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Catalytic effect of carbon in shaping Si(1 1 1) surfaces

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Abstract

This paper presents an experimental and theoretical study of the effect of carbon in the formation of pits on silicon surfaces. Experimentally we have searched for the best conditions to produce a homogeneous density of single shape pits in Si(1 1 1) using a C_2H_4 source. The result is that two steps are required: a rapid "precursor" process at relatively low temperature and high gas pressure and a longer "etching" step at higher temperature and lower gas pressure. Pits obtained with the two step process have a triangular shape that is not only due to the surface symmetry but also to the presence of carbon. In fact, we have found that the holes still remain after complete carbon removal by further annealing, but their shape becomes circular.

Motivated by these experimental results we investigated theoretically the beginning of the pit formation mechanism using a tight binding method. We have performed two types of calculations: structural optimization of Si slabs containing carbon at 0 K and high temperature molecular dynamics simulations. We have found that carbon atoms prefer to occupy substitutional sites near the surface rather than adsorbed or interstitial sites. Their presence weakens some Si–Si bonds near the surface and therefore induces surface silicon atoms to move away from their equilibrium position and to diffuse on the surface. This may start the pit formation. We have also found that there is an attractive interaction between substituted carbon atoms and surface vacancy clusters, which must certainly influence the pit growth.
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1. Introduction

In recent years there have been many experimental works studying the interaction of carbon atoms with silicon surfaces. Their aim has been twofold: either to eliminate carbon contamination [1,2] or to obtain size and shape controlled SiC structures on silicon [3–9]. In this work we show that a precisely controlled C gas source may provide a new method to shape the Si surfaces. The C

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atoms act catalytically, as they can be removed later, making the process a simple and cheap way to structure Si surfaces.

Previous studies have already reported that regular shape etch pits are obtained on Si surfaces by reaction with different carbon sources. For example, in 1985 Ishikawa et al. [1] obtained them by annealing a carbon contaminated sample at 900 °C. In 1990 Yang and Williams [2] observed etch pits in different silicon surfaces when carbon was deposited by desorption from the vacuum chamber walls. In 1999 Pacheco et al. [3] used propane (C_3H_8) as gas source and obtained a thin SiC film. Triangular and square voids appeared on Si(1 1 1) and Si(0 0 1), respectively, corresponding to the different surface symmetries. Some other works have used pyrolitic graphite as a solid carbon source, which is evaporated by electron beams [10,11].

Most of the works that produce SiC thin films use either C_2H_2 or C_2H_4 gas as carbon source. These experiments indicate that the molecules dissociate, leaving only atomic carbon on the surface [4–9]. De Crescenzi et al. [9] have shown that crystalline SiC can be pseudomorphically grown on Si(1 1 1) when the substrate temperature is between 600 and 700 °C, while at higher temperatures a carbonization process occurs with carbon atoms also occupying non-substitutional sites.

In spite of the large amount of experimental work, the atomistic mechanisms involved in each experiment are not completely understood. In the case of a molecular gas source this implies several processes: the surface mediated dissociation of the molecule, the carbon migration, the hydrogen desorption, and the carbon incorporation. Many ab initio calculations have been performed to study the energetics of C adsorption versus incorporation in near surface sites. Most of them were performed for the (0 0 1) orientation [12–18] and they all agree that carbon atoms prefer to be substituted rather than adsorbed, although they differ in which is the best substitutional site. Very recently, the interaction with the (1 1 1) surface has also been studied theoretically [19].

The purpose of this work is to understand the etch pit formation mechanism on the Si surfaces, both from the experimental and the theoretical point of view.

2. Experimental setup

Using C_2H_4 gas as carbon source, the best conditions to produce well defined holes of controlled size and shape on Si(1 1 1), have been systematically searched for. Experiments have been performed in an ultra high vacuum chamber, the sample being a small piece ($20\times2\times0.3$ mm^3) of a silicon (1 1 1) wafer. After ex situ cleaning in ethanol and hot acetone the sample is flashed in situ (under 10^{-10} Torr) by heating at 1250 °C and then annealed at 1150 °C for 1 h, in this way large atomic flat areas are obtained. A direct current of about 2–3 Å and a voltage of around 6–7 V are used in the heating process. High purity C_2H_4 is then introduced in the ultra high vacuum chamber by a controlled leak system. The doses can be controlled varying the gas partial pressure (between 10^{-9} and 10^{-6} Torr) or the exposure time. The sample is later studied ex situ at room temperature using optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

3. Method of simulation

In order to simulate the atomic scale processes involved in the experiment described above we have used a 12 layer Si slab with a two dimensional unit cell of 16 atoms per layer to represent the Si surface. C atoms are initially deposited in different sites of this slab and periodic boundary conditions in the directions parallel to the surface are applied. The Si–Si, Si–C and C–C interactions are described using a density functional based non-orthogonal tight binding Hamiltonian. In this model the Hamiltonian and overlap matrix elements are obtained from pseudo-atomic orbitals as a function of distance. Although only a minimal basis set is used, the method has been proved to be transferable, giving good results for clusters, surfaces and solids [20,21]. It uses only two center integrals and calculates the total energy as the sum of a band-structure term and a repulsive term, this last one being parameterized with experimental information. When performing the dynamical simulations at finite temperatures or obtaining the relaxed equilibrium structures, the atoms are moved according to the Hellmann–Feynmann forces and the equations of motion are integrated using Verlet's algorithm. Kinetic processes are studied by constant temperature molecular dynamics using a Berendsen's thermostat [22], each simulation run being about 10 ps long.

The relative stability of substitutional, adsorbed and interstitial carbon has been investigated by structural optimizations using successive quenches and simulated annealing, starting from different initial configurations. The bond orders or off-diagonal elements of the Mulliken Overlap Population Matrix, which are proportional to the bond strength between different atoms [23], are calculated for the optimized structures. Calculations for systems having different number of carbon atoms require some approximation concerning the carbon chemical potential but calculations for systems with the same number of carbon atoms are independent of this parameter. The adsorption or inclusion energies of C are calculated using as reference system the 192 atoms slab of Si and as chemical potentials the cohesive energies of Si and C in the diamond structure. If $E(M,N)$ is the total energy of a slab with M silicon atoms and N carbon atoms the formation energy of the slab with carbon is

$$E = E(M,N) - E(192,0) - (M-192)\mu_{\mathrm{Si}} - N\mu_{\mathrm{C}} \tag{1}$$

4. Results

4.1. Experimental results

Table 1 lists some of the different experimental conditions investigated. We describe them so as to indicate how we arrived at the final procedure. In case (I) the surface was exposed to the gas during a long time and at a high temperature. Pits did not appear, and the surface ended up covered by a C film. In case (II) a short "precursor" treatment at low temperature and high pressure [5] was followed by annealing at high temperature and ultra high vacuum (UHV) but again no pits were formed. These results suggested that more steps of gas exposure might be necessary to obtain a homogeneous density of single shape and similar size pits, and the results may depend on either the temperature or the gas pressure at the precursor stage. To test these hypothesis we considered situations (III)–(V). We noticed that while in (III) only irregular shaped pits were formed, in (IV) and (V) triangular pits were formed. Therefore we concluded that when a rapid precursor process at low temperature (either above or below the 7×7 to 1×1 transition temperature (830 °C)) and relatively high pressure is followed by a longer etching step at higher temperature and lower pressure, regular shaped pits can be successfully obtained. Figs. 1 and 2 show the images of case (V) obtained by optical microscopy and SEM, respectively. We

Table 1
Representative cases in the systematic search of experimental conditions to obtain regular shaped pits on Si(1 1 1)

Case	(I)	(II)	(III)	(IV)	(V)	(VI)	(Fig. 3(b))
T (°C)		700	900	880	700	700	700
P (10^{-6} Torr)		1	0.01	1	1	1	1
Time (sec)		30	30	30	30	30	30
T (°C)	1000		1000	1000	1000	1000	1000
P (10^{-8} Torr)	6		5	6	5	6	5
Time (h)	5		4	4	21	3	4
T (°C)		1130				1130	1250
P (10^{-10} Torr)		1				1	1
Time (h)		13				7	2

The first three lines are the temperature, C_2H_4 gas pressure and exposure time of the "precursor" step, the fourth to sixth lines correspond to the "etching" step and the last three lines to the final UHV "annealing".

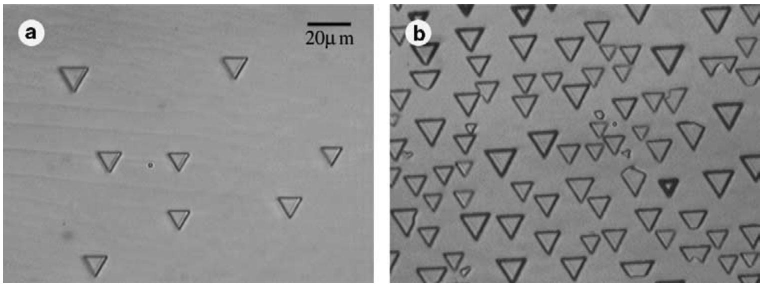

Fig. 1. Optical microscopy images of (a) case (V) and (b) case (VI) described in Table 1.

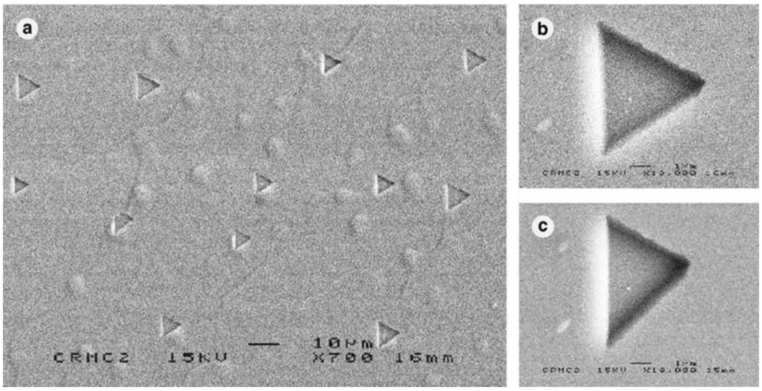

Fig. 2. SEM image of (a) case (V) in Table 1, (b) a single pit (top view) and (c) the same pit tilted 30°. The horizontal size of the images are 200 and 14 μm, respectively.

see in Fig. 2 that the pits are rather flat, their outline is triangular in the three ⟨1 1 0⟩ directions with {1 1 1} facets at the bottom and limited at the edge by three facets which have been indexed by SEM and AFM. One pit is further observed by SEM under two azimuths: top view and tilted. At a tilt angle of 30°, one facet is observed on side view proving that this facet is {1 1 3} in agreement with the observations of Ref. [2]. This has been confirmed by AFM, where a scan in the ⟨1 1 2⟩ direction, perpendicular to the side facet, allows to measure an angle of around 30° in comparison with the mean orientation of the sample. The pit depth is about 0.5 μm.

The polyhedral holes observed have sizes between 4 and 6 μm and their density is about 10^5 pits/cm^2. We have found that in order to increase the pit density, keeping a homogeneous distribution, further annealing is required. In fact, in case (VI) annealing under UHV at 1130 °C during 7 h was performed and the density of pits increased by an order of magnitude. This is shown in Fig. 1.

In the SEM image of Fig. 2 we observe bunches of monoatomic steps forming mounds of circular shape between the pits. One of these is shown in Fig. 3(a) using AFM. We believe that these mounds are formed by Si atoms pushed out of their equilibrium positions by C atoms, as their shape is close to that of an equilibrium thin flat *pancake* of pure silicon at 1000 °C (see Ref. [24]).

We wish to emphasize that the polygonal shape of the pits is related to carbon incorporation. In fact, carbon can be completely removed by annealing during 2 h at 1250 °C and the pits become circular. They are surrounded by a flange, the outside of which is quite similar to that of the mounds (see Fig. 3(b)). It is also interesting to note that the bottom of the pit (the {1 1 1} facet) does not present any circular step, in contrast to the positive mound in Fig. 3(a). If no nucleation of

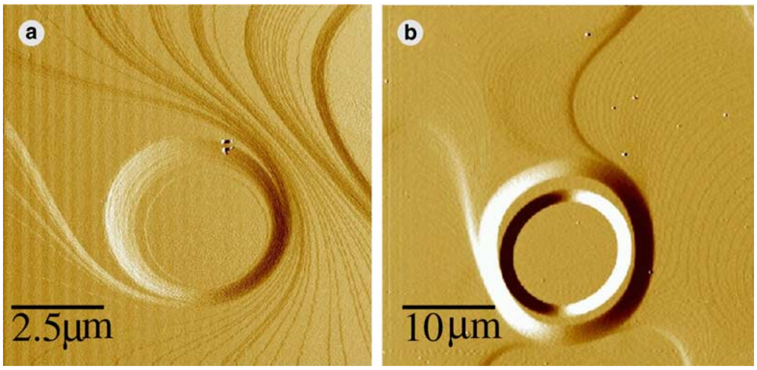

Fig. 3. (a) AFM image of a Si mound. The diameter is about 5 µm, the height 60 Å, the left edge angle 0.6° and the right one 2°. (b) AFM image of a circular pit (after C removal). The diameter is about 10 µm, the depth 0.14 µm and the internal angle between 7° and 8°.

new terraces takes place, the bottom facet remains perfectly flat, and this has been used to obtain very flat Si(1 1 1) surfaces on a large scale (100 µm × 50 µm) [25].

4.2. Simulation results

The previously described experimental results are performed only on Si(1 1 1). However, to be able to compare our results with previous calculations we have simulated both Si(0 0 1) and Si(1 1 1). Buckled dimers are present in the Si(0 0 1) surfaces but no reconstruction is considered in Si(1 1 1) as the pits are observed for two "precursor" temperatures, one above and one below the transition temperature to the 7×7 structure (see Table 1).

Because the experimental evidence is that the C_2H_4 molecule dissociates at the surface [4–9], leaving only atomic carbon on it we shall limit our calculations to this situation. Moreover, some previous and the present calculations show that while single C atoms interact strongly with silicon surfaces if a C_2 molecule is formed it desorbs quickly. Therefore, in the following our discussion will be concerned only with deposited single C atoms. Within these hypothesis we proceed along two lines: in the first one we study the very first stages of pit formation following the path of a carbon atom when it is deposited on a Si surface, using molecular dynamics at high temperature. In the second one we assume the existence of clusters of surface vacancies, arranged in a way consistent with the surface geometry, and calculate the equilibrium energy and the bond orders for carbon atoms in different positions in the slab. This allows us to estimate the interaction of C atoms with the vacancies and to infer the way these holes may grow.

4.2.1. First stages of pit formation: dynamics of C atoms in perfect Si slabs

To study the very first stages of pit formation we perform molecular dynamics simulations at high temperature ($T = 927$ °C and $T = 1227$ °C) for one adsorbed carbon atom on Si(1 1 1) and Si(0 0 1). We find that in all cases the C atom becomes substitutional in the first layers practically without diffusion. It pushes one Si atom to an adsorbed position, from which it can diffuse on the surface. This clearly shows that the diffusion barriers for C on Si(1 1 1) and Si(0 0 1) are higher than those for Si atoms. In all our simulations on Si(1 1 1) at 927 °C the carbon atom becomes substitutional in the first layer but at 1227 °C it often arrives at the subsurface layer. We believe that if the temperature or the simulation time were increased the probability of the C atoms to penetrate further in the silicon slab would also increase.

To find the preferential positions for C atoms in a slab we have calculated the energy of some high symmetry adsorption and interstitial sites as well

Table 2
Different configurations studied by 0 K energy relaxation for the Si(1 1 1) surface

Configuration	Si(1 1 1) slab		
	M	*N*	*E* (eV)
Substitutional in layer 1	191	1	0.8
Substitutional in layer 2	191	1	0.5
Substitutional in layer 3	191	1	1.3
Substitutional in layer 4	191	1	1.2
Adsorbed	192	1	2.5
Interstitial between layers 2 and 3	192	1	4.7
Tri-vacancy	189	0	1.5
Tri-vacancy + 1C in layer 1	188	1	1.4 (near) 2.2 (far)
Tri-vacancy + 1C in layer 4	188	1	1.5 (near) 2.6 (far)
Four-vacancy	188	0	1.4
Four-vacancy + 1C in layer 3	187	1	2.1 (near) 2.9 (far)

E is the energy calculated according to Eq. (1), *M* and *N* denote number of Si and C atoms in the slab. In the case of one substitutional carbon in presence of surface vacancy clusters the two energy values correspond to one substitutional carbon being: (near) as close as possible to and (far) far from the vacancies.

Table 3
Different configurations studied by 0 K energy relaxation for the Si(0 0 1) surface

Configuration	Si(0 0 1) slab		
	M	*N*	*E* (eV)
Substitutional in layer 1	191	1	0.8
Substitutional in layer 2	191	1	0.6
Substitutional in layer 3	191	1	0.7
Substitutional in layer 4	191	1	0.8
Adsorbed	192	1	1.8 (over dimer) 2.4 (far)
Interstitial between layers 1 and 2	192	1	1.4
Missing dimer	190	0	0.1
Missing dimer + 1C in layer 1	189	1	1.6 (near) 1.4 (far)
Missing dimer + 1C in layer 2	189	1	1.4 (near) 0.8 (far)
Missing dimer + 1C in layer 3	189	1	1.0 (near) 0.7 (far)
Missing dimer + 1C in layer 4	189	1	0.7 (near) 1.0 (far)

E is the energy calculated according to Eq. (1), *M* and *N* denote number of Si and C atoms in the slab. In the case of one substitutional carbon in presence of a missing dimer the two energy values correspond to one substitutional carbon being: (near) as close as possible to and (far) far from the vacancies.

as the substitutional sites, for both Si(1 1 1) and Si(0 0 1) slabs. Tables 2 and 3 show the results obtained.

The energy values are given with only 0.1 eV precision, as the different simulated annealings lead to minima that differ by this amount. It is clear that systems with one substitutional carbon atom have lower energy than those with one adsorbed or interstitial carbon, the best site being in the second layer for Si(1 1 1) and in the second (or third) for Si(0 0 1) [12–18]. It must be recalled that Si(1 1 1) presents bilayers, so that the first and second layers are close to each other, while the third one is much further away. When more than one Si atom is replaced by C in the Si(1 1 1) unit cell, the best configuration is a local SiC structure in the subsurface layer, that is, carbons not being nearest neighbors of one another.

Tight binding calculations not only give total energies but also provide information on the electronic structure, such as charge transfers and bond orders. Charge transfers are usually overestimated if the calculation does not include self-consistency, but their relative values are quite reliable. Electronic charge is transferred from Si to C and from the bulk to the surface atoms. In the buckled Si(0 0 1) surface dimers it is transferred from the lower to the higher atom. Bond orders, being indicative of bond strengths, can show some possible paths for bond breaking and subsequent pit formation. For example, in Si(0 0 1) the lowest energy configuration for two carbon atoms is when they replace a surface dimer [12]. However, when two substitutional carbon atoms are first neighbors in the surface of a silicon slab the equilibrium structure is such that their bond order is large, about 1.2 as if a C_2 molecule was formed, while the bond orders of each C atom with its other neighbors decreases with respect to that of a single substituted carbon (from 0.40 to 0.36). This result predicts what in fact happens in the high temperature simulations, the carbon dimer desorbs easily and leaves a surface dimer vacancy. This may be one possible starting process for hole formation.

The bond order between Si atoms in bulk silicon and in slabs is about 0.5 within this method of calculation. A carbon atom substituted in the silicon slab has a smaller bond order with its neighbor silicon atoms, on the average 0.4. This is different from bulk SiC, where the interatomic distances are smaller and therefore the bond orders are larger. A carbon atom substituted in the third or fourth layer of Si(0 0 1) weakens the bonding of a surface dimer close to it (from 0.5 to 0.4) keeping however the reconstruction c(4×2) and the dimer buckling. A carbon atom substituted in third or fourth layer of Si(1 1 1) weakens one or two bonds between surface and subsurface silicon atoms. This suggests a second possible mechanism for pit formation: a weak bond breaks up and leaves a surface vacancy and a mobile silicon atom on the surface. This one may end up in a mound.

4.2.2. Interaction of substituted C atoms with surface cluster vacancies: pit stability and growth

In this section we show, using 0 K energy calculations, that the interaction between surface vacancy clusters and nearby substituted carbon atoms is attractive. This happens both for Si(1 1 1) and Si(0 0 1) slabs but it is much more pronounced for Si(1 1 1). It is therefore energetically favorable to produce surface vacancies when the slab has carbon already incorporated. We have only studied the configurations suggested by symmetry, that is, the surface dimer vacancy in Si(0 0 1), as in [26], and triangular vacancy clusters on the surface of Si(1 1 1). These are of two types, either they have a second layer atom in the center of the triangle, in which case the cluster vacancy considered was of four atoms, or it does not have it and the cluster vacancy considered was of three atoms. Only a single carbon atom was substituted in different places of the unit cell.

In this calculation we compare the energy of a 192 atom slab without vacancies with that of the slab with the vacancies, in both cases with and without one substitutional carbon atom. The result is obviously independent of the chemical potentials, but the numerical value depends on the cell size. For the three vacancy cluster on Si(1 1 1) the more symmetric position in the fourth layer is almost degenerated with that of a neighbor site in the first layer and the formation energy of the triangular cluster of vacancies is appreciably reduced when a carbon atom is in one of those positions.

The lowest energy configuration for a carbon atom substituted in a Si(0 0 1) slab with a surface dimer vacancy is in the fourth layer, symmetrically located below the vacancy, as was also reported in [26]. The formation energy of a dimer vacancy is very small and it remains the same under carbon incorporation, within the error of our calculations.

Bond order analysis for Si(1 1 1) shows that with three vacancies one third of the bonds between surface and subsurface atoms in the unit cell change their bond order from 0.5 to 0.4, but not in a symmetric pattern. However, if a carbon atom is present in the fourth layer more bond orders decrease and they do so in a very symmetric way. Also, the bond orders between the second and third layer are further reduced, to 0.36.

For Si(0 0 1) the presence of a dimer vacancy weakens the bonding of neighbor dimers in the same row and also their interaction with second layer atoms. Substituted carbon atoms enhance these effects.

5. Discussion and conclusions

The experimental conditions that produce a homogeneous density of pits in Si(1 1 1) of the same size and shape, using a C_2H_4 source, have been found. These consist of a rapid “precursor” process and a second longer “etching” step. The pit density can be after increased, keeping a homogeneous distribution, by subsequent annealing at ultra high vacuum and high temperature. The pits have a triangular shape that is not only due to the surface symmetry but also to the presence of C, as when carbon is removed by further annealing they become circular.

From these experimental results and those in Ref. [5], the following mechanisms involved in the reaction of C atoms with Si surfaces can be inferred. If the molecule C_2H_4 is adsorbed on silicon at temperatures between 700 and 900 °C it dissociates and leaves single carbon atoms deposited on the surface. At lower temperatures the molecule does not dissociate and at higher temperatures a C film is formed. Those single carbon atoms on the silicon surface initiate the formation of etch pits, that increase in size if carbon is supplied continuously and if the temperature is high enough for silicon atoms to diffuse easily on the surface. In fact, the pits grow when silicon atoms are removed, diffuse on the surface and end up forming mounds, probably near surface defects. At very high temperature (1250 °C) carbon disappears from the vicinity of the surface, probably by dissolution in the bulk, and the pits change their shape, which becomes close to the equilibrium shape of a Si hole at the same temperature.

Using a tight binding molecular dynamics method we have performed numerical simulations in order to confirm the previously suggested mechanisms. Only the very beginning of the pit formation process was studied, as the size of the experimental pits is outside our computational possibilities. Calculations at finite temperatures show that an adsorbed C atom has a higher probability to incorporate in the substrate than to diffuse on the surface. If another adsorbed carbon atom comes close to the previously substituted one they tend to form a molecule and desorbs, thus starting the formation of a hole. At high enough temperatures the C atoms move to subsurface sites, and our calculations show that for Si(1 1 1) the second layer is energetically preferred. However, to maximize the configurational entropy, the atoms will penetrate further into the bulk and in this case the bond order analysis shows that some Si–Si bonds on the surface become weaker. These have a large probability of breaking, thus producing more pits and mounds.

Energy calculations at 0 K prove that it is easier to form a small surface vacancy cluster in Si(1 1 1) if there is a substituted carbon atom close to it. Also, because C atoms are attracted by surface vacancies they will tend to introduce themselves into the subsurface layers close to the pits and if a C atom arrives to the third or fourth layer due to thermal energy the probability of formation of vacancy clusters nearby will be enhanced. The calculations have been performed for very small vacancy clusters, not comparable in size to the experimental pits, but the bond order analysis allows us to infer possible growth mechanisms, as bonds are weakened symmetrically around the carbon-vacancy cluster structure.

The possibility that carbon incorporation could induce a new type of surface reconstruction [19,27], was not considered, but we believe that the same mechanisms are involved in such reconstruction and in the pit formation: i.e. the C substitution, induced Si–Si bond breaking and Si adsorption on the surface.

The C etching of Si and the elimination of C by annealing can be a simple and cheap way, in comparison with usual lithography, to shape the silicon surface.

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