THE EFFECT OF CLUSTER SIZE ON THE CHARACTERISTICS OF CHEMISORPTION IN THE MODEL GROWTH OF SILICON CRYSTALS*

Jaroslav Burda[a], Michal Bureš[b] and Čestmír Černý[b]

[a] *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6*
[b] *Department of Physical Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6*

The optimum cluster model size for the simulation of silicon crystal growth was sought by using the semiempirical CNDO/2 method. The Si_4H_9 system emerged as a reasonable compromise between the convergence of results and computation demands.

In the approach where a cluster model of the crystal is used to describe the interactions between atoms or molecules and the solid surface, small numbers of atoms are considered as representatives of the surface and the chemisorbed atom or molecule as a fictitious pseudomolecule. For this set, the wave function is determined and its properties are interpreted in substrate–adsorbate interaction terms. In models of this kind, the cluster surface can be increased by adding substrate atoms until the chemisorption properties become virtually independent of the cluster size. In practice, however, a compromise must be sought respecting the potential of the computer techniques.

The first problem emerging during the study of the cluster model is the determination of the number of substrate atoms necessary for the various properties of chemisorption to converge[1]. In cases where the interaction between substrate and adsorbate concerns few atoms of the former, it is usually sufficient to use the adjacent neighbours of the interacting cluster atom only[2]. Where this approach is applicable to actual systems, it gives relatively accurate results for the equilibrium geometry and force constants[1,3]; the energy values are rather only usable as a qualitative estimate for comparison purposes[4,5].

A next problem is associated with the existence of boundary effects appearing during the use of small-size clusters[6]. A high electron density gradient establishes on the cluster boundaries, affecting the quality of calculations[7]. Actually, these effects concern particularly metals, where electrons occupy the conductivity band and are not localized at the individual atoms. In semiconductors the boundary effects are

---

* Part I in the series Study of Silicon Crystal Surface Growth by the CNDO/2 Method.

lower, and the fixing of the cluster by hydrogen atoms causes additional reduction of these effects. The fixing is also performed for all the silicon atoms to have the sp^3 hybridization and the bonding condition to approach the crystal as closely as possible[8].

CALCULATION MODELS AND SIMULATION OF THE PROCESS OF ADSORPTION OF SiH$_3$

The silicon crystal is modelled by a substrate cluster with a variable size. A single silicon atom was considered as the simplest substrate; the SiH_3, Si_4H_9, $Si_{10}H_{15}$, $Si_{14}H_{19}$, $Si_{19}H_{27}$ and $Si_{23}H_{31}$ sets followed. The geometry in the Si_4H_9 and higher clusters corresponds to the situation observed[8,9] for the Si(111) plane.

The reaction coordinate of adsorption can be obtained by moving the SiH_3 radical towards the substrate surface. To a first approximation it is sufficient to consider the central interaction where the bond is directly formed between the silicon atoms of substrate and adsorbate. The reaction coordinate then can be regarded as a potential curve corresponding to the vibration of the Si(substrate)–Si(adsorbate) bond.

The calculation model employed was based on a constant optimized geometry of the SiH_3 radical, which was moved towards the substrate surface by the Si atom along a normal passing through the central silicon atom. The geometry of the species to be adsorbed was chosen such that, viewed from above, the silicon bonds on the trajectory straight line were mutually 60° displaced (Fig. 2a).

The model of detachment of substituents adsorbing to the silicon species was chosen similarly. Hence, these processes can be written in terms of the scheme

$$\text{substrate} + \text{SiH}_3 \quad \rightarrow \quad \text{cluster} \quad \rightarrow \quad \text{crystal} + \tfrac{3}{2}\,\text{H}_2 . \qquad (A)$$
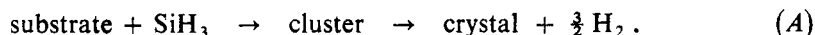
The energies of the two consecutive steps, along with the energy of interaction of the released atomic substituents of the adsorbate $(H_2$ dissociation energy$)$, provide information on the energy change of the epitaxial growth of a silicon single crystal. The energy balance of the first part of reaction (A) can be written as

$$\Delta E_{\text{int}} = E_{\text{cl}} - E_{\text{sub}} - E_{\text{ads}} , \qquad (1)$$

where ΔE_{int} is the energy of the substrate–adsorbate interaction, E_{cl} is the total energy of the cluster and E_{sub} and E_{ads} are the total energies of substrate and adsorbate, respectively.

Important for the further crystal growth is particularly the process

$$\text{cluster}\,(\text{sub–ads}) \quad \rightarrow \quad \text{crystal}\,(\text{sub–Si}) + \tfrac{3}{2}\,\text{H}_2 . \qquad (B)$$
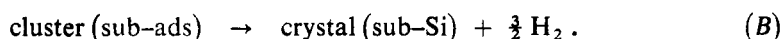
For obtaining the energy balance one has to determine the energy taken up for the detachment of the adsorbate substituents and the energies released during their

recombination,

$$H + H \rightarrow H_2 . \tag{C}$$

Decisive for whether or not the adsorbate substituents will detach and the silicon atom will be incorporated in the crystal lattice is the energy balance

$$\Delta E_g = E_{cr} + \tfrac{1}{2}E_{H_2} - E_{cl} \tag{2}$$

where ΔE_g is the energy associated with the crystal growth, E_{cl} is the total energy of the cluster, E_{cr} is the energy of the forming crystal (substrate + Si), and E_{H_2} is the dissociation energy of the substituents. If ΔE_g is negative, silicon in adsorbate can be expected to release its substituents and become part of the crystal.

CALCULATIONS AND DISCUSSION

The semiempirical CNDO/2 method[10] was applied to all the systems modelled. The bonding in the SiH$_3$ radical was first calculated based on optimization calculations for SiH$_3$; the data obtained are $d(Si—H) = 1\cdot628 . 10^{-10}$ m, $\alpha(HSiH) = 108\cdot633°$ and $E = -163\cdot800$ eV. Measurements on a silicon single crystal gave a bond length[11] of $d(Si—Si) = 2\cdot350 . 10^{-10}$ m. Based on preliminary calculations for silicon systems including optimization of the Si—Si bond, a standard internuclear distance for silicon atoms in clusters of $d(Si—Si) = 2\cdot328 . 10^{-10}$ m was adopted. The bond angles in the silicon clusters were based on the theoretical value of 109°28′, the Si—H bond length (for the cluster fixing) was $d(Si—H) = 1\cdot63 . 10^{-10}$ m. The ground energies of the clusters are given in Table I, their geometric arrangement is shown in Fig. 1.

Unlike the Si$_4$H$_9$, Si$_{10}$H$_{15}$ and Si$_{19}$H$_{27}$ clusters which simulate the situation in the first three planar layers, the Si$_{14}$H$_{19}$ and Si$_{23}$H$_{31}$ systems reach as far as the fifth layer of the silicon crystal. Moreover, in the cluster considered, the inner silicon atoms are closed in cyclic formations reminding of adamantane, which are characteristic of the diamond structure. From the true structure they only differ in the bonding in the fourth layer. This difference is a result of the above efforts to reach deeper (at least the fourth and fifth) layers of the lattice and to maintain the correct central interaction, and of the calculation compromise, i.e. the use of the lowest possible number of atoms in the cluster.

After basic information on the substrate and adsorbate was acquired, calculations of the processes could be commenced; these included the sorption of the species on the surface, and liberation of its substituents. The resulting optimized $d(Si(sub-strate)-Si(adsorbate))$ distances for modelling the process of adsorption of the SiH$_3$ radical on the crystal surface, along with the total energy, are given in the first part

of Table II. This table demonstrates the convergence of the equilibrium Si(ads)–
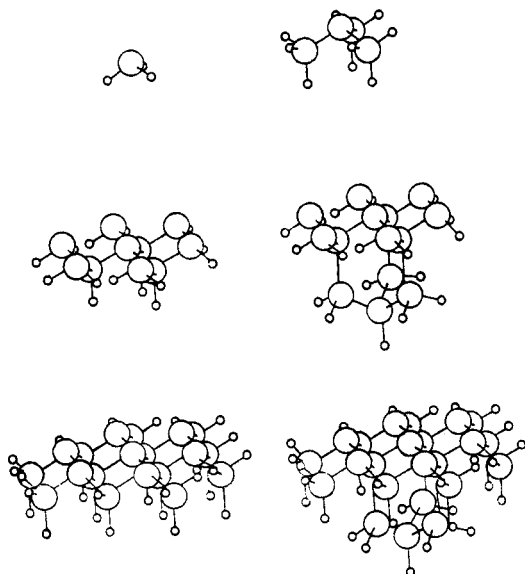–Si(sub) distance with the cluster size.

FIG. 1

Models of silicon clusters: SiH_3, Si_4H_9, $Si_{10}H_{15}$, $Si_{14}H_{19}$, $Si_{19}H_{27}$ and $Si_{23}H_{31}$
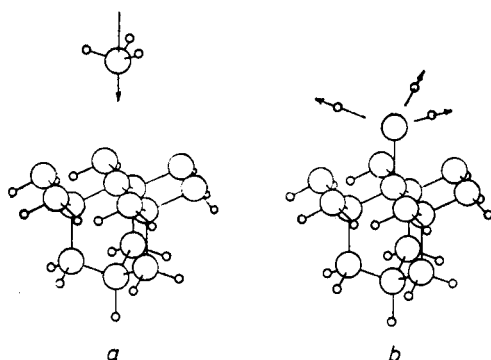

a b

FIG. 2

Trajectory of the SiH_3 radical for the simulation of the process of a sorption on the $Si_{14}H_{19}$
cluster, b crystal surface growth

TABLE I

Substrate clusters used

Cluster	Energy eV	Cluster	Energy eV
Si	$-106 \cdot 0$	$Si_{14}H_{19}$	$-1\,945 \cdot 5$
SiH_3	$-163 \cdot 8$	$Si_{19}H_{27}$	$-2\,667 \cdot 9$
Si_4H_9	$-620 \cdot 8$	$Si_{23}H_{31}$	$-3\,205 \cdot 9$
$Si_{10}H_{15}$	$-1\,406 \cdot 4$		

TABLE II

Optimized d(Si–Si) distances and total energies of the substrate–SiH_3 and substrate–Si sets

Substrate	Substrate–SiH_3		Substrate–Si	
	d^{opt} 10^{-10} m	E^{tot} eV	d^{opt} 10^{-10} m	E^{tot} eV
Si	$2 \cdot 386$	$-276 \cdot 7$	$2 \cdot 030$	$-219 \cdot 3$
SiH_3	$2 \cdot 434$	$-339 \cdot 1$	$2 \cdot 385$	$-276 \cdot 7$
Si_4H_9	$2 \cdot 446$	$-795 \cdot 4$	$2 \cdot 360$	$-733 \cdot 4$
$Si_{10}H_{15}$	$2 \cdot 444$	$-1\,580 \cdot 8$	$2 \cdot 032$	$-1\,518 \cdot 9$
$Si_{14}H_{19}$	$2 \cdot 450$	$-2\,119 \cdot 3$	$2 \cdot 271$	$-2\,057 \cdot 0$
$Si_{19}H_{27}$	$2 \cdot 444$	$-2\,842 \cdot 3$	$2 \cdot 257$	$-2\,780 \cdot 4$
$Si_{23}H_{31}$	$2 \cdot 452$	$-3\,380 \cdot 3$	$2 \cdot 273$	$-3\,318 \cdot 7$

TABLE III

Calculated energies of adsorption ΔE_{int} and energies of crystal growth ΔE_g

Substrate	ΔE_{int} kJ mol^{-1}	ΔE_g kJ mol^{-1}
Si	$-657 \cdot 3$	$-280 \cdot 3$
SiH_3	$-1\,112 \cdot 4$	$214 \cdot 0$
Si_4H_9	$-1\,038 \cdot 4$	$174 \cdot 3$
$Si_{10}H_{15}$	$-1\,020 \cdot 3$	$202 \cdot 3$
$Si_{14}H_{19}$	$-962 \cdot 2$	$203 \cdot 2$
$Si_{19}H_{27}$	$-1\,023 \cdot 3$	$170 \cdot 4$
$Si_{23}H_{31}$	$-1\,021 \cdot 1$	$144 \cdot 3$

Furthermore, the total energy of the Si–substrate system was determined for the optimum Si(atom)–Si(substrate) bond length. These sets correspond to the situation where after detachment from its substituents, a silicon atom adds to the crystal lattice (Fig. 2b). The calculated values for the clusters considered are given in the second part of Table II.

Table II demonstrates that the small substrate systems, SiH_3 and Si_4H_9, exhibit a systematic deviation in the equilibrium Si–Si(substrate) distance. The shorter distances in the remaining cluster systems are due to the other silicon atoms reacting through their lone electrons with the trapped silicon whose one electron takes part in the Si–Si(substrate) sigma bond whereas the remaining three electrons remain unbonded after releasing the substituents; a partial overlap takes place, whereupon the bond grows shorter.

The last value requisite for evaluation of the energy change in process (B) is the recombination energy for the formation of the H_2 molecule (reaction (C)). Data necessary for calculating the ΔE_g value according to Eq. (2) concern the H_2 molecule. For the optimized equilibrium distance $d(H—H) = 0.746 . 10^{-10}$ m, the computer program employed gave the total energy of $E_{H_2} = -40.126$ eV.

The final evaluation of the model reaction (A) is summarized in Table III, which includes the energies of the two processes involved for a temperature of 0 K, based on the calculations. The data demonstrate that the process of adsorption on the substrate surface brings about an appreciable decrease in the total energy of the system. Furthermore, the interaction energies give evidence of a sufficient size of the substrates chosen; transition to a considerably larger substrate system is associated with no substantial change in the quality of the data obtained. This indicates, among other things, considerable localization of the interaction: the basic properties of the sets are predicted by a cluster as small in size as SiH_3.

The convergence of the energy change in the two processes with respect to the cluster size shows how appreciably an Si atom as a cluster differs from the remaining substrate sets; the SiH_3 substrate system, although only little larger in size than the Si atom alone, provides a markedly better energy estimate owing to the better approaching bonding situation.

CONCLUSIONS

When considering a silicon atom as the substrate, the system energy values obtained are unusable even as a crude estimate. This can be explained in terms of the electron arrangement in the Si substrate being entirely different from that in actual silicon crystals. Mere fixing of this single silicon atom by means of hydrogen atoms, however, gives rise to conditions for local interaction approaching that in a real crystal. The results are also crudely indicative of the qualitative trends, although the Fock matrix rank increased by three only. Additional extension of the substrate system

to Si_4H_9 bears out the predictions made for the SiH_3 substrate. Table III gives evidence that the energy trend found for the SiH_3 and Si_4H_9 clusters can be, within the model used, considered to be qualitatively correct.

REFERENCES

1. Hermann K., Bagus P. S.: Phys. Rev., B 20 1603 (1979).
2. Schaefer H. F. III: *The Electronic Structure of Atoms and Molecules*, p. 352. Addison–Wesley Reading, Massachusetts 1972.
3. Cavell R. G., Kowalczyk S. P., Ley L., Pollak R. A., Wills B., Shirley D. A., Perry W.: Phys. Rev., B 7 5313 (1973).
4. Rowe J. E.: Surf. Sci. 53, 461 (1975).
5. Sakurai T., Hagstrum H. D.: Phys. Rev., B 12 5349 (1975).
6. Seel M., Bagus P. S.: Phys. Rev., B 23 5464 (1981).
7. Hermann K., Bagus P. S.: Phys. Rev., B 17 4082 (1978).
8. Fujiware K.: Phys. Rev., B 26 2036 (1982).
9. Kittel C.: *Úvod do fyziky pevných látek*, p. 42. Academia, Prague 1985.
10. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. McGraw Hill, New York 1970.
11. Ibach H., Rowe J. E.: Surf. Sci. 43, 481 (1974).

Translated by P. Adámek.