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Carbon-induced reconstructions on Si(111) investigated by RHEED and molecular dynamics

C. Koitzsch[a,*], D. Conrad[b], K. Scheerschmidt[b], F. Scharmann[c],
P. Maslarski[c], J. Pezoldt[c]

[a]*Institut of Physics, Universite de Fribourg, Perolles, CH-1700 Fribourg, Switzerland*
[b]*Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany*
[c]*Institut of Solid State Physics, Technische Universität Ilmenau, D-98684 Ilmenau, Germany*

Abstract

The adsorption of carbon trimers on Si(1 1 1) 1 × 1 is investigated by means of empirical molecular dynamics based on a Tersoff potential. A priori unknown carbon terminated Si(1 1 1) surfaces are modeled. The energetics of different adsorption sites, specifically the S5, T4 and H3 sites are investigated. The obtained structural models are used to simulate their response to a RHEED experiment. This enables us to further elucidate on the feasibility of the models by comparing theoretical data to in situ RHEED observations during the MBE experiments. Implications of the models to growth of 3C SiC by carbonization are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

SiC received increasing attention due to its attractive properties for electronic applications [1]. An interesting material inherent property is the occurrence of more than 220 different polytypes. The most prominent ones are the wurtzite type hexagonal phase and their various stacking sequences and the cubic zincblende structure. So far bulk single crystals of the 6H, 4H polytype are commercially available, the cubic phase in contrast can only be obtained as epitaxial thin film on a compliant substrate. Especially growth of 3C SiC on silicon, and hence the incorporation into current silicon technology would be desirable from a processing standpoint. Unfortunately the prerequisite for that, the high quality epitaxial growth of 3C SiC on silicon has remained an experimental challenge so far. The state-of-the-art method for chemical vapor deposition of 3C SiC on silicon is a two-step technique, where first an ultrathin film is obtained by carbonization and subsequently a film is grown by standard CVD. Apparently functionality and structure of the carbonized seed layer is not fully resolved yet. From this point of view the understanding of the silicon carbon interaction is of crucial importance for the investigation of the SiC nucleation on Si and the formation of a nearly perfect and flat interface in the SiC/Si system. RHEED shows unambiguously a

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[*] Corresponding author. Tel.: +41-26-3009088;
fax: +41-26-3009747.
E-mail address: christian.koitzsch@unifr.ch (C. Koitzsch).

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transition from the initial Si(1 1 1) 7 × 7 reconstruction towards a carbon-induced $\sqrt{3} \times \sqrt{3}R\,30^\circ$ superstructure developing upon carbonization. We report on possible adsorption geometries of carbon on a Si(1 1 1) surfaces causing this reconstruction. Energetics upon relaxation of the initial models is investigated by means of semi empirical molecular dynamics, the feasibility of the models is tested by comparing RHEED patterns with simulated diffractograms based on MD optimized structures.

2. Structural models and MD simulation

The semiclassical molecular dynamics calculation was performed in the NVT ensemble (constant number of atoms, volume and temperature). The simulated supercells comprised four bilayers of silicon and additional surface carbon atoms, which yielded more than 300 atoms for the whole slab. Periodic boundary conditions were applied in the *xy*-plane, while the bottom silicon layer was fixed to the initial position, which may approximately describe the connection to the bulk. Silicon–carbon interactions were modeled with a semi-empirical potential, which was initially introduced by Tersoff [3,4]. Previously it was shown, that this potential is able to describe some SiC surface reconstructions with satisfactory accuracy [5,6]. The results obtained for SiC(0 0 0 1) are in promising agreement to experimental results from *I–V* LEED [7] and theoretical ab initio calculations in the framework of density functional theory [8,9].

The outcome of MD simulations can severely depend on the starting point on the potential energy surface, hence an initial guess at best motivated by physical reasoning might decide upon finding the lowest energy structure. Starting from an ideal Si(1 1 1) 1 × 1 surface, crystallographic considerations suggest three high symmetry adsorption sites. Adsorption can take place in a tetragonal four-fold coordination (T4) directly above atoms of the second layer (Fig. 1), in a subsurface five-fold coordination (S5) in between the third and second layer (Fig. 2) and in a three-fold coordinated hollow (H3) site (middle of surface honeycomb) above silicon atoms of the third layer (Fig. 3). Nominally a surface coverage of approximately 1/3 monolayer can yield the observed $\sqrt{3} \times \sqrt{3}R\,30^\circ$ reconstruction. In situ chemical

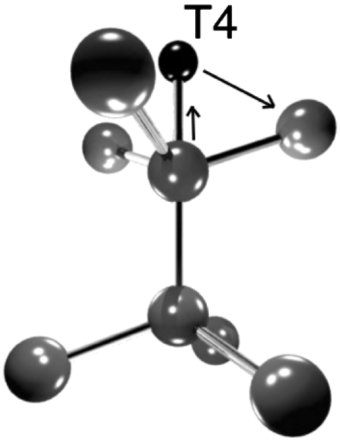

Fig. 1. T4 adsorption site.

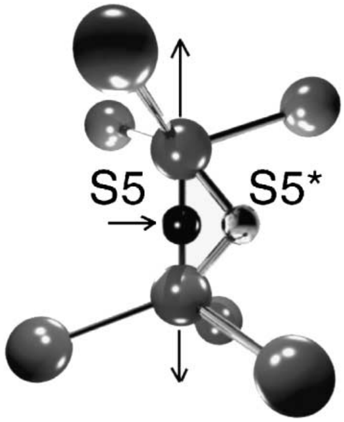

Fig. 2. S5 adsorption site.

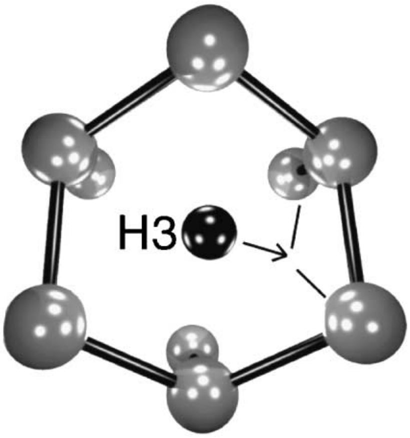

Fig. 3. H3 adsorption site.

analysis by XPS [2], however, showed that the carbon coverage for the reconstruction is approximately one monolayer. The excess carbon can be explained by two different scenarios. First the reconstruction might be due to adsorbed carbon clusters and not just monomers, secondly carbon might diffuse randomly into interstitial sites of the topmost silicon layers (solid solution), giving rise to a strong carbon signal for element specific techniques, such as XPS [2]. The random distribution of a solid solution is not responsible for a reconstruction. Consequently we modeled as a first carbon deficient approach the adsorption of monomers in S5, T4 and H3 sites.

2.1. Modeling of monomers

Simulation of monomers does not fulfill the requirements imposed by stoichiometric analysis, which suggest a monolayer coverage for the $\sqrt{3} \times \sqrt{3}R\,30^\circ$ reconstruction. Nevertheless the simulation of these structures might give physical insight in crucial carbon-induced relaxation mechanisms. Especially the question, whether low energy sites exist within the silicon host lattice might be easier accessed by investigating the incorporation of single carbon atoms, thus neglecting carbon–carbon interactions in more complicated arrangements.

The simulation of the S5 geometry reveals two major carbon-induced relaxation mechanisms. The necessary bond length for the vertical Si–C–Si structure is achieved by a push-out of the carbon atoms out of the chain (Fig. 2). Furthermore, the two silicon atoms are pushed away from (1 1 1) plane centered at the carbon atoms, which ultimately yields a flatter surface compared to the clean Si(1 1 1) case.

Simulation of carbon in T4 sites showed a pull out motion of silicon atoms underneath the adsorbed carbon. Furthermore a tendency to move out of the T4 spots towards the three bordering silicon atoms could be observed especially at elevated temperatures (900 K) (Fig. 1). Such a movement would contribute to an improved bond saturation of the carbon atoms.

Simulation of adsorption on H3 sites served a twofold purpose, first the hollow nature of this site might provide a path for diffusion in subsurface layers. Second the low interaction to the silicon environment might give more insight into a possible solid solution scenario. A tendency is noted that carbon atoms move off center of the honeycomb towards a higher coordinated position (Fig. 3). Table 1 shows the potential energy in terms of the Tersoff potential for all three slabs after intensive heating cycles in order to relax the system. Energetically the T4 scenario can be clearly ruled out, while the geometrically rather similar relaxed H3 and S5 positions are very close in potential energy in terms of the Tersoff potential. Though T4 adsorption might still exist if the adsorption leads to a kinetically-induced semi-stable arrangement. Nevertheless it has to be pointed out, that a simulation of monomer adsorption does not yield a single domain, periodic arrangement of carbon atoms in S5/T4/H3 sites if all carbon atoms in the slab are considered.

2.2. Modeling of trimers

After the discussion of monomer coverages, the simulation focuses now on trimer arrangements. They are better suited to the full monolayer coverage indicated by stoichiometric analysis at the maximum of the reconstruction. Table 2 shows the resulting energies for the three investigated geometries, as in Table 1 the S5 configuration is energetically preferred.

The simulation shows that, among the three investigated geometries an adsorption in S5 sites is energetically favored. Furthermore this structure is stable to temperatures exceeding 600 K, which is not the case for T4 and H3. Again we note a push out motion in the topmost silicon layer with a $\sqrt{3} \times \sqrt{3}R\,30^\circ$ periodicity. Therefore, this structure might be understood as a carbon mediated reconstruction of silicon

Table 1
Monomer simulation

Arrangement	Si–C bond length (Å)	Energy (eV)	Remarks
S5 final	1.80	−1300	Stable for 900°C
T4 final	1.75	−1280	At 900°K off center movement
H3 final	1.91	−1299	Next atom in honeycomb 1.94 Å

Table 2
Timer simulation

Arrangement	Energy (eV)	Remarks
S5	−1404	Domain arranged such that single C is in H3
T4	−1392	Carbon shows no interaction, no reconstruction
H3	−1361	Formation of Si–C ring structures, polymerization

(Fig. 4). Another reason for the energy gain of S5 with respect to T4 might be the better coordination of the carbon atoms. A distance of 3.4 Å clearly does not facilitate a C–C bond [10], but distance analysis shows that every carbon atom is closely coordinated to two silicon atoms. Since carbon is of valency 4, this still leaves two dangling bonds. An adsorption of single carbon in T4 would even leave three bonds unaccounted for. The results for H3 trimers are very similar to the S5 arrangement, which was already indicated by the simulation of monomers. The two-fold coordination might induce the formation of ring-like structures, which so far have not been experimentally observed. The feasibility of polymerization in a Si–C system was already proposed by [11] for SiC(0 0 0 1) 3 × 3.

3. RHEED simulation and comparison to experimental results

The simulation of electron diffraction pattern is possible within dynamical or kinematical theory. While the latter considers only single scattering events, dynamical scattering considers also multiple scattering. Due to the small angle of incidence in the case of RHEED, the interaction volume is strongly elongated in the beam direction and therefore multiple scattering is very likely. Thus, dynamical theory would be the more reliable description of the experiment, but only if the scattering data are well known. However, the accuracy of the parameters are still in debate. The penetration depth, e.g. of the electrons during the multiple scattering effects ranges in the literature from five bilayers [12] up to 100 layers [13]. On the other hand in kinematical theory there is a general agreement about the interaction depth of approximately 1 nm [14–17]. The kinematical simulation offers two advantages, the simplicity of the calculation and the straight forward dependence of the results on the input structure [15]. In addition the kinematical theory offers a correct description of the geometry of the diffraction patterns and a sufficient approximation of the intensities besides the well-known limitations.

Our RHEED pattern simulation is based on the kinematical model described in [15] modified for

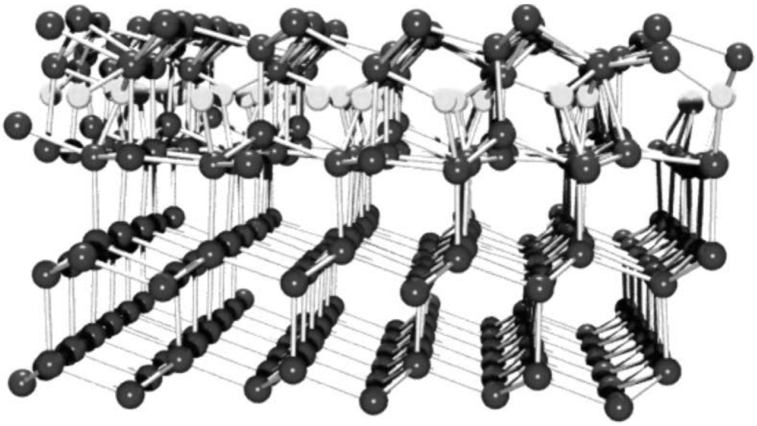

Fig. 4. Side view of S5 trimer adsorption.

(1 1 1) surfaces. In contrast to other available simulation packages [16] the reduced intensity of the elastic scattering due to the thermal motion of the atoms was included via a modified Debye–Waller factor [18]. The electron scattering factors were taken into account by using Doyle–Turner potentials [19].

The interaction of the electrons with the atoms depends strongly on the distance to the surface of the crystal. Since the kinematical theory neglects multiple scattering events, the scattering form factor has to be reduced according to the probability of subsequent scattering events. As in [15,16] we assume a kinematical form factor proportional to an exponential term $e^{-0.21z}$ [14], where z is the vertical distance (Å) between scattering event and surface.

Another important parameter for the calculation of the RHEED pattern is the mean inner potential (MIP). The MIP of the silicon bulk was estimated via Kikuchi lines to be 11.7 V employing the method described in [20,21]. The best agreement between the experimental and calculated RHEED pattern is achieved with nearly half of the generally used bulk mean potential. For our simulation we have chosen 6.4 V for the MIP of the reconstructed near surface layer.

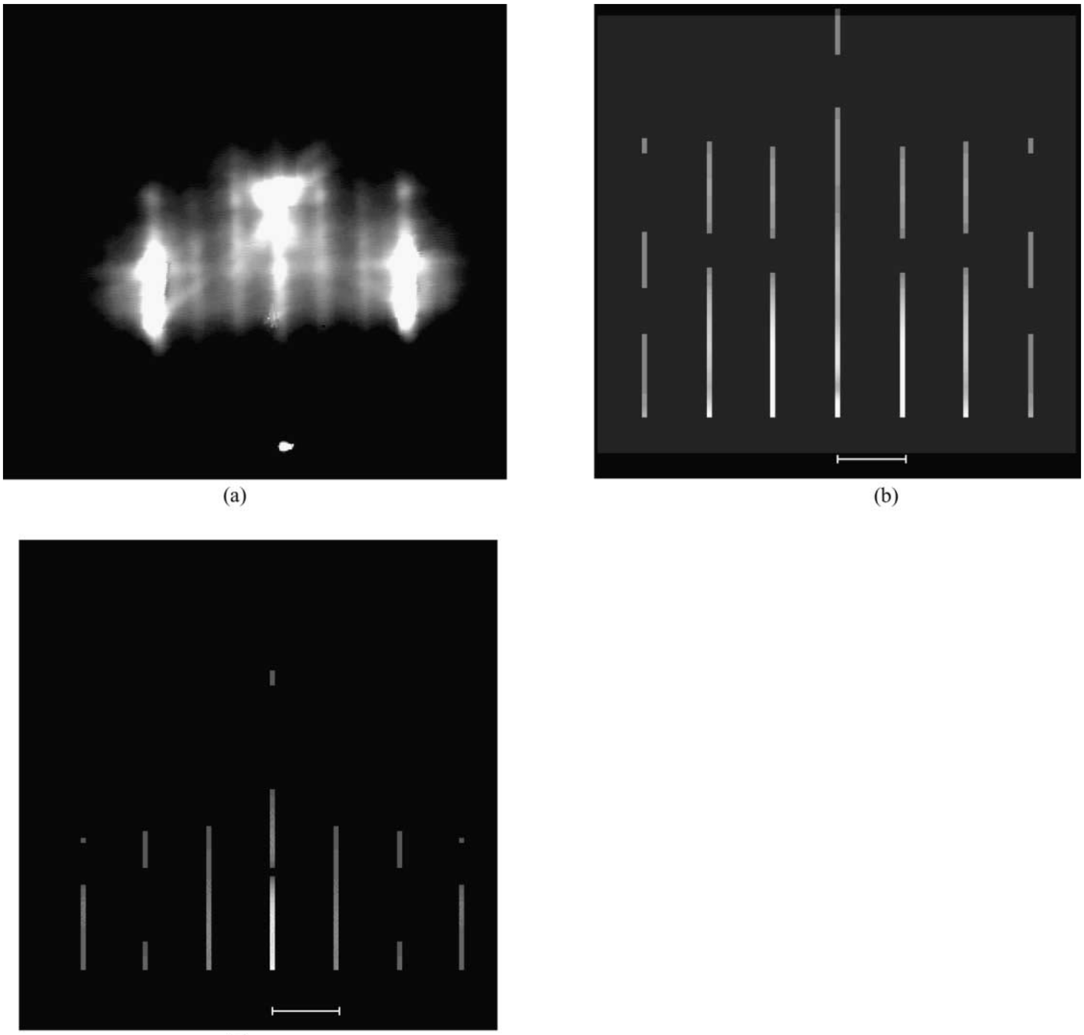
(a) (b) (c)

Fig. 5. (a) Experimental RHEED; (b) simulated RHEED S5 monomer; (c) simulated RHEED S5 trimer.

The RHEED pattern simulations were carried out for the unstable monomer and stable trimer configurations. For both cases the S5 arrangement yields the best results compared to the H3 and T4 structures in terms of line numbers and overall intensity distribution (Fig. 5). Especially the bell-shaped decay from the (0 0) to the (1 1) reflection was solely achieved for the S5 configurations. Therefore, we conclude from the RHEED pattern simulation that the carbon incorporation into S5 sites might be preferred and both cases can exist. The carbon incorporation into the S5 position is supported by the observation that in hydrogen poor environments (1 1 1) silicon carbide layers with a silicon polarity are formed [22]. The differences between the experimental and simulated RHEED pattern can be caused by a formed $Si_{1-x}C_x$ solid solution in the near surface layer. Such a scenario cannot be included in the models at the present stage. Furthermore the solid solution might stabilize other carbon configurations, i.e. monomers. To clarify this point scanning tunneling and X-ray photoelectron diffraction investigations have to be carried out.

4. Conclusion

Simple single domain periodic structural models for the incorporation of 1/3 monolayer do not exist within the framework of molecular dynamics based on Tersoff potential. Nevertheless monomer models were optimized by good reasoning (bond length and angle). The simulation of RHEED diffraction patterns from these models indicates that a S5 arrangement resembles very much the experimental pattern. MD was used to simulate structures with additional carbon. Here again an incorporation of carbon below the silicon surface is favored energetically. Carbon was found to occupy interstitial sites. The optimized structure is supported by RHEED simulations. The resulting Si terminated surface, i.e. carbon incorporation into the second layer of the (1 1 1) bilayer is in agreement with observations during molecular beam epitaxial growth of SiC on Si, which showed a SiC surface with Si polarity.

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