INTERACTIONS OF THE SiH$_x$Cl$_y$ SILICON SPECIES WITH THE Si$_4$H$_9$ CLUSTER*

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The CNDO/2 method was applied to the investigation of the surface reaction occurring during the epitaxial growth of silicon single crystals. The aim of the work was to find silicon species from which the crystal growth is possible under the reaction conditions chosen to comply with the application of the CVD technological method. Calculations suggest that the SiH$_2$, SiHCl and SiH$_3$ species are feasible for the further growth.

Silicon semiconductor platelets are conventionally manufactured by the CVD (Chemical Vapour Deposition) technique, consisting in the deposition of layers of the solid on the surface of a suitable substrate, the former arising from a heterogeneous chemical reaction of the starting gaseous substances[1].

During the deposition process, the gaseous substances in the reactor are transported from the inlet to the deposition section, where the starting substance diffuses from the bulk to the substrate surface. During the diffusion, the starting substances can react with hydrogen to give various intermediates. The solid separates on the substrate surface, and the silicon atoms released from the adsorbed species can migrate along the substrate surface until they occupy a site with an energy suitable for embedding into the crystal structure of the substrate. After the deposition, the gaseous reaction products diffuse back into the bulk and are carried in the main stream away to the reactor outlet.

The aim of the present work was to simulate the epitaxial growth of a silicon single crystal from the gas phase. Silicon species are adsorbed on the crystal surface, and after the substituents detach, the silicon atoms become part of the crystal. The choice of the species was determined by the most frequently employed deposition media — SiCl$_4$, SiCl$_2$H$_2$ or SiH$_4$ with a fraction of hydrogen. During the deposition,

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the starting substances react in the gas bulk giving rise to a plethora of silicon species. We concentrated on the following ones: SiH, SiCl, SiH$_2$, SiCl$_2$, SiHCl, SiH$_3$, SiH$_2$Cl, SiHCl$_2$ and SiCl$_3$.

EPITAXIAL GROWTH MODEL

The crystal is modelled by a cluster with a variable size. Previous calculations have indicated[2] that Si$_4$H$_9$ is a reasonable compromise between the computer time demands and the convergence properties of clusters in dependence on their size. Results for the SiH$_3$ cluster are also given for a comparison. The geometric situation in the Si$_4$H$_9$ cluster corresponds to that found[3,4] for the Si(111) crystal plane.

The treatment is based on the chemisorption process model described previously[2]. The mechanism is divided into two consecutive processes, viz. adsorption on the substrate surface, and detachment of substituents (X, Y):

$$\text{substrate} + \text{adsorbate} \rightarrow \text{cluster} \rightarrow \text{crystal} + \text{XY}. \qquad (A)$$
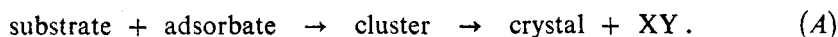
The energy balance of the first part of the process can be expressed by the relation

$$\Delta E_{int} = E_{cl} - E_{ads} - E_{sub} + \Delta E^{dang}, \qquad (1a)$$

where ΔE_{int} is the energy associated with the particle adsorption on an active centre of the substrate, E_{cl} is the total energy of the cluster, E_{ads} and E_{sub} are the energies of the adsorbing particle and of substrate, respectively, and ΔE^{dang} is an additional correction with respect to the adsorption process model employed. Whether or not the adsorbate substituents will detach and the silicon atom embed into the crystal structure is determined by the energy balance

$$\Delta E_g = E_{cr} + E_{XY} - E_{cl}, \qquad (1b)$$

where ΔE_g is the energy determining the substrate growth, E_{cr} is the energy of the growing crystal (substrate + Si), and E_{XY} is the dissociation energy of the adsorbate substituents.

The energies of the silicon systems were calculated by using the semiempirical CNDO quantum-chemical method[5] in version 2 with parametrization by Pople, Seagal and Santry.

RESULTS AND DISCUSSION

First, the bonding in the adsorbed silicon species was determined based on optimization calculation. The optimum Si—H bond length for the SiH$_4$ molecule was found to be $d(\text{Si—H}) = 1\cdot616 \cdot 10^{-10}$ m, which differs slightly from the experimental

value[6] of $1.4789(4) . 10^{-10}$ m. The CNDO/2 ground energy difference for the two bond lengths is -108 kJ mol^{-1}.

All silicon species employed in the cluster model as adsorbents were optimized by the CNDO/2 method. The parameters of the substrate sets, their geometries and energies were taken from ref.[2].

The next step was the determination of the reaction coordinate of adsorption of the species on the cluster. As in the preceding work, the model adopted involved the gradual approach towards the substrate surface along a normal intersecting the substrate in the site where the central silicon atom is located. The geometrical arrangement of the adsorbing species was regarded constant during the adsorption, the Si atom being oriented towards the substrate; the σ-bonds of the SiH and SiCl species were parallel to the trajectory, whereas the triangular SiH$_2$, SiHCl and SiCl$_2$ species were so oriented that the trajectory passed through the X—Si—Y angle and, viewed in the direction of the trajectory, the Si—X σ-bond (in the case of SiHCl, the Si—H bond for energy reasons) eclipsed the substrate Si—Si bond. The orientation of the trisubstituted species was chosen such that in the direction of the normal the bonds of the central and approaching silicon atoms were $60°$ displaced and the straight line of the trajectory coincided with the axis of the SiXYZ pyramid. The resulting parameters for the adsorption of the species on the surface are summarized in Table I.

The moving of the SiX and SiXY species towards the substrate surface was considered such that the adsorbate atoms formed a straight line perpendicular to the

TABLE I

Optimized Si—Si distance of the particle from the cluster surface and the energy of adsorption

Species	SiH$_3$		Si$_4$H$_9$	
	d^{opt} 10^{-10} m	E^{tot} eV	d^{opt} 10^{-10} m	E^{tot} eV
SiH	2·382	−297·0	2·375	−753·2
SiCl	2·358	−728·9	2·374	−1 185·1
SiH$_2$	2·374	−315·9	2·380	−772·2
SiHCl	2·379	−748·0	2·399	−1 204·3
SiCl$_2$	2·382	−1 180·1	2·384	−1 636·4
SiH$_3$	2·434	−339·1	2·446	−795·4
SiH$_2$Cl	2·438	−771·1	2·450	−1 227·4
SiHCl$_2$	2·443	−1 203·0	2·447	−1 659·4
SiCl$_3$	2·448	−1 635·0	2·450	−2 091·4
Si	2·385	−276·7	2·360	−733·4

cluster surface and apexes of a triangle whose plane was perpendicular to the substrate plane, respectively. These configurations are consistent with the sp and sp^2 hybridization geometries, respectively, but not with the bonding angles of adsorbed silicon in the newly formed pseudomolecule. Therefore, additional correction ΔE^{dang} was introduced to account for the transition from the planar state to the sp^3 hybridization (Fig. 1).

Data of Table II document that in the case studied, sp^3 hybridization really is energetically more convenient than sp or sp^2 hybridization. The table includes the total energies of the cluster–SiH, cluster–SiCl, cluster–SiH$_2$, cluster–SiHCl and cluster–SiCl$_2$ systems against the optimized Si—Si—X or Si—Si—m angle (the

TABLE II

Energy corrections ΔE^{dang} for the tilting of the SiX and SiXY species with respect to the cluster surface. The correction is defined as $\Delta E^{\text{dang}} = E(\alpha_{\text{opt}}) - E(180°)$

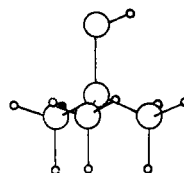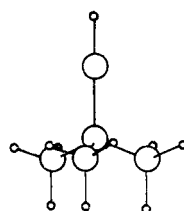| Species	α_{opt} deg	ΔE^{dang}, eV	
		SiH$_3$	Si$_4$H$_9$
SiH	100	−2·210	−2·581
SiCl	105	−2·641	−3·103
SiH$_2$	135	−0·303	−0·466
SiHCl	135	−0·409	−0·601
SiCl$_2$	135	−0·539	−0·734

FIG. 1

The optimized Si(Si$_3$H$_9$)—Si distance corrected for the actual $sp \rightarrow sp^3$ hybridization (associated with additional decrease in the total energy system)

symbol Si—m stands for the median of the SiXY triangle), assuming that the Si—H (Si—Cl) distances and X—Si—Y angles did not change with respect to the optimized values for the species themselves. Table II demonstrates that the CNDO/2 method correctly predicts the establishing of geometries roughly corresponding to the sp^3 hybridization. For SiX, the Si—Si—X angle is 100 to 105°, hence, somewhat lower than the theoretical 109°28′. For the tilting of the SiXY species, Table II gives an optimum departure of the SiXY triangle from the initial adsorption plane of 45 to 50°, which implies the Si—Si—X(Y) angle within the range of 115 to 118°. This is a value higher than as corresponds to sp^3 hybridization, but since the initial optimized X—Si—Y angle is, on the other hand, lower than 100°, the lone electron pairs of the Si atom in the species under consideration can be assumed to be more diffuse than the bonding electrons.

Furthermore, the reaction coordinate of interaction of the adsorbate silicon atom with the substrate (Si–sub) was determined. These sets represent a situation where the silicon atom, after detaching from its substituents, attaches to the crystal lattice. Having been given in detail in ref.[2], the values are only included in the last row of Table I to facilitate orientation in the results. The last quantity requisite for evaluation of process (A) is the recombination energy E_{XY} in Eq. (1). Only three reactions during which molecules of H_2, Cl_2 and HCl are formed are conceivable.

Due to the inaccurate prediction of the heats of dissociation provided by the CNDO/2 method, the following energy balances use, within the calculation consistency, energies for the recombination of adsorbate substituents to molecules of hydrogen and chlorine only (in the corresponding stoichiometric ratios).

TABLE III

Final changes in energies for the process of interaction of silicon species with the substrate surface

Species	Adsorption on SiH_3		Adsorption on Si_4H_9	
	ΔE_{int} kJ mol^{-1}	ΔE_g kJ mol^{-1}	ΔE_{int} kJ mol^{-1}	ΔE_g kJ mol^{-1}
SiH	$-1\ 209{\cdot}8$	$241{\cdot}4$	$-1\ 161{\cdot}4$	$228{\cdot}3$
SiCl	$-1\ 159{\cdot}6$	$434{\cdot}2$	$-1\ 117{\cdot}5$	$426{\cdot}4$
SiH$_2$	$-515{\cdot}1$	$-56{\cdot}1$	$-456{\cdot}9$	$-80{\cdot}1$
SiHCl	$-487{\cdot}5$	$129{\cdot}6$	$-432{\cdot}7$	$109{\cdot}0$
SiCl$_2$	$-459{\cdot}2$	$313{\cdot}3$	$-405{\cdot}6$	$294{\cdot}0$
SiH$_3$	$-1\ 112{\cdot}4$	$214{\cdot}0$	$-1\ 038{\cdot}4$	$174{\cdot}3$
SiH$_2$Cl	$-1\ 075{\cdot}2$	$374{\cdot}5$	$-1\ 003{\cdot}7$	$337{\cdot}2$
SiHCl$_2$	$-1\ 044{\cdot}5$	$535{\cdot}5$	$-975{\cdot}2$	$500{\cdot}5$
SiCl$_3$	$-1\ 017{\cdot}1$	$696{\cdot}6$	$-949{\cdot}5$	$663{\cdot}6$

The values given in Tables I and II were employed to calculate the energy changes in the processes described by reaction (A). The resulting energy balances of the processes of adsorption and growth are summarized in Table III. The data indicate that the process of adsorption on the substrate surface is associated with an appreciable decrease in the total energy of the system. Comparison of the ΔE_{int} values for the various groups demonstrates that the energy of adsorption of the SiXY species is about one-half with respect to the SiX and SiXYZ systems. This can be explained in terms of the SiXY species having even numbers of electrons in closed shells, so that the resulting state is a singlet one; the SiX and SiXYZ systems, on the other hand, have one unpaired electron in the SOMO (Single Occupied Molecular Orbital), hence, the species are in the doublet state and thus chemically more reactive.

It is possible to assess which of the species treated are low stable and can release the silicon atom on the substrate surface. Basically, it can be predicted that crystal growth may take place from the SiH_2 species. The SiHCl and SiH_3 species are also conceivable, their ΔE_g energy being relatively low $(\Delta E_g < 200 \text{ kJ mol}^{-1})$; detailed description, however, would also require kinetic factors to be taken into account.

CONCLUSIONS

Despite the considerable simplicity of the semiempirical CNDO/2 quantum-chemical method (chosen to cope with computation problems) and of the models employed for the description of the elementary phenomena, the results obtained correlate significantly with the experimental facts; it can be inferred that for the further crystal growth, silicon atoms will be probably released from the SiH_2 species and perhaps also from the SiHCl and SiH_3 species.

The other systems studied may only adsorb on the pure surface of the growing crystal. Another phenomenon is also conceivable, although it was not addressed for the complexity of its treatment, viz. mutual interaction of the various species either in the gas phase or on the crystal surface. Investigation into this problem would require an approach more accurate than as can be achieved with the CNDO/2 method. Probably, *ab initio* calculations would have to be used with a sufficiently good base, at least $6-31$ G, augmented with the calculation of the correlation energy. The existence of such interactions particularly at so high temperatures (1 000 to 1 500 K) has been indicated by extensive experimental work[7,8].

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