



Universiteit
Leiden
The Netherlands

The dynamics of plasma-surface interaction

Gou, F.

Citation

Gou, F. (2007, February 28). *The dynamics of plasma-surface interaction*. Retrieved from <https://hdl.handle.net/1887/11007>

Version: Corrected Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/11007>

Note: To cite this publication please use the final published version (if applicable).

Chapter 7

Molecular dynamics simulation of CH₃ interaction with Si (100) surface

Abstract: Molecular dynamics simulations of the CH₃ interaction with Si (100) were performed using the Brenner potential. The H/C ratio obtained from the simulations is in good agreement with available experimental data. The results show that H atoms preferentially react with Si. SiH is the dominant form of SiH_x generated. The amount of hydrogen that reacts with silicon is essentially energy-independent. H atoms do not react with adsorbed carbon atoms. The presence of C-H bonds on the surface is attributed to molecular adsorption.

7.1 Introduction

Hydrocarbon thin films deposited by plasma enhanced chemical vapor deposition (PECVD) are important for many applications because their structure can be varied over a wide range [1]. Their property of high hardness makes them suitable as wear-resistant coatings, for example as protective layers in fuel injection valves and in very thin wear-resistant coatings on magnetic discs and magnetic read/write heads. The deposition of these films has been an active topic in fundamental research [2]. Hydrocarbon interactions are also important for the performance and the design of the ITER fusion reactor [3; 4]. Carbon is proposed as the material for the ITER divertor target [5]. Chemical sputtering of this wall will lead to the release of hydrocarbon compounds, which can be re-deposited elsewhere in the vessel. A better knowledge of film formation processes and transport of hydrocarbon species is useful in attempting to predict and minimize dust formation [6-8].

Although hydrocarbon films have been intensively investigated during recent years [9-12], the growth mechanism is still poorly understood due to limitations of in-situ and real-time measurement techniques for surface reactions in a plasma environment. Atomic scale molecular dynamics (MD) is a potential complement for experimental techniques when seeking to understand hydrocarbon-surface interaction mechanisms [7; 13; 14]. There have been many studies on MD simulations of hydrocarbon-surface interactions [15]. The initial

film growth on the substrate, the steady-state deposition coefficients, and the H/C ratios of the deposited layers can be independently studied as a function of energy and molecular exposure.

7.2 Description of molecular dynamics model

The present investigation was performed on the basis of molecular dynamics simulation of CH₃ interacting with silicon surfaces. In an MD model, all atoms in the system are traced by Newtonian mechanics. Particles move under the influence of forces, derived from an interatomic potential. In this work, the Brenner-Tersoff type potential for C-H-Si system is used [16-24].

A (2x1) reconstructed Si (100) crystal consisting of 4x4x6 unit cells with a lateral area of ~500 Å² and a depth of ~35 Å was created. The simulation cell had periodic boundaries in the x- and y-directions. The bottom two layers were held rigid in order to maintain the structure. At the beginning of each impact, the incident CH₃ molecule was placed at a distance above the substrate beyond the cutoff of the potential. The position of the incident molecule in the x- and y-directions was chosen randomly. Each trajectory is run for 1000x0.5 fs, giving a total of 0.5 ps per impact. The spatial trajectories of the atoms were integrated explicitly using the velocity Verlet scheme [25]. The substrate temperature was kept constant at 300 K, using the Berendsen heat bath algorithm [26]. The deposition process was simulated by exposing the substrate sequentially to CH₃ molecules. All impacts were normal to the surface. Energies of 60, 100 and 150 eV per molecule were simulated.

The simulated films were characterized based on coordination number, mass densities and corresponding depth profiles. The coordination of an atom was determined using the first minimum of the pair correlation function as the cutoff length. Depth profiles were calculated by averaging over intervals of 1.3575 Å. In this article twofold, threefold and fourfold coordinated carbon atoms are referred to as *sp*1, *sp*2 and *sp*3 hybridized, respectively.

7.3 Results and Discussion

After CH₃ collides with the surface, some C and H atoms are deposited. Figure 1(a) shows the number of H atoms sticking to the surface as a function of exposure for different energies.

With increasing exposure, the number of H atoms deposited on the surface increases for all incident energies. The deposition of H is largest for 60 eV incident energy. At 100 and 150 eV the deposition rates are effectively identical. For the range of exposures studied, an upper limit to the uptake of H was not observed. During the initial stages of exposure, the rate of H adsorption is highest. After ~7 ML exposure, steady-state deposition is established at a lower rate. At steady-state the deposition rates, defined as the number of H atoms deposited on the surface per incident CH₃, are 0.39, 0.19 and 0.16 for 60, 100 and 150 eV incident energies, respectively. Figure 1(b) shows the H/C ratio deposited on the surface as a function of exposure to CH₃ at the three different incident energies. In each case the H/C ratio initially

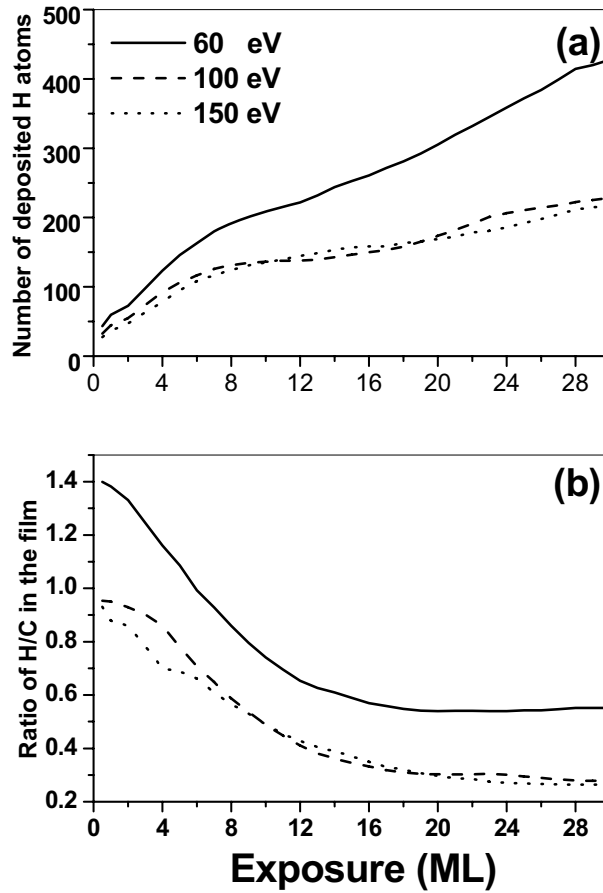


Figure 1: (a) Number of H atoms on the substrate as a function of exposure to CH_3 with incident energies of 60, 100 and 150 eV. (b) H/C ratio on the substrate as a function of exposure to CH_3 with incident energies of 60, 100 and 150 eV.

decreases rapidly before reaching a constant value. For 60 eV, the H/C ratio drops from ~ 1.4 during the early stages to ~ 0.54 after 15 ML exposure. For 100 and 150 eV, a steady-state H/C ratio of ~ 0.29 is obtained after 20 ML exposure. This is in good agreement with experimental data by Plank et al [10]. They measured H/C ratios at room temperature ranging between 0.3 and 0.4. Their HC ratio was effectively independent of the incident energy for energies from 150 to 3.0 keV. Our simulations suggest that this independence extends down to 100 eV.

Figure 2 shows the depth profiles of Si, H and C atoms in the films for 60, 100 and 150 eV after 30 ML exposure. From the figure, we note that the densities and distributions of H atoms are strongly dependent on the incident energy, whereas the C densities and distributions are relatively unchanged. With increasing energy, the C atoms penetrate somewhat deeper into the substrate, but the overall shape and intensity of the distribution are largely unaffected. In contrast, the distribution of H atoms shows major changes as the incident energy is increased. At all energies, this distribution contains 2 peaks. One is located above the position of the initial surface and the other is located beneath it. With increasing incident energy, the intensity of the H peak above the initial surface decreases, while the intensity of the peak below the initial surface is relatively unchanged but shifts to deeper in the bulk. For 60 eV, most C and H atoms are concentrated above initial surface and some Si atoms are shifted outward from

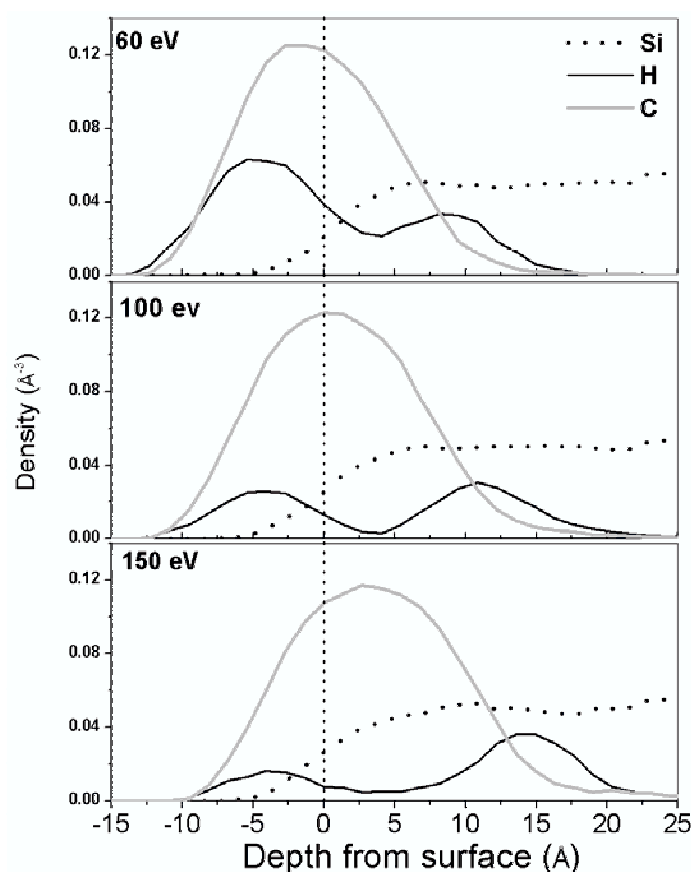


Figure 2: Atomic density as a function of substrate depth after exposure of Si(100) to the equivalent of 40 ML of CH_3 with incident energies of 60, 100 and 150 eV.

their initial position. At the top of the adlayer, the C/H ratio is approximately 1. For 100 eV, the amounts of C and H atoms above and below the initial surface are almost equivalent. For 150 eV, most C and H atoms are located beneath the initial surface.

From figure 2 we note the position of the lower peak always coincides with the interface between the bulk silicon lattice and the mixed Si/C interfacial layer. The upper H peak is located at the outer surface region of the growing adlayer. The double peak structure suggests that, as the deposition progresses, hydrogen atoms are depleted from the adlayer bulk. The previous figures demonstrate that C and H atoms penetrate the Si structure. These atoms may react with Si to form Si-C and Si-H bonds. The distributions of these bonds will influence the properties of the film. Figure 3 shows the densities of Si-C and Si-H bonds as a function of the depth from the initial surface. From figure 3(a), it is seen that most Si-C bonds are concentrated beneath the initial surface. These bonds do not show a strong energy dependence. With increasing incident energy, the density maximum shifts deeper, the distribution becomes broader and the density of the Si-C bonds increases. From figure 3(b), we note that practically all Si-H bonds are located beneath the initial surface. With increasing incident energy, the density maximum shifts deeper into the bulk. At 150 eV, the density maximum is located at ~ 15 Å beneath the initial surface. Combining this figure with figure 3, the second peak in the H atom profile can be attributed to Si-H bonds. Unlike the Si-C distribution, the width of the Si-H distribution does not change significantly with increasing incident energy. Instead, broad

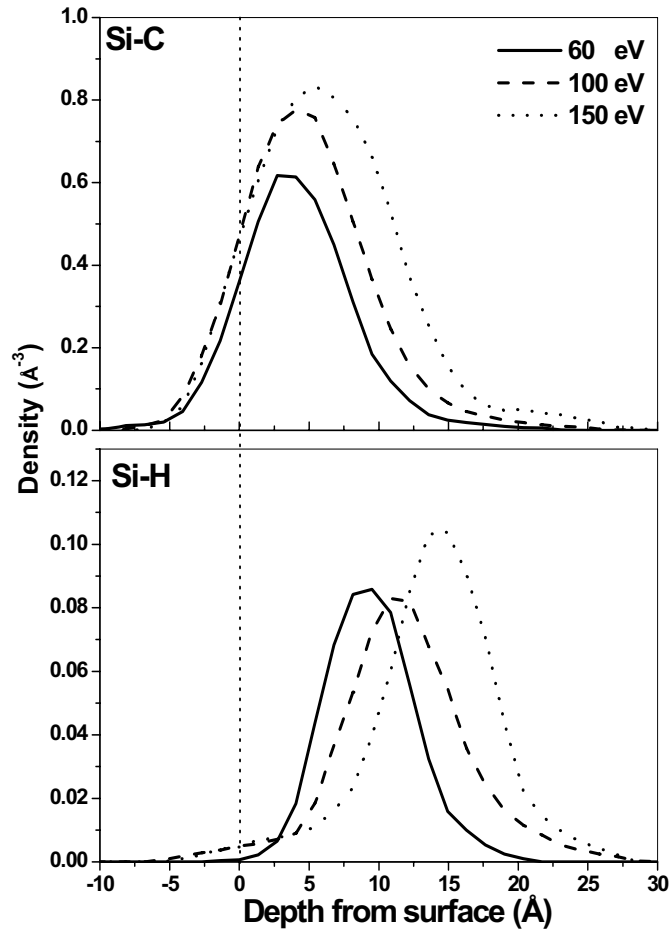


Figure 3: Bond density profiles of Si-C and Si-H as a function of substrate depth after exposure of Si(100) to the equivalent of 40 ML of CH_3 with incident energies of 60, 100

wings develop on either side of a sharp central distribution. Figure 4(a) shows the density of *Csp1-Csp1*, *Csp2-Csp2* and *Csp3-Csp3* bonds as a function of the depth for 60, 100 and 150 eV after 30 ML exposure. *Csp3* bonds are an indication of diamond-like carbon, while *Csp2* bonds are indicative of graphitic carbon. *Csp1* bonds are more molecular in nature and indicate a more porous, amorphous structure. From the figure, we note that most of *Csp1-Csp1* and *Csp2-Csp2* bonds are concentrated above the initial surface. At 60 eV, no *Csp1-Csp1* bonds are found. For 100 and 150 eV, both *Csp1-Csp1* and *Csp2-Csp2* bonds are present. With increasing incident energy, the total density of *Csp3-Csp3* bonds decreases, while *Csp2-Csp2* bonds increase. Hence, the deposition shifts from a predominantly diamond-like structure toward a more graphitic structure. Figure 4(b) shows the density of H-*Csp1*, H-*Csp2* and H-*Csp3* as a function of the depth from surface for 60, 100 and 150 eV. From the figure, it is seen that most H-C bonds are concentrated above the initial surface, contributed to the outer peak of H atoms in figure 3. In the films, the amount of H-*Csp1* is the smallest, while H-*Csp3* is dominant. With increasing the incident energy, the density of these bonds decreases. This decrease coupled with the weak adsorption of hydrogen evident from figure 1(b) suggests that

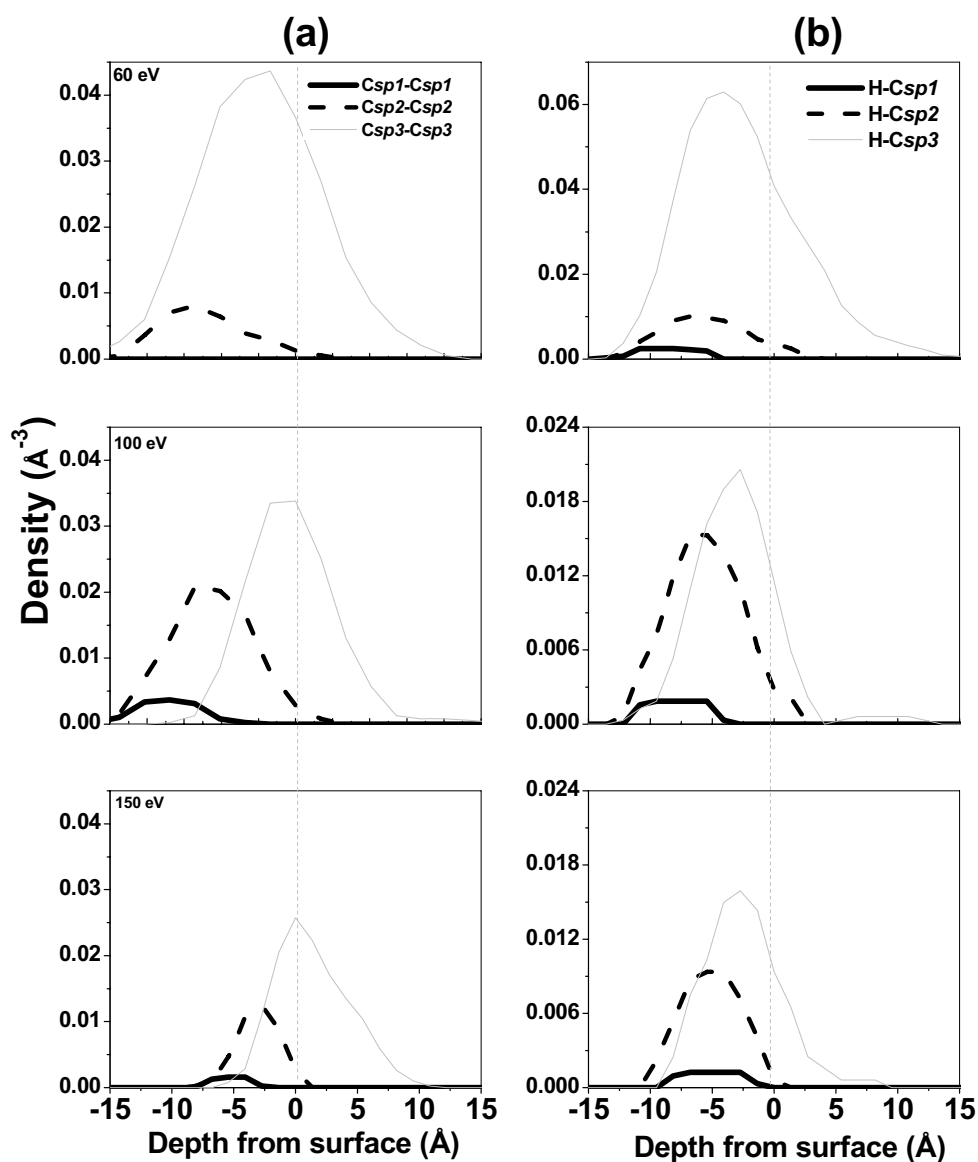


Figure 4: (a) Bond density profiles of sp^1 -, sp^2 - and sp^3 -hybridized C-C bonds as a function of substrate depth after exposure of Si(100) to the equivalent of 40 ML of CH_3 with incident energies of 60, 100 and 150 eV. (b) Density of H-Csp1, H-Csp2 and H-Csp3 as a function of the depth from surface for 60, 100 and 150 eV.

most C-H species arise from molecular-adsorption rather than from H reaction with pre-adsorbed C.

Figure 5(a) shows the relative fractions of CH_x on the modified surface ($x=1-4$). From the figure, we note that in the films, CH species are dominant. For 60 eV, all 4 species are present, while for 100 and 150 eV, no CH_3 and CH_4 species are evident. This can be attributed to enhanced collision-induced dissociation. With increasing incident energy, the CH_2 fraction decreases. From 60 eV to 100 eV, this fraction decreases sharply, while from 100 eV to 150 eV, the decrease is comparatively small. Figure 5(b) shows the corresponding relative fraction of SiH_x ($x=1-4$) on the surface. The relative fraction of SiH_x species is not very sensitive to

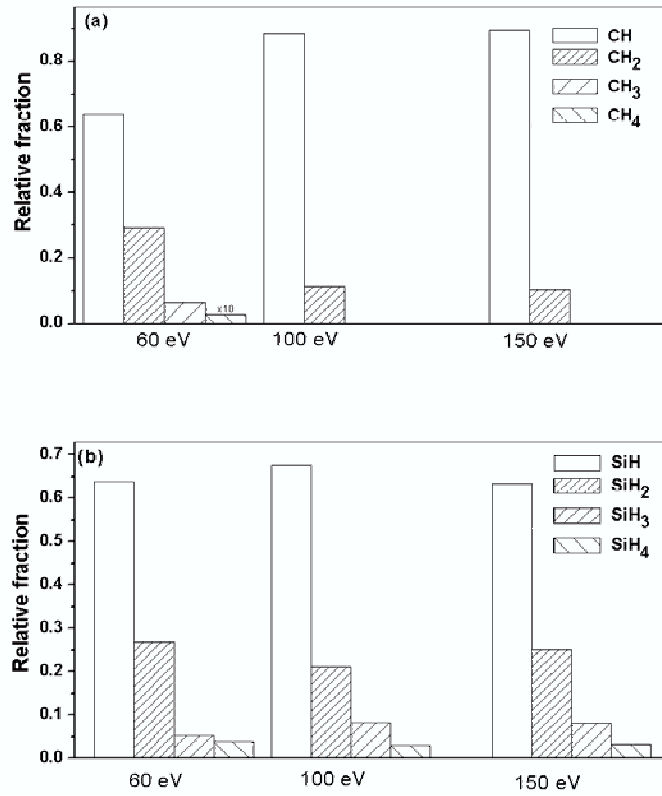


Figure 5: Relative fractions of **(a)** CH_x and **(b)** SiH_x on the surface after exposure of Si(100) to the equivalent of 40 ML of CH₃ with an incident energy of 100 eV.

the incident energy. Combined with figure 1(b) and figure 2, the results suggest that there is a finite amount of H that will react with Si atoms, which is independent of the incident energy. In contrast, the steady-state uptake of H is mainly due to CH_x adsorption.

7.4 Conclusions

The hydrogen distributions observed in the current simulations can be attributed to two independent processes. The first is reaction of H with Si. The hydrogen atoms are provided by dissociation of the incident CH₃. This process occurs during the early stages of exposure and is not very energy independent. The weak-energy dependent changes that are observed can be attributed to enhanced penetration and roughening as the energy is increased. As the total exposure increases, the initial Si-H layer is covered by a mixed Si/C/H adlayer. Thus, the SiH forms an interface layer between the Si bulk and the growing adlayer.

The second process is molecular adsorption of CH_x species. This is strongly energy dependent, since enhanced dissociation at higher energies will lead to less hydrogen on the surface. However, hydrogen atoms are depleted from the bulk of the hydrocarbon adlayer, most probably as a result of sputtering/etching of hydrogen atoms. At all incident energies, the bulk of the adlayer was composed of diamond-like carbon, while the surface was graphitic in

nature. The relative amounts of diamond-like and graphitic carbon were energy dependent, with a more graphitic surface being formed at higher energies.

References

- [1] A. von Keudell, W. Jacob, W. Fukarek, *Appl. Phys. Lett.* 66 (1995) 1322.
- [2] A. von Keudell, W. Jacob, *Prog. Surf. Sci.* 76 (2004) 21.
- [3] J. Roth, *Phys Scripta T124* (2006) 37.
- [4] I. I. Arkhipov, V. L. Bukhovets, A. K. Buryak, G. Federici, A. E. Gorodetsky, C. Ibbott, D. A. Komarov, A. N. Makhankov, A. Markin, I. V. Mazul, R. Tivey, I. G. Varshavskay, S. P. Vnukov, A. P. Zakharov, A. V. Ulianov, R. K. Zalavutdinov, *J. Nucl. Mater.* 313 (2003) 342.
- [5] A. J. M. Buuron, J. J. Beulens, P. Groot, J. Bakker, D. C. Schram, *Thin Solid Films* 212 (1992) 282.
- [6] W. Jacob, *Thin Solid Films* 326 (1998) 1.
- [7] C. Hopf, A. von Keudell, W. Jacob, *J. Appl. Phys.* 93 (2003) 3352.
- [8] C. Hopf, A. von Keudell, W. Jacob, *J. Appl. Phys.* 94 (2003) 2373.
- [9] W. Moller, W. Fukarek, K. Lange, A. vonkeudell, W. Jacob, *Jpn. J. Appl. Phys.* 34 (1995) 2163.
- [10] H. Plank, W. Wang, W. Eckstein, R. Schworer, H. J. Steffen, J. Roth, *J. Appl. Phys.* 78 (1995) 5366.
- [11] W. M. Wang, W. Eckstein, R. Schwörer, H. Plank, J. Roth, *J. Nucl. Mater.* 222 (1995) 1033.
- [12] W. M. Wang, J. Roth, W. Eckstein, R. Schwörer, H. Plank, M. H. Du, *Nucl. Instrum. Meth. B* 129 (1997) 210.
- [13] E. Neyts, A. Bogaerts, R. Gijbels, J. Benedikt, M. C. M. van de Sanden, *Nucl. Instrum. Meth. B* 228 (2005) 315.
- [14] E. Neyts, A. Bogaerts, R. Gijbels, J. Benedikt, M. C. M. van de Sanden, *Diam. Relat. Mater.* 13 (2004) 1873.
- [15] B. J. Garrison, P. B. S. Kodali, D. Srivastava, *Chem. Rev.* 96 (1996) 1327.
- [16] S. Ramalingam, D. Maroudas, E. S. Aydil, *J. Appl. Phys.* 86 (1999) 2872.
- [17] S. Ramalingam, P. Mahalingam, E. S. Aydil, D. Maroudas, *J. Appl. Phys.* 86 (1999) 5497.
- [18] J. Tersoff, *Phys. Rev. B* 39 (1989) 5566.
- [19] J. Tersoff, *Phys. Rev. B* 37 (1988) 6991.
- [20] J. Tersoff, *Phys. Rev. B* 38 (1988) 9902.
- [21] J. Tersoff, *Phys. Rev. Lett.* 61 (1988) 2879.
- [22] J. Tersoff, *Phys. Rev. Lett.* 56 (1986) 632.
- [23] D. W. Brenner, *Physical Review B* 42 (1990) 9458.
- [24] C. F. Abrams, D. B. Graves, *J. Vac. Sci. Technol. A* 16 (1998) 3006.
- [25] L. Verlet, *Phys. Rev.* 159 (1967) 98.
- [26] H. J. C. Berendsen, J. P. M. Postma, W. F. v. Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.* 81 (1984) 3684.