Interaction of F and Cl with silicon surfaces

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We have performed local-density-approximation calculations on clusters modeling the Si(111) surface with adsorbed and subsurface F and Cl atoms. These calculations explicitly show that the anomalously low effective binding energy U_0 of SiF and SiCl radicals to the Si substrate in plasma etching conditions is entirely due to the presence of subsurface halogen atoms. The different behavior of subsurface Cl and F is discussed; in the latter case we also discuss the dependency of the SiF U_0 on the flux of incoming F atoms.

I. INTRODUCTION

The chemical enhancement of silicon sputtering by ion bombardment in the presence of F- or Cl-containing gases has been studied extensively.[1–8] These experiments, combined with theoretical studies,[9,10] show that the mechanism of chemical sputtering by F or Cl atoms has the following qualitative features. Generally, the halogen-containing gases chemisorb dissociatively on the silicon surface.[1,9] For Si(111), the halogen atoms stick with almost unit probability to the onefold "top" sites[9,10] (see Fig. 1). In addition to dissociative chemisorption, also penetration of halogen atoms into the bulk takes place under the influence of a beam of, e.g., Ar^+ ions to which the Si surface is exposed.[1–8] It is supposed that these subsurface halogen atoms play an important role in the etch rate enhancement.[2–6] The Ar^+ beam causes sputtering of Si mostly in the form of halogen-containing compounds.

Experiments show that in the presence of F or Cl the energy needed to remove a surface Si atom (the effective binding energy U_0) is "anomalously" low. Whereas the measured U_0 for a top Si atom to the substrate in the absence of F or Cl is equal to 7.8 eV (Ref. 3) [this roughly corresponds to the binding energy of three Si—Si bonds in bulk Si, 7.0 eV (Ref. 11)], the measured U_0 under etching conditions for, e.g., the SiCl and SiF compounds are of the order 0.4 eV (Refs. 3 and 8) and 2.5 eV (Ref. 7), respectively; the SiF value decreases to about 0.8 eV when the flux of incoming F atoms is increased.[7] The "real" U_0 values of the SiF and SiCl molecules may be somewhat higher since internal excitation of the sputtered molecule can decrease its kinetic energy and therefore the measured U_0 value.[12] Several authors believe that the decrease of U_0 of the sputtered Si atoms is one of the main factors responsible for the chemical enhancement of Si sputtering.[2,3,7,8] It is, however, by no means clear how U_0 can decrease so much. It is often assumed that the subsurface halogen atoms can, in some way, give rise to such a decrease.[2–4,6–8] Some authors suggest that the silicon-halogen compounds be present in "voids" of the damaged Si crystal, where they are loosely bound to their environment.[3,4,6] However, in view of the high chemical reactivity of, especially, SiF and SiCl radicals, one would expect that even in voids these species are more tightly bound to the Si crystal than only by about 0.5 eV.

It is the purpose of the present paper to explain the low effective surface binding energy of SiF and SiCl under

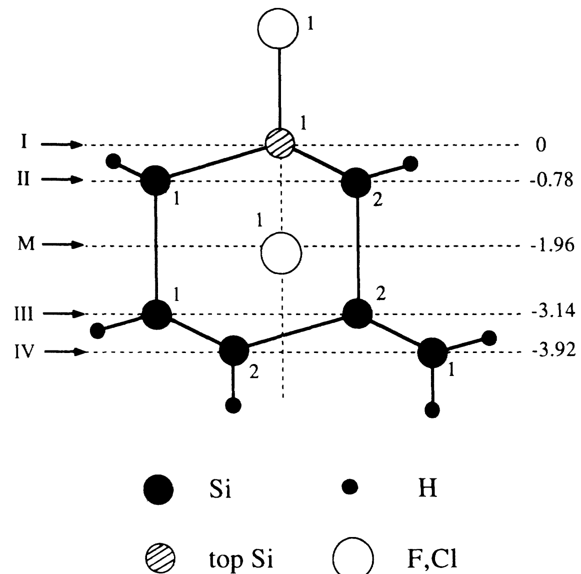

FIG. 1. Cluster modeling the (unreconstructed) Si(111) surface with an on-top chemisorbed and a subsurface halogen atom. The cluster is seen in a projected view along the [1$\bar{1}$0] direction. The numbers next to each atom indicate the real nr. of cluster atoms this atom represents in the projected view. The first, second, etc., layer positions are indicated by I, II, etc. The position halfway between the first and fourth layer is indicated by "*M*." The vertical dashed line indicates the threefold symmetry axis below the top Si atom. The numbers to the right indicate the vertical position (in Å) below the surface.

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etching conditions. To this end we performed electronic structure calculations on clusters modeling the Si(111) surface in interaction with F and Cl atoms. Earlier theoretical work on these systems has shown that the cluster approach is reasonably well suited in this case: the convergence of, e.g., binding energies, equilibrium geometries, and vibrational frequencies with cluster size is quite good.[10] From the results of our calculations, we explain how a subsurface halogen atom can give rise to a very low U_0 for SiF and SiCl. Furthermore, we discuss the differences between the interactions of F atoms with bulk Si and of Cl atoms with bulk Si. Our conclusions about these differences agree qualitatively with earlier theoretical work.[10] Finally, we discuss the possible influence of increasing the flux of supporting fluorine gas on the U_0 of SiF.

Section II of this paper gives an outline of the calculational method used. This section also describes the model clusters. In Sec. III we present and discuss results. Finally, Sec. IV summarizes the results.

II. METHOD

A. General

Self-consistent-field linear-combination-of-atomic-orbitals[13] (SCF-LCAO) calculations have been performed, using the local-density approximation (LDA) in a parametrization from Vosko, Wilk, and Nusair,[14] in combination with a correction proposed by Stoll.[15] Matrix elements were evaluated using a recently developed numerical integration scheme.[16] We used standard[17] (double-ζ) Slater-type-orbital (STO) basis sets, together with a $3d$ function, for the F and Cl atoms. For Si and H, we used the same basis sets as in an earlier study.[18] In the calculations, the F $1s$ and Si and Cl $1s$, $2s$, and $2p$ orbitals were kept frozen.

The interaction energy between the atoms (fragments) of a molecule (cluster) was calculated using Ziegler's transition state method.[19] The expression for the interaction energy ΔE is

$$\Delta E = \Delta E_{\mathrm{el}}(\rho) + \Delta E_X(\rho) + \Delta E_{\mathrm{TS}}(\rho,\bar{\rho}) , \quad (1)$$

where the electron density ρ is given by the sum of the atomic (fragment) densities, $\rho = \sum_A \rho_A$, and $\bar{\rho}$ is the fully converged molecular (cluster) SCF density. Expressions for ΔE_{el}, ΔE_X, and ΔE_{TS} are given in, e.g., Ref. 19. Only the last term, ΔE_{TS}, depends on the molecular (cluster) SCF density $\bar{\rho}$. If we use in Eq. (1) instead of the SCF density $\bar{\rho}$, the density ρ^0, which is obtained from the antisymmetrized product of atomic (fragment) wave functions, we obtain the exchange (Pauli, Born) repulsion ΔE^0,

$$\Delta E^0 = \Delta E_{\mathrm{el}}(\rho) + \Delta E_X(\rho) + \Delta E_{\mathrm{TS}}(\rho,\rho^0) , \quad (2)$$

between the atoms (fragments) of the molecule (cluster). The exchange repulsion is a measure for the overlap between *occupied* atomic (fragment) orbitals: a high overlap gives a high ΔE^0. If ΔE^0 is very high, the energy-lowering electron relaxation $\rho^0 \rightarrow \bar{\rho}$ may not be sufficient to make the net interaction energy ΔE attractive; this is the case for subsurface Cl as we will see below. An extensive discussion of the characteristics of ρ^0 and ΔE^0 has been given in Ref. 20.

B. Clusters

Figure 1 shows the cluster modeling the Si(111) surface in a projected view along the $[1\bar{1}0]$ direction; also chemisorbed (on the onefold top site) and subsurface halogen atoms are indicated. Next to each Si or halogen atom is a number indicating the actual number of cluster Si or halogen atoms this atom "represents" in the projected view. The Si atoms in the cluster are saturated by hydrogen atoms in such a way that they are tetrahedrally coordinated.[18]

III. RESULTS AND DISCUSSION

A. Test calculations

We have performed test calculations on the gas-phase SiF, SiCl, and Si_2H_6 molecules and on the "surface embedded" SiF and SiCl molecules, i.e., F and Cl atoms chemisorbed on the top site of the Si(111) surface. Table I shows our calculated binding energies (D_e), equilibrium distances (r_e), and vibrational frequencies (ω_e) or force constants (k_e) [Table I(a)] in comparison with experiment [Table I(b)] and with other calculations [Table I(c)]. In Table I(c), the calculations on the gas-phase molecules include electron correlation, whereas the calculations on the "embedded" SiF and SiCl molecules are calculations at the SCF level. In general, the agreement with our results is quite satisfactory, as we can see from Table I. Our calculated binding energies tend to be somewhat too high, but this is a general property of LDA-type calculations.[32] In contrast, Hartree-Fock (HF) binding energies tend to be too low,[32] which explains the difference between our calculated D_e values for the embedded SiF and SiCl molecules and those of Ref. 30. The very low D_e values of Ref. 10 are largely due to the absence of d functions in the silicon and halogen basis sets, as has been noted earlier.[30]

B. Chemisorption of F and Cl on "on-top" Si(111)

As we can see from Table I(a), the embedded SiF and SiCl molecules have a lower D_e and ω_e and a larger r_e than their gas-phase "counterparts" [note that we cannot compare the D_e's of the gas-phase and embedded SiF and SiCl molecules in Table I(c), due to different calculational procedures]. This can be explained by a small charge transfer (ca. 0.1 e) from the embedding Si crystal towards the Si—F and Si—Cl bonds; this charge goes into antibonding orbitals. However, most of the electron charge that the electronegative chemisorbed halogen atoms receive comes from the on-top Si atoms to which they are attached; this observation is in agreement with previous work.[10] Therefore the on-top chemisorption of halogen atoms hardly disturbs the bonds between the top (first-layer) and second-layer Si atoms. This suggests that the mere adsorption of halogen atoms causes only a very small decrease of the effective binding energy U_0 of the

TABLE I. Calculated D_e (binding energy), r_e (equilibrium distance), and ω_e (vibrational frequency) or k_e (force constant) for some molecules, compared with experiment and other calculations.

	D_e (eV)	r_e (Å)	ω_e (cm^{-1})	k_e (mdyn/Å)
		(a) this work		
Si—F (gas)	6.7	1.66	792	
Si—Cl (gas)	4.8	2.12	498	
$H_3Si—SiH_3$ (gas)	3.6	2.35		1.54
Si—F (emb)	6.0	1.75	572	
Si—Cl (emb.)	4.2	2.21	318	
		(b) experiment		
Si—F (gas)	5.7[a]	1.60[f]	857[f]	
Si—Cl (gas)	4.7[a]	2.06[f]	536[f]	
$H_3Si—SiH_3$ (gas)	3.5[a]	2.33[g]		1.78[k]
Si—Cl (emb.)		2.03[h]		
		(c) other theoretical work		
Si—F (gas)	5.45[b]	1.67[b]	733[b]	
Si—Cl (gas)	4.28[c]	2.10[i]	525[i]	
$H_3Si—SiH_3$ (gas)	3.12[b]	2.38[b]		2.32[l]
Si—F (emb.)	3.2[d]	1.68[d]		
	4.4[e]	1.61[e]	708[e]	
Si—Cl (emb.)	1.6[d]	2.24[d]	325[d]	
	3.6[e]	2.09[e]	362[e]	
		2.02[j]	338[j]	

[a]Reference 21.
[b]Reference 26.
[c]Reference 27.
[d]Reference 10.
[e]Reference 30.
[f]Reference 22.
[g]Reference 23.
[h]Reference 25.
[i]Reference 29.
[j]Reference 31.
[k]Reference 24.
[l]Reference 29.

top Si atom to the Si crystal. This is indeed the case, as we can see from Table II. This table shows the effective binding energies U_0 of the top Si atoms (or the SiF or SiCl radicals containing these atoms) to the Si substrate for a number of cases. In the absence of F or Cl, the calculated U_0 for the top Si is equal to 7.6 eV; this value nicely agrees with the measured U_0 of 7.8 eV (Ref. 3) and the literature bond energy of three bulk Si-Si bonds [7.0 eV (Ref. 11)]. The absorption of halogen atoms causes only a small decrease of U_0 (ca. 0.6 eV) as is clear from the second and fifth rows of Table II.

TABLE II. Calculated effective binding energies U_0 (in eV) of the top Si atom (or SiF or SiCl radical containing the top Si atom) to the Si substrate (left column); experimental U_0 (right column).

	U_0 (calc.)	U_0 (expt.)
Without F or Cl	7.6	7.8[a]
Adsorbed F atoms	6.9	
Adsorbed plus subsurface F		
"Low" F flux	3.0	2.5[b]
"High" F flux	0.3	0.8[b]
Adsorbed Cl atoms	7.0	
Adsorbed plus subsurface Cl	1.2	0.4[c]

[a]Reference 3.
[b]Reference 7.
[c]Reference 8.

C. Subsurface F and Cl atoms

In this subsection we discuss the influence of subsurface F or Cl atoms on the effective binding energy of SiF or SiCl radicals containing the top-layer Si atom. We start by considering the incorporation of a (subsurface) halogen atom into the Si crystal; next we will discuss what happens when we remove the SiF or SiCl radical from the surface.

We have calculated the interaction energies ΔE and exchange repulsions ΔE^0 between subsurface halogen atoms and the Si crystal (with chemisorbed halogen atoms) for various positions of the subsurface atoms along the threefold symmetry axis below the top Si atom (see Fig. 1). The results are shown in Fig. 2. From this figure, we can see that the incorporation of subsurface F is exothermic, whereas for Cl it is endothermic. Consequently, Cl cannot penetrate by itself into the solid, contrary to F.[10] This explains the fact that F can spontaneously etch silicon, whereas in the case of Cl this is much more difficult.[33] The reason for this difference between F and Cl also follows from Fig. 2: the exchange repulsion

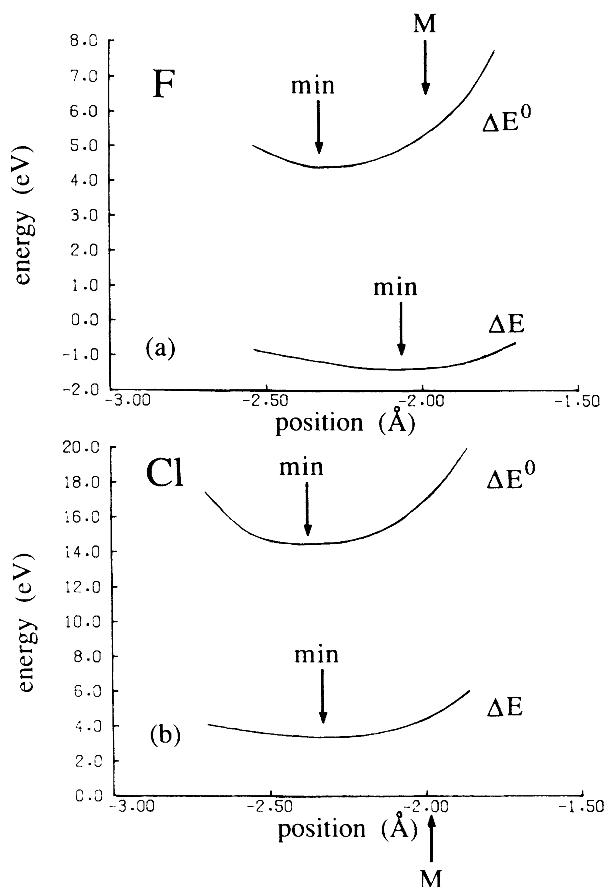

FIG. 2. Interaction energy (ΔE) and exchange repulsion (ΔE^0) curves for subsurface F [Fig. 2(a)] and Cl [Fig. 2(b)] at different positions along the threefold symmetry axis below the top Si atom (see Fig. 1). The positions are defined with respect to the top Si atom. The minima of the energy curves are indicated by arrows. Also is indicated position "M" (see Fig. 1).

ΔE^0 between Cl and the Si crystal is about three times as large as the exchange repulsion between F and the Si crystal. The ΔE^0 of Cl is so large that the energy-lowering relaxation of the electron density ($\rho^0 \rightarrow \bar{\rho}$) cannot compensate for this; therefore the net interaction energy ΔE is still repulsive. Since in the case of F the ΔE^0 is much smaller, the net interaction energy ΔE can be attractive. Figure 2(b) shows that for Cl, the behavior of ΔE is dominated by ΔE^0: the minima of the curves for ΔE and ΔE^0 coincide. This is not the case for F [Fig. 2(a)], where bonding to the Si(II) atoms (see Fig. 1) causes an upward shift of the minimum of ΔE with respect to the ΔE^0 minimum. Since ΔE^0 is a measure for the overlap between occupied orbitals, we expect from the difference between F and Cl shown in Fig. 2 that the occupied orbitals in Cl are much larger than in F. This is indeed the case, as we can see from Table III: the Cl 3s and 3p orbitals are about 1.5 times larger than the F 2s and 2p orbitals.

As a next step, let us consider the removal of the SiF or SiCl radical containing the top Si atom, in the presence of subsurface F or Cl. We expect that, due to this removal, the subsurface halogen atoms will relax towards new equilibrium positions. Figure 3 shows that this is indeed

TABLE III. Expectation values $\langle r \rangle$ for some F and Cl atomic orbitals (in a_0). For comparison, the $\langle r \rangle$ value of the hydrogen 1s orbital is also given, as calculated by LDA and HF methods (the HF value is exact for H).

H		F		Cl	
1s (LDA)	1.7	2s	1.0	3s	1.6
1s (HF)	1.5	2p	1.1	3p	1.9

the case. Here, the interaction energies ΔE and exchange repulsions ΔE^0 between the subsurface halogen atom and the Si crystal in the absence of the top SiF or SiCl radical are plotted as a function of the position of the halogen atom. From this figure, it is clear that there will be a considerable relaxation towards a new equilibrium position, especially in the case of Cl, where the repulsive interaction energy at the subsurface position changes into an attractive interaction energy at an equilibrium position above the surface. This relaxation causes, especially for Cl, a considerable decrease of the net amount of ener-

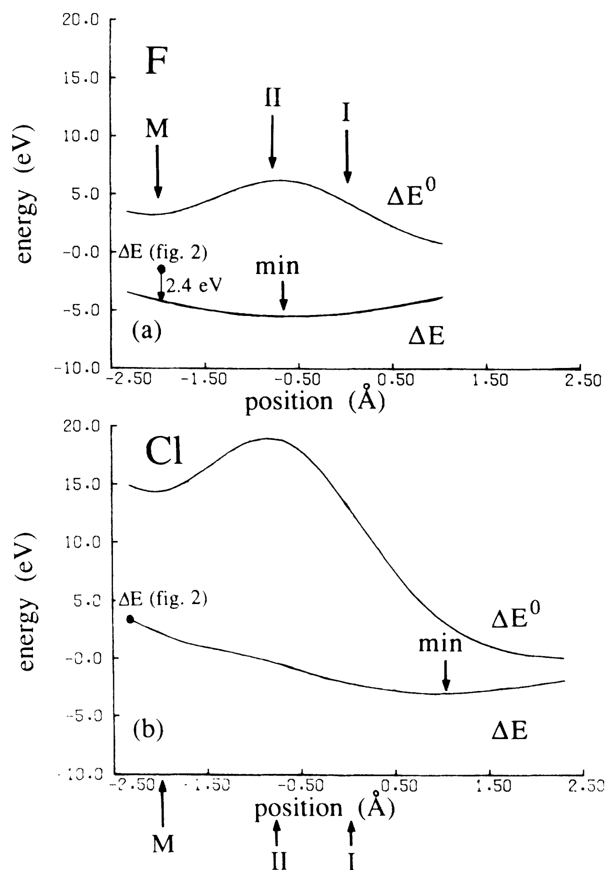

FIG. 3. Interaction energy (ΔE) and exchange repulsion (ΔE^0) curves for (a) subsurface F and (b) Cl at different positions along the threefold symmetry axis (see Fig. 1) in the *absence* of the top Si atom (and adsorbed halogen atom). The positions of the minima in the ΔE curves are indicated by arrows. Also are indicated the first and second layer positions, and position "M" (see Fig. 1).

gy needed to remove a SiF or SiCl radical from the surface. Since, on the average, an ejected SiF or SiCl radical moves over a distance only of the order of 1 Å on the time scale of lattice vibrations, it is reasonable to assume that subsurface halogen atom relaxation indeed influences the effective binding energy U_0.

The first column of Table II lists the calculated net amounts of energy needed to remove an SiF or SiCl from the Si surface, i.e., the effective surface binding energies U_0 of SiF and SiCl in the presence of a subsurface halogen atom. In the second column, the experimental values for U_0 are given. The large reduction of U_0 noted in the experiments is nicely reproduced in the calculations. This strongly suggests that the experimentally observed reduction of U_0 is due to subsurface atoms. The precise cause of the reduction is somewhat different for subsurface F and Cl. The subsurface F atom, although it has a net bonding interaction with the surrounding Si cage, obviously has a repulsive interaction with the top Si atom [Si(I), see Fig. 1], or alternatively is able to considerably strengthen its bonds to the three Si(II) atoms when the Si(I) leaves. This accounts for 2.4 eV out of the total calculated reduction of 3.9 eV in U_0 due to subsurface F [see Fig. 3(a)]. The additional 1.5 eV comes from the relaxation of the F atom to an equilibrium position almost within the Si(II) layer. At this position the distance between the F atom and the Si(II) atoms is minimal (2.22 Å).

In the case of subsurface Cl, the (repulsive) interaction with the cage does not change much if the Si(I) atom leaves [note that the subsurface Cl is somewhat more removed from Si(I) than subsurface F]. Here, the lowering of U_0 is almost completely due to the relaxation of the Cl atom to a position which is even above the original position of the Si(I) atom. Figure 3(b) shows that when the Cl moves to its new equilibrium position, the initial energy lowering is due to a strengthening of the Cl—Si(II) bonds, which more than compensate for the increase in exchange repulsion with the Si(II) atoms when the Cl atom moves to the "narrow" site in the Si(II) layer. However, the Cl moves on to a position above the Si(II) plane since this results in a rapid decrease of the repulsive interaction ΔE^0 with the Si(II) layer which is far more important than the decrease of the bonding interaction with Si(II).

Finally, we consider the dependence of the effective binding energy U_0 on the flux of supporting halogen gas. The experimental U_0 of SiF can be decreased even more by increasing the flux of incoming F atoms.[7] Our calculations suggest that this may be due to the fact that a second subsurface F atom in the same Si cage (in addition to the relaxed F atom in the absence of the top SiF radical) gives an additional lowering of the total energy of the system by about 2.7 eV; consequently, the U_0 of SiF can be lowered to 0.3 eV (Table II). Of course, in the case of Cl such a second subsurface atom will be energetically highly unfavorable. Therefore we do not expect a decrease of the effective binding energy of SiCl if the Cl flux is increased.

IV. CONCLUSIONS

We have shown that the very low effective surface binding energies U_0 of SiF and SiCl molecules to the Si substrate can be explained by the presence of subsurface F or Cl atoms. The relaxation of these atoms upon removal of SiF or SiCl molecules from the surface lowers the net amount of energy needed to remove these molecules, i.e., their effective surface binding energy. The detailed interactions of F and Cl with the Si crystal show considerable differences. In the case of F, the possibility of an energy-lowering configuration in which a second subsurface F atom is present, can further lower U_0 as a function of flux of incoming F atoms.

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[1]J. W. Coburn and H. F. Winters, J. Appl. Phys. **50**, 3189 (1979).

[2]R. A. Haring, A. Haring, F. W. Saris, and A. E. de Vries, Appl. Phys. Lett. **41**, 174 (1982).

[3]J. Dieleman, *Second Conference for the Study of Dry Etching in Microelectronics, Grenoble, France, 1983,* Le Vide les Couches Minces Suppl. No. 218 (1983), p. 3.

[4]F. H. M. Sanders, A. W. Kolfschoten, J. Dieleman, R. A. Haring, A. Haring, and A. E. de Vries, J. Vac. Sci. Technol. A **2**, 487 (1984).

[5]T. Mizutani, C. J. Dale, W. K. Chu, and T. M. Mayer, Nucl. Instrum. Methods B **7/8**, 825 (1985).

[6]J. Dieleman, F. H. M. Sanders, A. W. Kolfschoten, P. C. Zalm, A. E. de Vries, and A. Haring, J. Vac. Sci. Technol. B **3**, 1384 (1985).

[7]D. J. Oostra, A. Haring, A. E. de Vries, F. H. M. Sanders, and K. Miyake, Appl. Phys. Lett. **46**, 1166 (1985); D. J. Oostra, A. Haring, A. E. de Vries, F. H. M. Sanders, and G. N. A. van Veen, Nucl. Instrum. Methods B **13**, 556 (1986).

[8]D. J. Oostra, A. Haring, R. P. van Ingen, and A. E. de Vries, J. Appl. Phys. **64**, 315 (1988).

[9]P. K. Larsen, N. V. Smith, M. Schlüter, H. H. Farrell, K. M. Ho, and M. L. Cohen, Phys. Rev. B **17**, 2612 (1978).

[10]M. Seel and P. S. Bagus, Phys. Rev. B **28**, 2023 (1983).

[11]K. A. Gschneidner, in *Solid State Physics,* edited by F. Seitz and O. Turnbull (Academic, New York, 1964), Vol. 16, p. 344.

[12]H. M. Urbassek, Nucl. Instrum. Methods B **18**, 587 (1987).

[13]E. J. Baerends, D. E. Ellis, and P. Ros, Chem. Phys. **2**, 41 (1973).

[14]S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[15]H. Stoll, C. M. E. Pavlidou, and H. Preuss, Theor. Chim. Acta **49**, 143 (1978).

[16]P. M. Boerrigter, G. te Velde, and E. J. Baerends, Int. J. Quant. Chem. **33**, 87 (1988).

[17]J. G. Snijders, P. Vernooijs, and E. J. Baerends, Atom. Data Nucl. Data Tables **26**, 483 (1981); Internal Report, Free University, Amsterdam, 1981 (unpublished).

[18]P. J. van den Hoek, W. Ravenek, and E. J. Baerends, Phys. Rev. Lett. **60**, 1743 (1988); P. J. van den Hoek, W. Ravenek, and E. J. Baerends, Surf. Sci. (to be published).

[19]T. Ziegler and A. Rauk, Theor. Chim. Acta **46**, 1 (1977).

[20]P. J. van den Hoek, A. D. Tenner, A. W. Kleyn, and E. J. Baerends, Phys. Rev. B **34**, 5030 (1986).

[21]*Handbook of Chemistry and Physics* (Chemical Rubber, Boca Raton, 1983).

[22]Huber and Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).

[23]B. Beagly, A. R. Conrad, J. M. Freeman, J. J. Monaghan, and B. G. Norton, J. Mol. Struc. **11**, 371 (1972).

[24]W. J. Hehre and W. A. Lathan, J. Chem. Phys. **56**, 5255 (1972).

[25]P. H. Citrin, J. E. Rowe, and P. Eisenberger, Phys. Rev. B **28**, 2299 (1983).

[26]B. J. Garrison and W. A. Goddard III, J. Chem. Phys. **87**, 1307 (1987).

[27]P. Ho, M. Coltrin, J. S. Binkley, and C. F. Melius, J. Phys. Chem. **89**, 4647 (1985).

[28]R. K. Gosavi and O. P. Strauss, Chem. Phys. Lett. **131**, 243 (1986).

[29]L. Snyder and Z. Wasserman, Chem. Phys. Lett. **51**, 349 (1977).

[30]F. Illas, J. Rubio, and J. M. Ricart, Phys. Rev. B **31**, 8068 (1985).

[31]G. B. Bachelet and M. Schluter, J. Vac. Sci. Technol. B **3**, 726 (1983); Phys. Rev. B **28**, 2302 (1983).

[32]G. S. Painter and F. W. Averill, Phys. Rev. B **26**, 1781 (1983).

[33]Y. Y. Tu, T. J. Chuang, and H. F. Winters, Phys. Rev. B **23**, 823 (1981); H. F. Winters and F. Houle, J. Appl. Phys. **54**, 1218 (1983).