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Nonempirical cluster-model study of the chemisorption of atomic hydrogen on the (111) surface of diamondlike crystals

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The interaction of atomic hydrogen with C_4H_9, Si_4H_9, and Ge_4H_9 model clusters has been studied using all-electron and pseudopotential *ab initio* Hartree-Fock computations with basis sets of increasing flexibility. The results show that the effect of polarization functions is important in order to reproduce the experimental findings, but their inclusion only for the atoms directly involved in the chemisorption bond is usually sufficient. For the systems H-C_4H_9 and H-Si_4H_9 all-electron and pseudopotential results are in excellent agreement when basis sets of comparable quality are used. Besides, semiempirical modified-neglect-of-differential-overlap computations provide quite reliable results both for diamond and silicon and have been used to investigate larger model clusters. The results confirm the local nature of chemisorption and further justify the use of minimal X_4H_9 model clusters.

I. INTRODUCTION

Extensive efforts have been made to analyze and explain at a microscopic level the details of the interaction of atoms and molecules with semiconductor surfaces in view of the technological importance of some of these processes. The chemisorption of hydrogen on the (111) surfaces of diamondlike crystals is probably the most studied among these processes and the ultraviolet-photoemission spectra of cleaved Si and Ge (111) 2×1 surfaces undergo dramatic changes on exposure to atomic hydrogen.[1-3] In particular, the large peak just near the valence-band maximum (VBM), which is associated with the dangling bonds of surface atoms, disappears,[4-7] while a new peak appears at about 5.0 eV below the VBM. Furthermore, the low-energy electron diffraction pattern changes to the primitive 1×1 structure. All these trends can be easily explained by considering, that because of the saturation of the dangling bonds, the surface atoms of the semi-infinite lattices do not relax or undergo a Jahn-Teller distortion (which led to the 2×1 reconstruction of the free crystals). In fact, atomic hydrogen is easily adsorbed up to monolayer coverage (monohydride phase) directly on the surface atoms, whereas further exposure produces a trihydride phase[8,9] where SiH_3 radicals are bonded to the surface Si atoms. On the other hand, molecular hydrogen does not seem to react with Si(111) probably because of the large dissociation energy of H_2 [4.48 eV (Ref. 10)]. The experimental studies concerning the chemisorption of hydrogen on C(111) are comparatively quite recent[11-13] and were first interpreted in terms of a reduced reactivity of diamond with respect to silicon and germanium. The most recent studies,[14,15] however, indicate that hydrogen exposures at an elevated sample temperature revert the 2×2 or 2×1 surface of diamond to the 1×1 structure. Also, in this case, further exposure to atomic hydrogen produces a trihydric phase,[15] whereas molecular hydrogen is always relatively inert.[14]

In spite of these studies, several questions remain open about the detailed mechanism of chemisorption and the possible differences between different diamondlike crystals (diamond, silicon, and germanium), which can be more directly answered by theory than by experiment. Most of the theoretical studies performed until now have been based on band-structure-type models (where a two-dimensionally periodic adsorbate layer corresponding to monolayer coverage is considered) and were especially concerned with spectroscopic characteristics.[16-20] Here, however, we are concerned with the study of equilibrium geometries, force constants, and binding energies in the low-coverage limit. In this connection the cluster-model approach[21-29] remains competitive since these observables are generally local in character. In the very small clusters that can, at present, be studied by refined quantum-mechanical procedures, however, the boundaries may play a decisive role.[30,31] It is therefore our purpose to perform extensive computations on small model clusters [the only available results concern Si (Refs. 32 and 33)] in order to select an optimal procedure (i.e., the best compromise between computation time and reliability of the results) for the study of larger clusters. In fact, even using the minimal X_4H_9 cluster models to mimic the surface, extended-basis-set all-electron *ab initio* computations, which are quite feasible in the case of carbon, become out of the question in the case of germanium. In order to solve such a dilemma, the use of *ab initio* atomic pseudopotentials (hereafter referred to as PP's) is very valuable and, as only valence electrons are treated explicitly, the study of the same models for C(111), Si(111), and Ge(111) surfaces using extended basis sets is possible at the same level of accuracy and with the same computational effort. As the inclusion of polarization functions seems to be necessary, several basis sets of different complexity are used, and mixed basis sets are also proposed. For purposes of comparison the computations for C and Si cluster models have been performed with comparable basis sets also at the all-electron level. Finally, the same clusters have been investigated by the much cheaper semiempirical modified-neglect-of-differential-overlap (MNDO) method[34] in order to test its reliability in view of its use for much larger clusters and of some criticism on its performance in the case of silicon compounds.[35]

II. METHOD

Embedding H atoms are used to form a tetrahedral bulk environment for the substrate atoms and to effectively allow for sp^3 hybridization. Several studies have shown that for covalently bonded crystals this is a very satisfactory procedure and does not alter significantly the computed energetic and geometric parameters, provided that sufficiently large clusters are used.[21–25,36]

The chemisorption process was studied by adding an H atom, denoted H_a to distinguish it from the embedding H atoms, above cluster models containing just one surface atom, indicated as $X(1)$ (see Fig. 1). The first model (X_4H_9) has been largely used in previous studies and is small enough to allow the use of quite large basis sets. It represents therefore an ideal model for selecting appropriate basis sets for the study of larger clusters. The second model ($X_{10}H_{15}$) includes four layers and is used to examine the possible effect of boundaries on the computed properties.

All-electron (AE) computations were performed using the GAUSSIAN/80 (Ref. 37) package, whereas pseudopotential (PP) calculations were performed using the PSHONDO program.[38] Inner shells of X atoms are represented by minimal basis sets of Gaussian functions (AE computations) or replaced by the pseudopotentials determined by Durand and co-workers[39] (PP computations). All-electron computations were first performed by a minimal basis set (hereafter referred to as AE-min) in which each atomic orbital is represented by a Slater-type orbital, which, in turn, is fitted by a linear combination of three Gaussian functions (known as the STO-3G basis set[40]). In all the other computations the basis set for embedding hydrogens is of double-ζ quality, the four initial Gaussian primitives being contracted through a $3+1$ procedure. Several basis sets have instead been used for the other atoms, which can be summarized as follows.

Basis 1. In this kind of basis set (which will be hereafter referred to as AE-2ζ or PP-2ζ) the valence s orbitals of all the atoms and the $2p$ orbitals of carbon are described by four primitives, which are contracted by means of a $3+1$ procedure. Since at the AE level the inner-shell orbitals are represented by four Gaussians, the basis set is known as 4-31G.[41] A $2+2$ contraction scheme was, instead, adopted for the $3p$ orbitals of Si and the $4p$ orbitals of Ge.

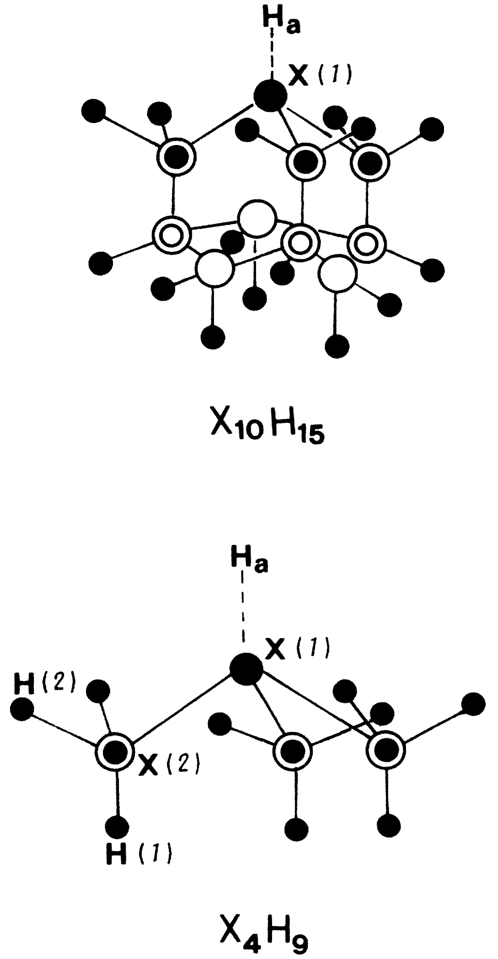

FIG. 1. Schematic drawing of the model clusters H-X_4H_9 and H-$X_{10}H_{15}$ used in the study of hydrogen chemisorption on the (111) surfaces of diamondlike crystals.

Basis 1′. In this basis set (referred to as AE-$2\zeta^*$) inner orbitals are described by six Gaussians, the valence orbitals are as in the previous AE basis set, and a set of d orbitals is added to nonhydrogen atoms;[42] p orbitals on hydrogen were not included in view of their negligible importance in similar compounds.[43]

Basis 2. This basis set (hereafter referred to as PP-$2\zeta^+$) includes the effect of polarization on the adatom by adding a single p function (with $\zeta_p=0.8$) to the previous basis set of H_a.

Basis 3. This basis set (hereafter referred to as PP-$2\zeta^{++}$) includes also the polarization of the surface X atom by adding a single d function [$\zeta_d=0.70$ for C (Ref. 44), 0.45 for Si, and 0.20 for Ge (Ref. 29)].

Basis 4. This basis set (hereafter referred to as PP-$2\zeta^*$) is of double-ζ plus polarization quality on all atoms except embedding hydrogens.

Only low-spin wave functions were considered as possible ground states, i.e., singlet states for $(X_4H_9)H$ clusters and doublet states for X_4H_9 clusters. The doublet states were treated by the unrestricted Hartree-Fock method at the all-electron level and by the effective Hamiltonian proposed by Nesbet,[45] at the MNDO and pseudopotential levels.

The vibrational frequencies for the vibration perpendicular to the surface were computed from the binding-energy curves in the harmonic approximation and by assuming an infinite mass for the substrate. Accordingly, the vibrational energy can be expressed as

$$\hbar\omega_e = \hbar(k/m_{\mathrm{H}})^{1/2} ,$$

m_{H} being the hydrogen mass. Such an approximation has been widely used in dealing with atomic chemisorption on model clusters and, together with the limitation of the basis sets and the lack of electron correlation, leads to typical errors of 10% on the computed vibrational frequencies.[46]

All the computations were carried out in the C_{3v} symmetry group and, consequently, the number of integrals to be computed is greatly reduced and the molecular orbitals belong to the irreducible representations of the C_{3v} point group.

As is the case for many surfaces, $X(111)$ relaxes and reconstructs; i.e., the positions of the atoms in the first few layers of the crystals change from their positions in the bulk.[47] In the cluster models used here these changes are neglected and the X atoms are chosen to have their bulk geometry (tetrahedral angles were used throughout and G—C, Si—Si, and Ge—Ge bond distances of 2.90,[48] 4.44,[49] and 4.63 bohrs,[50] respectively). The C—H, Si—H, and Ge—H bond lengths (taken from X_2H_6 compounds) are 2.06,[51] 2.80,[52] and 2.91 bohrs,[53] respectively.

The binding energy D_e is defined, as usually, as the difference between the total energy of the adsorbate-cluster system and the total energies of the isolated fragments, using the same basis set in both cases. This can be expressed as

$$D_e = [E_{\mathrm{tot}}(\mathrm{cluster}) + E_{\mathrm{tot}}(\mathrm{H})] - E_{\mathrm{tot}}(\mathrm{cluster\text{-}H}) .$$

III. RESULTS AND DISCUSSION

The geometric, energetic, and electronic characteristics of the bare X_4H_9 and $X_{10}H_{15}$ clusters obtained at the all-electron (Refs. 26 and 54), pseudopotential (Refs. 29 and 54), and MNDO (Ref. 24) levels have been previously reported and are not repeated here. The corresponding data for the adducts obtained upon hydrogen chemisorption are given in Table I.

From the results of the table it can be seen that comparable basis sets give very similar results at the PP and AE levels concerning equilibrium distances, vibrational frequencies, and ionization potentials. The lower binding energies obtained by AE computations are due to the different treatment of the naked clusters, which are open shell systems: in fact, the unrestricted Hartree-Fock procedure (used in AE computations) *always* gives lower total energies with respect to the Nesbet approximation (used in PP computations) for *identical* basis sets.

A further apparent characteristic of Table I is the closeness of the results obtained by mixed and complete basis sets in the pseudopotential approach. These results indicate that inclusion of polarization functions only for the atoms directly involved in the chemisorptive bond gives results essentially identical to those obtained by the use of an extended basis set for the whole substrate.

Considering the correlation error for the D_e of a single two-electron bond, we would expect the self-consistent-field (SCF) D_e to be too small by about 1 eV.[32] However, the calculated values are much closer to the available experimental data and the convergence of D_e for various cluster sizes (Refs. 32 and 33 and MNDO results in Table I) suggests that the value will not change by more than about 0.2 eV for larger cluster representations of the surface. Thus the experimental D_e are likely to be in error and the actual binding energies of $H/X(111)$ systems could be 4.5, 3.5, and 3.2 for C, Si, and Ge, respectively.

The SCF ω_e are 10% larger than the available experimental values. These errors are characteristic for SCF vibrational frequencies of real molecules. There is no experimental information for r_e; however, the SCF values are reasonable ones. They are close to both the SCF and experimental distances in X_2H_6 molecules and, in the case of Si, to the r_e value obtained from band-structure computations.[16]

The atomic net charges obtained by AE and PP computations show some difference, but it is well known that Mulliken population analysis is very sensitive to the treatment of inner shells. A more detailed partition of electron populations is given in Table II only for the pseudopotential results. All-electron results are not reported since inner shells are not exactly neutral and, more importantly, the treatment of d orbitals (a redundant set of six functions is used) results in the inclusion of a part of the s population in the d one.[29] As a first point it is quite apparent that the electron populations of the embedding hydrogen atoms are almost constant with all the basis sets used in this work and practically identical with the values obtained for the naked clusters. This is a further indication of the adequacy of hydrogen saturators in the treatment of covalent solids. Furthermore, the populations of the silicon atoms belonging to the second layer are also identical before and after hydrogen chemisorption, so that the essential of adatom-substrate charge transfer is related to $X(1)$. This gives further support to simplified models based on the treatment of an X-H surface molecule embedded in the rest of the solid, which plays, at most, the role of an electron reservoir.[55] From a computational point of view the different behavior of mixed basis sets is quite remarkable. In fact, the addition of polarization functions to the adsorbing hydrogen does not alter the electron distribution of the whole system (results obtained by 2ζ and $2\zeta^{+}$ basis sets in Table II), whereas the unbalanced treatment of the X atoms in the substrate leads to significant alterations ($2\zeta^{++}$ and $2\zeta^{*}$ results). As already observed, however, the comparison of Mulliken populations obtained by different basis sets is not too meaningful, especially in view of the remarkable agreement obtained both for all the observables computed (see Table I) and for the electron redistribution caused by chemisorption.

TABLE I. Net atomic charges on the adatom (q_{H_a} in a.u.); equilibrium bond lengths (r_e in Å), vibrational frequencies (ω_e in meV), ionization potentials (IP in eV), and binding energies (D_e in eV) obtained for the X_4H_9 clusters according to different methods. The definition of the basis sets is given in the text.

Method	q_{H_a}	r_e	D_e	ω_e	IP
		C_4H_9			
MNDO	0.023	1.137	4.15		12.2
AE-min	0.047	1.085	4.81	401	10.8
AE-2ζ	0.158	1.087	3.87	382	12.3
AE-2ζ^*	0.158	1.085	3.82	392	12.2
PP-2ζ	0.140	1.095	4.03	367	12.3
PP-2ζ^+	0.091	1.095	4.10	373	12.3
PP-2ζ^{++}	0.097	1.096	4.12	370	12.3
PP-2ζ^*	0.084	1.094	4.16	369	12.3
MNDO[a]	0.023	1.114	4.20		11.3
AE-min[a]	0.047	1.091	4.78	395	9.7
Expt.			4.2[b]	360[c]	
		Si_4H_9			
MNDO	−0.149	1.421	3.09		10.4
AE-min	−0.160	1.423	4.42	295	7.8
AE-2ζ^*		1.486[d]	3.00[d]	282[d]	
PP-2ζ	−0.060	1.489	2.94	269	10.4
PP-2ζ^+	−0.120	1.475	3.07	294	10.4
PP-2ζ^{++}	−0.088	1.481	3.27	271	10.4
PP-2ζ^*	−0.109	1.484	3.23	271	10.5
MNDO[e]	−0.159	1.432	3.02		9.8
Expt.			3.2[d]	257[d]	
		Ge_4H_9			
PP-2ζ	−0.104	1.551	2.76	268	10.0
PP-2ζ^+	−0.148	1.542	2.86	265	10.0
PP-2ζ^{++}	−0.079	1.555	2.96	269	10.0
PP-2ζ^*	−0.094	1.556	2.94	268	10.0

[a] $C_{10}H_{15}$ cluster.
[b] From Ref. 11.
[c] From Ref. 15.
[d] From Ref. 33.
[e] $Si_{10}H_{15}$ cluster.

As is well known, the chemical properties of Si and Ge are very similar and this is very well reflected by the results of Table I. In fact, the binding energies of H do not differ by more than 0.2 eV and the vibrational frequencies are virtually identical. The characteristics of carbon are, on the other hand, somewhat different due to the more covalent character of the C—H bond and the consequent greater strength and force constant. All these results are perfectly coherent with the known properties of small saturated molecules formed by C, Si, and Ge.

From another point of view, the results obtained by nonempirical methods are very similar to those provided by the much cheaper MNDO method, both for carbon and silicon clusters. On these grounds we considered it interesting to analyze by the MNDO method the effect on the computed properties obtained, increasing the dimensions of the model clusters employed to simulate the substrate. The results reported in Table I for the clusters $C_{10}H_{15}$ and $Si_{10}H_{15}$ show that the adatom-substrate charge transfer, the chemisorption energy, and the $H_a-X(1)$ bond length are not sensitive to cluster size, whereas the obtainment of reasonable spectroscopic properties (as exemplified by the ionization potentials) demands the use of quite large model clusters. This trend is further confirmed by a STO-3G computation on the H-$C_{10}H_{15}$ system.

IV. CONCLUDING REMARKS

In this study we have used quantum-mechanical methods at different levels of sophistication in order to gain insight into the nature of chemisorption of hydrogen on the (111) surfaces of diamondlike crystals. The main results can be summarized as follows.

(i) The method of pseudopotentials gives results in excellent agreement with the available experimental data and extended basis-set all-electron computations.

(ii) Polarization functions introduce significant varia-

TABLE II. Orbital and total atomic populations for the different $(X_4H_9)H$ clusters obtained by the pseudopotential method using several basis sets. The atoms are labeled as in Fig. 1 and the basis set as in Table I, except for the dropping of the prefix PP. Δq indicates the variation of the total charge between H-X_4H_9 and X_4H_9 systems; negative values are used when the electron population is lower in the naked cluster.

	Diamond				Silicon				Germanium			
	2ζ	$2\zeta^+$	$2\zeta^{++}$	$2\zeta^*$	2ζ	$2\zeta^+$	$2\zeta^{++}$	$2\zeta^*$	2ζ	$2\zeta^+$	$2\zeta^{++}$	$2\zeta^*$
$X(1)$												
s	1.26	1.24	1.21	1.13	1.41	1.38	1.36	1.31	1.40	1.38	1.35	1.24
p	3.02	2.96	3.06	3.01	2.79	2.74	2.72	2.64	2.72	2.68	2.87	2.66
d			0.08	0.08			0.12	0.12			0.17	0.14
Tot.	4.28	4.21	4.35	4.22	4.20	4.12	4.20	4.07	4.12	4.06	4.38	4.04
Δq	−0.14	−0.08	−0.04	0.01	0.06	0.14	0.12	0.14	0.10	0.15	0.11	0.12
$X(2)$												
s	1.20	1.20	1.17	1.15	1.30	1.30	1.28	1.25	1.29	1.29	1.25	1.23
p	3.14	3.14	3.12	3.20	2.20	2.20	2.19	2.20	2.13	2.14	2.07	2.37
d				0.06				0.16				0.19
Tot.	4.34	4.34	4.29	4.40	3.49	3.50	3.47	3.61	3.42	3.43	3.32	3.79
Δq	0.02	0.02	0.00	0.00	0.03	0.02	0.00	0.00	0.03	0.01	0.00	0.00
H(1)												
s	0.88	0.88	0.88	0.86	1.15	1.15	1.15	1.12	1.17	1.17	1.18	1.06
Δq	0.00	0.00	0.00	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01
H(2)												
s	0.87	0.87	0.87	0.85	1.14	1.14	1.14	1.11	1.17	1.17	1.18	1.06
Δq	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	0.00	0.00	−0.01	0.00	0.00	0.00
H_a												
s	0.86	0.88	0.88	0.89	1.06	1.11	1.08	1.10	1.10	1.14	1.07	1.08
p		0.03	0.02	0.03		0.01	0.01	0.01		0.01	0.01	0.01
Tot.	0.86	0.91	0.90	0.92	1.06	1.12	1.09	1.11	1.10	1.15	1.08	1.09
Δq	0.14	0.08	0.10	0.08	−0.06	−0.11	−0.09	−0.11	−0.10	−0.15	−0.08	−0.09

tions in the results and their use is mandatory for quantitative predictions. However, the use of mixed basis sets shows that very reliable results are obtained, limiting the inclusion of polarization functions to the atoms directly involved in the chemisorption bond. The use of pseudopotentials and mixed basis sets is thus very promising since it would allow, in the near future, the inclusion of correlation effects at a reasonable cost.

(iii) In the case of very small clusters (X_4H_9) the MNDO method gives results in close agreement with extended basis-set nonempirical computations concerning charge-transfer and chemisorption energy, but the equilibrium $X(1)$-H_a distances are somewhat underestimated. The low computational cost of MNDO has allowed the study of quite large clusters and the demonstration that atom chemisorption on semiconductor surfaces is a local phenomenon, and only negligible changes are obtained increasing the dimensions of the model clusters.

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