H_2$	2.70 eV	2.04 eV	20*
$Si_2H_6 \rightarrow SiH_3SiH + H_2$	1.91 eV	2.32 eV	20*
$Si_2H_6 \rightarrow SiH_4 + SiH_2$	2.03 eV	2.27 eV	20*

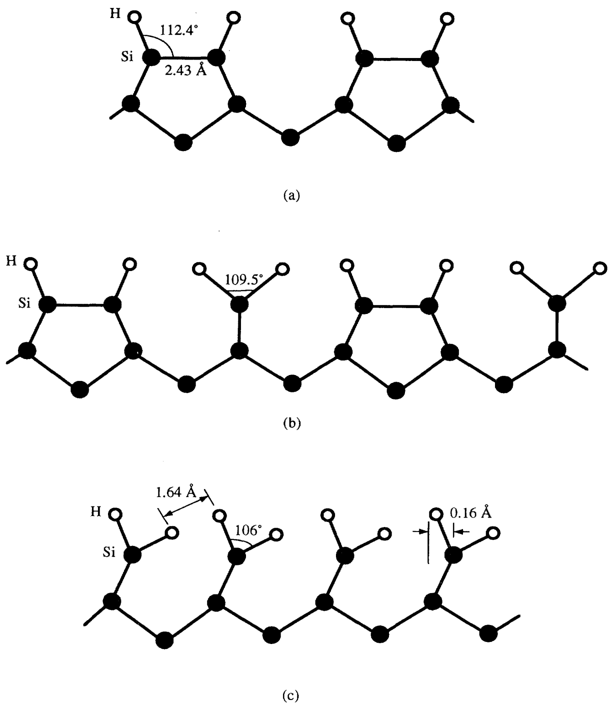

FIG. 2. The different hydrogen-induced reconstructions of the silicon surface. (a) The (2×1) monohydride structure with a hydrogen coverage $\theta=1$ ML, (b) the (3×1) structure with alternate monohydride and dihydride units at $\theta=1.33$ ML, and (c) the (1×1) dihydride structure with $\theta=2$ ML. The dimensions are according to the Si-H potential.

dimer bond was also reported in the semiempirical[29] and *ab initio* cluster calculations.[30] The H-Si-Si bond angle was found to be 112.4° compared to the values of 110.2° (Ref. 31) and 114.7° (Ref. 29) reported in the literature. The wave number of the symmetric stretch mode was $2144\ \mathrm{cm}^{-1}$ compared to the experimental value of $2099\ \mathrm{cm}^{-1}$.[30] At a coverage of 1.33 ML, a (3×1)-reconstructed surface consisting of alternate monohydride and dihydride units is obtained.[8,32] The H-Si-H angle in the dihydride units was found to be 109.5°, in agreement with the first-principles calculations.[33] At a coverage of 2 ML, the surface reverts to a (1×1) structure. There is strong repulsion between H atoms bonded to neighboring Si atoms. A canted-row structure was found to have a lower energy than the symmetric dihydride structure. The H-Si-H angle in the canted-row structure is about 106°, compared to 100° in the symmetric structure. The Si surface atoms are displaced by about 0.16 Å from their bulk positions in the canted-row structure. Although the difference of $0.02\ \mathrm{eV}/(1\times1)$ pair is small, it is significant that a symmetry-breaking displacement produces a structure close in energy to the symmetric structure. Such a canted-row structure was shown to be the lowest-energy structure using the local-density approximation in Ref. 33. A somewhat larger difference of $0.18\ \mathrm{eV}/(1\times1)$ pair and a Si surface-atom displacement of 0.6 Å was reported in these calculations. At low coverages, hydrogen atoms have been observed experimentally to pair up.[8] The difference in energy between an isolated H atom and a H atom in a dimer pair was found to be 0.015 eV, with the isolated atom having lower energy. This difference, albeit small, is contrary to the experimental observation. Using the configuration-interaction method, it was shown in Ref. 31 that the H atom in a dimer pair had a lower energy by ~ 0.05 eV. The driving force for a pairing of H atoms thus appears to be small. A 1-ML hydrogen coverage on the Si(111)-1×1 surface gave a Si-H bond length of 1.48 Å and a stretch mode of $2137\ \mathrm{cm}^{-1}$. The experimental value for the stretch mode is $2084\ \mathrm{cm}^{-1}$.[30] An interesting result is the possibility of formation of a bond-centered Si-H-Si site on the surface. Although this has never been observed for silicon, such a bridge-bonded site was recently observed experimentally on the GaAs surface.[34] It is noted that none of the surface properties were fitted to the potential, and the above results may be considered as predictions of the potential.

The interstitial positions of hydrogen in silicon have been studied extensively using first-principles techniques. The important sites of atomic hydrogen can be found in Ref. 35. All the energies mentioned below are with respect to H atoms in free space and bulk Si atoms. The minimum-energy site has been shown to depend on the charge state of hydrogen.[10] For both neutral H and H^+, the bond-centered (BC) site is the minimum-energy site.[10,11] The set of parameters (labeled IIb in Table I) in the potential were adjusted to produce a minimum energy of atomic H at the BC site. The Si-H bond length in this site is 1.54 Å, and the second-nearest-neighbor atoms are displaced by 0.10 Å. The bridged Si-H bond length in the radical $\mathrm{H_3Si\text{-}H\text{-}SiH_3}$ is 1.58 Å. This increase is due to the free motion of the $\mathrm{SiH_3}$ units in the outward direction. The Si-H bond lengths of 1.58 and 1.72 Å were obtained in the BC site and the radical, respectively, in *ab initio* cluster calculations.[11] The energy at the BC site is 1.26 eV compared to 1.05 eV in Ref. 36. A site near C (on the line between C and T) was found to be 0.2 eV higher in energy compared to the BC site. This site was reported to be the saddle point for H diffusion between BC sites[10] with an activation energy of about 0.2 eV. Among the other sites, the antibonding site AB was not a metastable site. At both the tetrahedral interstitial T and the hexagonal interstitial H sites, the H atom did not interact with any Si atoms. While this is clearly an oversimplification, *ab initio* calculations have shown that there is very little relaxation of Si atoms when a H atom is placed at these sites.[11,37] In the $\mathrm{H_2}$ molecule oriented in the $\langle 100\rangle$ direction at the tetrahedral interstitial site, the H atoms were too far from the Si atoms to interact. The energy per H atom was therefore 2.38 eV, the same as in the free $\mathrm{H_2}$ molecule. A value of 1.92 eV per H atom and an increase of 0.03 Å in the H-H bond length for the $\mathrm{H_2}$ molecule was reported with the local-density approximation.[36] The energy per H atom in the H_2^* complex (H atoms in adjacent BC and AB positions) was 1.50 eV compared to 1.65 eV in Ref. 36.

There are several dynamic situations where one could apply the classical potential described here. A brief analysis of the strengths and weaknesses of the potential is thus appropriate. An area of considerable interest is the low-temperature chemical-vapor deposition of silicon from precursors such as SiH_4 and Si_2H_6. The potential might be used to study the dissociative adsorption of these molecules on the Si(001) surface. However, one must be more cautious with the dissociation of these molecules in the gas phase because of the inadequate description of the Si_2H_4 molecule and the presence of ionized species. Situations where a Si-H-Si configuration is important must be interpreted cautiously. Although the bond-centered site in bulk Si is reasonably described, the potential predicts unusually high stability for bridge-bonded hydrogen in small molecules such as H_3Si-H-SiH_3. This metastability can be removed by substituting potential III for IIb (with a consequent loss of the description of bridge-bonded sites). Hydrogen-terminated silicon surfaces are fairly well described by the potential. Thus the potential may be used to study various physical vapor deposition techniques such as molecular-beam epitaxy and sputter deposition of silicon. Another area of application might be modeling of hydrogenated amorphous silicon. This seems reasonable, since the Si-H bond lengths and the stretching and bending modes in hydrogenated amorphous silicon are not very different from those of the SiH_4 molecule and the hydrogen-terminated silicon surface.[38]

An empirical interatomic potential has been developed to describe the Si-H interactions. The potential gives a reasonable description of the various gas-phase species and hydrogen-terminated silicon surfaces. The potential is computationally efficient and may be used, with caution, for molecular-dynamics investigations of the processing of hydrogen-terminated silicon surfaces and hydrogenated amorphous silicon.

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[1] T. Ohmi, T. Ichikawa, H. Iwabuchi, and T. Shibata, J. Appl. Phys. **66**, 4756 (1989).

[2] D. L. Smith, C.-C. Chen, G. B. Anderson, and S. B. Hagstrom, Appl. Phys. Lett. **62**, 570 (1993).

[3] D. J. Eaglesham, G. S. Higashi, and M. Cerullo, Appl. Phys. Lett. **59**, 685 (1991).

[4] M. V. R. Murty and H. A. Atwater, Phys. Rev. B **49**, 8483 (1994).

[5] J. Tersoff, Phys. Rev. B **38**, 9902 (1988).

[6] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[7] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).

[8] J. J. Boland, Adv. Phys. **42**, 129 (1993).

[9] C. Astaldi, A. Bianco, S. Modesti, and E. Tosatti, Phys. Rev. Lett. **68**, 90 (1991).

[10] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 1079 (1989).

[11] S. Estreicher, Phys. Rev. B **36**, 9122 (1987).

[12] I. Kwon, R. Biswas, and C. M. Soukoulis, Phys. Rev. B **45**, 3332 (1992).

[13] P. M. Agrawal, D. L. Thompson, and L. M. Raff, J. Chem. Phys. **88**, 5948 (1988).

[14] T. Ohira *et al.*, in *Amorphous Silicon Technology—1994*, edited by E. A. Schiff, M. Hack, A. Madan, M. Powell, and A. Matsuda, MRS Symposia Proceedings No. 336 (Materials Research Society, Pittsburgh, 1994), p. 177.

[15] M. V. R. Murty and H. A. Atwater, in *Mechanisms of Thin Film Evolution*, edited by S. M. Yalisore, C. V. Thompson, and D. J. Eaglesham, MRS Symposia Proceedings No. 317 (Materials Research Society, Pittsburgh, 1994), p. 355.

[16] J. Tersoff, Phys. Rev. B **39**, 5566 (1989).

[17] The angular term in the Tersoff potential was simplified since $c \gg d^2$, $d \gg h$, and $\beta \ll 1$ for the Si-Si potential.

[18] *Handbook of Chemistry and Physics*, 72nd ed. (CRC, Cleveland, 1991).

[19] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986).

[20] M. S. Gordon, T. N. Truong, and E. K. Bonderson, J. Am. Chem. Soc. **108**, 1421 (1986).

[21] *JANAF Thermochemical Tables*, 3rd ed. (Dow Chemical Company, Midland, MI, 1985).

[22] B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monaghan, B. G. Norton, and G. C. Holywell, J. Mol. Struct. **11**, 371 (1972).

[23] J. R. Durig and J. S. Church, J. Chem. Phys. **73**, 4784 (1980).

[24] S. D. Peyerimhoff and R. J. Buenker, Chem. Phys. **72**, 111 (1982).

[25] R. D. Verma and P. A. Warsop, Can. J. Phys. **41**, 152 (1963).

[26] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **52**, 2594 (1970).

[27] C. Yamada and E. Hirota, Phys. Rev. Lett. **56**, 923 (1986).

[28] P. W. Atkins, *Molecular Quantum Mechanics*, 2nd ed. (Oxford University Press, New York, 1983).

[29] B. I. Craig and P. V. Smith, Surf. Sci. **226**, L55 (1990).

[30] Y. J. Chabal, G. S. Higashi, K. Raghavachari, and V. A. Burrows, J. Vac. Sci. Technol. A **7**, 2104 (1989).

[31] C. J. Wu and E. A. Carter, Chem. Phys. Lett. **185**, 172 (1991).

[32] Y. J. Chabal and K. Raghavachari, Phys. Rev. Lett. **54**, 1055 (1985).

[33] J. E. Northrup, Phys. Rev. B **44**, 1419 (1991).

[34] H. H. Qi, P. E. Gee, and R. F. Hicks, Phys. Rev. Lett. **72**, 250 (1994).

[35] S. M. Myers *et al.*, Rev. Mod. Phys. **64**, 559 (1992).

[36] C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).

[37] *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic, New York, 1991).

[38] R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, New York, 1991).