Chemical sputtering of Si related to roughness formation of a Cl-passivated Si surface

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Chemical sputtering of Si in a chlorine environment has been examined with molecular dynamics simulations. It is found that chemical sputtering correlates with the roughness formation of Cl-passivated Si surfaces during low-energy ion bombardment. The chlorine passivation of the Si surface prevents the flattening of the surface due to the high activation barrier for surface diffusion. The rough surface contains reactive intermediates that can be desorbed into the gas phase when, after an ion impact, the region has a large energy content. The observed products and the increase of the sputtering yield are in agreement with experimental observations.

I. INTRODUCTION

High-aspect ratio (vertical) dry etching of thin films is imperative for high-quality pattern transfer in the production of present day very- and future ultra-large scale integrated circuits. The dominant dry etching technique used for this purpose is reactive ion etching, a technique in which a gas plasma reactor provides simultaneously chemically reactive species that adsorb on the film surface and ions that bombard this surface.[1,2] Although inert ion bombardment (physical sputtering) itself can provide the desired high-aspect ratio and resolution, it does so with little selectivity. The function of the added chemistry is to improve this selectivity by enhancing the removal rate of the film to be patterned and/or reducing that of the other films present (e.g., the mask). To obtain the desired high-aspect ratios and narrow size tolerances at useful etch rates, the reactant species should preferably only enhance the etching effect of the ion bombardment of the film to be patterned and should not etch spontaneously. In addition, to keep damage to underlying films within workable limits, the ion energies should be as low as possible.

In this article molecular dynamics simulations are presented of chemical sputtering of Si in a Cl environment. In this introduction we will first discuss and summarize the results of beam studies. After this discussion the outline is presented for the molecular dynamics simulations.

Major problems in the assessment of fundamental limitations and possibilities of reactive ion etching are its complexity and its inaccessibility to many diagnostic techniques. To partly overcome these difficulties the main features of the technique have been simulated by exposing thin film surfaces in (ultra) high vacuum simultaneously to beams of chemically reactive species and energetic ions.[3,4] Particularly, since chlorine-based plasmas satisfy the above mentioned conditions quite well, simulations using a molecular Cl_2-and an Ar^+ (Xe^+, Ne^+, or He^+) ion beam have been studied thoroughly. Around 300 K Cl_2 chemisorbs dissociatively on Si up to a saturation coverage of about one monolayer, forming mainly SiCl surface species and some $SiCl_2$ and $SiCl_3$.[5] Spontaneous etching under these conditions is negligible.[3] Simultaneous exposure of Si at 300 K to fluxes of Cl_2 and energetic Ar^+ ions with Cl_2/Ar^+ flux ratios higher than about 10^2 results in etching with an enhancement factor of about 5 as compared to pure Ar^+ ion sputtering at keV ion energies.[6,7] This enhancement increases to even higher values, while keeping considerable etch rates, when reducing the ion energy to values as low as 50 eV.[8] Flux ratios of Cl_2/Ar^+ much lower than 10^2 lead to a smaller etch rate enhancement, which is undesirable for practical purposes. For that reason, results obtained under the latter conditions will largely be left out of the discussion here. Since the ion energies in reactive ion etching seldom reach values higher than a few hundred eV, most of the results to be discussed here will be from beam studies with Ar^+ (Xe^+, Ne^+, or He^+) ion energies less than 1 keV.

The results of mechanistic studies in this parameter range comprise studies on the influence of

(1) the angle of incidence of the ion beam on (i) mixing of Ar and Cl into the top atomic Si layers, (ii) the formation of displaced Si atom densities in the top atomic Si layers, and (iii) cross sections for Cl removal from Si;[9,10]

(2) projectile mass[6] and Cl_2/Ar^+(Ne^+,He^+) flux ratios on enhancement factors; and

(3) projectile mass,[11] Cl_2/Ar^+ flux ratio, ion energy, Si target temperature[12–15] and ion angle-of-incidence[15] on (i) product distributions and (ii) on time-of-flight (TOF) distributions of products.

Before summarizing the main results of these studies, attention must be paid to discrepancies between results obtained in three different laboratories.[11–15] It has been shown[16] that conventional ion beam chopping without distortion of TOF distributions by mixing of fast and slow molecules from successive chopper gate openings (ion beam on) and with a reasonable time resolution leads to

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very poor signal-to-noise ratios or unduly long measuring times. In the same article it was also shown how pseudo-random chopping at gate openings much shorter than the flight times to be measured, followed by cross-correlation deconvolution, could be used to increase measurement efficiency by orders of magnitude, producing statistically significant results in a reasonable time. Some groups have used this technique and used a long flight path and collected over a small solid angle.[11,12,15] Their results, gathered from different setups, agree very well with one another and will be used in the comparison with and the discussion of the outcome of the molecular dynamics simulations given in this article.

TOF measurements combined with mass spectrometry on the products of this reaction process[3,11,12,15] have shown that the main products are Si, Cl, SiCl, $SiCl_2$, and Ar(Xe) with minor contributions of $SiCl_3$ and $SiCl_4$. The relative amount of more chlorinated products increases with increasing Cl_2/Ar^+ flux ratio and with decreasing temperature, ion energy and ion angle-of-incidence (as measured from the surface normal). The TOF distributions of Si and Cl correspond to binding energies higher than 1 eV, typical for physical sputtering. The TOF distributions of SiCl and $SiCl_2$($SiCl_3$,$SiCl_4$) consist each of three contributions: one fitted with a collision cascade (CC) distribution at surface binding energies of a few tenths of an eV, a second fitted well with a Maxwell–Boltzmann distribution (MB_l) at the target temperature and a third fitted well with an MB distribution with a temperature of about 2500 K (MB_l) appearing below an Ar^+ energy of roughly 500 eV and increasing in relative importance as the Ar^+ energy decreases. The binding energies of the CC distribution, which dominate at and above 250 eV, increase from about 0.2 eV to values as high as about 0.6 eV by changing the experimental conditions such that a Cl-poor surface is formed in the steady state. The use of Xe^+ instead of Ar^+, leading to a higher energy deposition in the near surface region, favors the MB_h over CC. The relative contribution of MB_l in the TOF distributions of $SiCl_3$ and $SiCl_4$ may be as high as 50%, whereas the MB_l contribution for SiCl or $SiCl_2$ is always below about 20%.

Using Rutherford backscattering spectrometry, secondary ion mass spectroscopy, and ion surface scattering as analytical techniques,[9,10] it has been shown that the combined exposure of a Si crystal surface to a 1 keV $Ar^+(Ne^+)$ beam, and a thermal energy Cl_2 beam, sufficiently intense to maintain saturation surface coverage, leads to incorporation of Ar(Ne) and Cl into subsurface Si up to values of 10^{14}–10^{15} atoms cm^{-2} and produces large densities of displaced Si atoms. The densities of all three decrease with increasing angle-of-incidence of the bombarding ion.

The cross section for removal of Cl from the surface increases from about 1 Cl atom/ion at normal incidence to about 40 Cl atoms/ion at 70°. In contrast, the etch rate of Si (about 5 Si atoms/ion) decays only slightly over this range of angles of incidence. Given the 40 Cl to 5 Si atoms/ion etch rate difference and the etch products listed above, bombardment at grazing angles of incidence causes mainly very efficient removal of adsorbed Cl from the surface in a form not bound to Si. Since the etch rate of Si does not show an increase at higher angles of incidence, the above results strongly suggest a direct relation between the relative amount of Cl incorporated below the surface and the etch rate enhancement.[10]

Whereas the use of a high $Cl_2/Ar^+(Ne^+,He^+)$ flux ratio in combination with 1 keV ions incident along the normal produces an etch rate enhancement of about 5 for Ar^+ and Ne^+ as compared to pure Si sputtering, this enhancement is about 14 for He^+. It has been suggested that this is due to the fact that He^+ is more effective in stimulating processes that need small amounts of energy, i.e., processes in a hot spot.[6]

All models put forward to explain all or part of the above observations,[3,4,9–12,15,17] agree about the importance of ion bombardment-induced bond breaking and the formation of a Si-Cl mixed subsurface layer. The low binding energies observed for the CC part of the SiCl and $SiCl_2$ distributions may be explained by their presence as subsurface void molecules or by an exceptionally low frequency factor for further thermal reaction. At the same time the MB_l part may be explained by ion bombardment-enhanced diffusion of these void molecules to the surface where they desorb.[3,12,15] Another proposal is reformation of small molecules after ion impact and ejection of the molecules in the tail of the same collision cascade.[17] This model emphasizes the necessity of ion bombardment induced mixing of Cl into subsurface layers. Yet another proposal assumes direct formation of molecules during the very first stages after impact and sputtering of these molecules by the tail of the same collision cascade.[4] There is general agreement about the model for the MB_h contribution: this is due to reaction in the hot spot immediately after the collision cascade has ended.[3,4,11]

It is the aim of the present article to use molecular dynamics simulations to study (i) the suggested relation between a subsurface mixed Si-Cl layer and etch rate enhancement, (ii) the type of products, (iii) their kinetic energy distributions, and (iv) to test proposed mechanisms. In order to be able to observe possibly both CC and MB_h distributions, an Ar^+ ion energy of 200 eV and full Cl surface coverage are chosen for the simulations.

II. DESCRIPTION OF THE CALCULATIONS

In the molecular dynamics simulations an unreconstructed Si(111) surface of a microcrystallite that consists of six layers of 60 atoms per layer is used. The bombardment is performed with 200 eV Ar^+ ions at normal incidence. Periodic boundary conditions in plane of the surface are applied in order to minimize boundary effects. The size of the microcrystallite is sufficiently large to prevent interference due to the periodic boundary conditions and its finite size. The bottom layer atoms are coupled to their initial positions with a harmonic force. The value of the force constant is 10^{-8} N m^{-1}. In order to correct for the dissipation of energy due to the shock wave shortly after impact,the potential energy build up in the bottom atoms is removed from these atoms as long as their temperature

TABLE I. Two-body potential parameters.

	a	b	c	r_{cutoff}	p	q
Cl-Cl	8.611	0.789	0.5795	2.0862	6	5
Si-Cl	28.0	0.67	1.3	1.8	2.2	0.9
Si-Si	7.050	0.602	1	1.8	4	0

exceeds the temperature of the external bath. A temperature control is added to mimic the heat flow to the bulk. The method described by Berendsen *et al.*[18] is used to couple the atoms in the bottom half of the crystallite to an external bath at constant temperature. In the simulations, the coupling is to a bath at $T=300$ K with a time constant $\tau=400$ fs. With this value the crystallite is cooled down to 300 K within a few ps after the ion impact. The simulations utilize potentials of the type introduced by Stillinger and Weber for the Si-F system.[19] To incorporate more repulsive interactions at small internuclear separations, the potentials are splined to a Moliere potential with a screening length of 0.83 times the Firsov value.[20] The attractive Ar-Ar, Si-Ar, and Cl-Ar interactions may be neglected under the experimental conditions. The repulsive Ar-Ar, Si-Ar, and Cl-Ar interactions are described by a Moliere potential, also with a screening length of 0.83 times the Firsov value. The interaction of Ar with Ar, Si, and Cl is described with a two-body potential only. The potential energy Φ used in the Si-Cl system is built up from two-body and three-body interactions ($A\equiv$Si, $B\equiv$Cl) (where Stillinger and Weber reduced units are used with energy unit $\epsilon=2.17$ eV and length unit $l=2.0951$ Å):

$$\Phi=\Sigma v_{AA}^{(2)}+\Sigma v_{AB}^{(2)}+\Sigma v_{BB}^{(2)}+\Sigma v_{AAA}^{(3)}+\Sigma v_{AAB}^{(3)}+\Sigma v_{ABB}^{(3)}+\Sigma v_{BBB}^{(3)}. \quad (1)$$

The two-body potential is of the form

$$v^{(2)}=\begin{cases} a(br^{-p}-r^{-q})\exp\left(\dfrac{c}{r-r_{cutoff}}\right) & r<r_{cutoff} \\ 0, \quad r\geqslant r_{cutoff} \end{cases}, \quad (2)$$

with the parameters for the different atom-atom combinations shown in Table I. With this choice of two-body potential parameters, the equilibrium distances are 1.96 and 2.06 Å and the dissociation energies 2.47 and 3.96 eV for Cl_2 and SiCl respectively.

Each $v^{(3)}$ is expressed as a sum of three triad functions $h_{XYZ}(r,s,\theta)$, where θ is the vertex angle at atom Y and r and s are the lengths of the two 'legs'.[19] The original Si and the five new Si-Cl heteratomic triad functions have been assigned as follows:

$$h_{AAA}=21\left(\cos\theta+\frac{1}{3}\right)^2\exp\left(\frac{1.2}{(r-1.8)}+\frac{1.2}{(s-1.8)}\right), \quad (3)$$

$$h_{AAB}=15\left(\cos\theta+\frac{1}{3}\right)^2\exp[(r-1.8)^{-1}+(s-1.8)^{-1}], \quad (4)$$

$$h_{ABA}=50\exp[(r-1.8)^{-1}+(s-1.8)^{-1}], \quad (5)$$

$$h_{ABB}=15\exp[(r-1.8)^{-1}+(s-1.8)^{-1}], \quad (6)$$

$$h_{BAB}=[30(\cos\theta-\cos 103°)^2-0.5]\exp[(r-1.8)^{-1}+(s-1.8)^{-1}], \quad (7)$$

$$h_{BBB}=3(rs)^{-2.056}\exp\left(\frac{0.5795}{r-2.0862}+\frac{0.5795}{s-2.0862}\right)+23.778(2.0-\cos^2\theta)\exp\left(\frac{1.7386}{r-1.6226}+\frac{1.7386}{s-1.6226}\right) \quad (8)$$

and each of the triad functions is taken to be zero if a distance variable exceeds the essentially singular cutoff value. The interactions defined lead to reasonable structures for various gas-phase silicon chlorides.[21,22] In particular $SiCl_2$ is a bent trimer, $SiCl_3$ is a pyramid with C_{3v} symmetry, and $SiCl_4$ is tetrahedral (symmetry T_d). These lowest energy structures are in reasonable agreement with experiment and exhibit moderately good bond lengths and energies and the $SiCl_4$ molecule exhibits virtually no tendency to add a fifth chlorine atom. Similar to the Si-F system the potentials do not describe the variation in Si-Cl dissociation energy in the $SiCl_x$ molecules Also the small variations in Si—Cl bond length (2.02–2.06 Å) and Cl—Si—Cl bond angle (106°–110.9°) are not exactly described by this choice of parameters. No claims are made that the interaction functions and the parametrization are an optimal choice, but the major features of the relevant structural chemistry are at least qualitatively reproduced.

In the simulations the surface is bombarded with 200 eV Ar^+ ions at normal incidence. For 200 eV Ar^+ ions the physical sputtering is expected to be still important, while for the chemical sputtering there is still sufficient yield[8,11] to obtain statistically relevant information from the simulations. In the first simulation, (a) the unreconstructed Si(111) surface is bombarded. The data obtained provide a basis for determining the effects of Cl adsorption, e.g., whether it enhances the yield. A set of trajectories is developed by uniform sampling of a representative area reflecting the underlying symmetry of the crystal.[23] With every new trajectory, a fresh surface is bombarded with the ion. The simulation of a trajectory is finished when there are no atoms in the crystallite that have enough kinetic energy to overcome the surface binding energy. In order to investigate the underlying mechanism of creation and desorption of volatile molecules the same simulation is performed but now with the Si(111) surface passivated with Cl(b). The chemisorption position of Cl on the Si(111) surface is derived from experiment to be the one-fold top site on the Si(111) surface.[24] Again, a set of trajectories is developed by uniform sampling of a representative area reflecting the underlying symmetry of the crystal and with every new trajectory, a fresh surface is bombarded with the ion. In the third simulation (c), the effect of a higher ion dose on the structure of a Cl-passivated surface is studied. The crystallite is bombarded continuously with 200 eV Ar^+ ions without refreshing the lattice. The calculation of a trajectory is continued until the temperature of the crys-

tallite is returned to about room temperature. The time covered by these molecular dynamics simulations is about 3 ps per impact. The behavior at room temperature during the time between two impacts, which is of the order of a second, cannot be simulated. The etch yield per ion obtained for the 3 ps periods will be compared with experimental values and the importance of processes during this room temperature period will be discussed. Because the lattice is not refreshed, the symmetry is broken after the first impact. To simulate the experimental situation as well as possible, the impact points of the incident Ar^+ ions are randomly taken on the total surface of the crystallite.

In the most favorable experimental situation, the Cl_2 flux is always much larger than the Ar^+ flux and thus the surface will be completely passivated with chlorine. This is taken into account in the simulation by passivating the surface with Cl after finishing each trajectory. The positions of the introduced Cl atoms are determined by a search for the potential energy minima for an additional Cl atom on the surface. The first introduced Cl atom is positioned on the minimum potential energy position. The next Cl atom is positioned on the next minimum as long as this position is not too close to another Cl surface atom and the binding energy is larger than 1 eV. The minimum Cl-Cl distance is taken equal to the Cl-Cl separation on an unreconstructed Si(111)-Cl surface.

A surface as prepared with these high-dose simulations is then bombarded to obtain statistical information on the product formation caused by the sputtering with Ar^+ ions. The impact points are chosen randomly over the total surface. With every new trajectory, the same rough surface is bombarded.

Finally, sputtering simulations are performed on clean Si surfaces prepared in a similar way as described above but prepared without Cl atoms (d).

III. RESULTS AND DISCUSSION

In this section we describe the results of the simulations for the three different situations. The simulation results are compared with the experiments and are used to explain the mechanism of surface roughness formation and chemical sputtering.

A. Clean, flat, pristine Si(111)

Ion bombardment of clean, flat, pristine Si(111) [case (a)], in 61 trajectories. Four sputtered Si atoms are observed with kinetic energies 3.0, 5.3, 5.5, and 6.6 eV giving the number of sputtered Si atoms per incident ion (the Si sputter yield), $Y_{Si}=4/61=0.07$. The yield agrees with both the experimental results of Stansfield *et al.*[25] and the simulation results of Smith *et al.*[26]

The Si atoms escape within about 200 fs after the impact of the incident ion. A visual analysis of the trajectories shows that the Si atoms are sputtered with a linear collision-cascade mechanism. In the linear collision-cascade the incident ion produces several recoil atoms in the crystallite. The recoil atoms collide with atoms in the lattice, which have very little kinetic energy. Some of the recoil atoms have enough kinetic energy to help overcome the surface binding energy for Si surface atoms. After a few hundred femtoseconds the kinetic energy is distributed among many atoms in the crystallite creating a hot spot in the impact region of the ion. After this time no individual atom has enough kinetic energy to overcome the high surface barrier. This surface barrier U_0 for an atom to escape from the surface is known to correspond quite well to the sublimation energy per atom in a wide variety of materials. For Si the surface barrier is about 5 eV, and it can be understood that, from the moment that the 200 eV kinetic energy of the incident ion is distributed among the 360 crystallite atoms, there are not many surface atoms whose kinetic energy is larger than U_0.

B. Flat, pristine Si(111)-(1×1)Cl

In order to investigate the underlying mechanism of creation and desorption of molecules the same simulation as in case (a) is performed with the Si(111) surface passivated with Cl. Two individual events where a $SiCl_2$ molecule is sputtered and one event where a SiCl molecule is sputtered are observed. No sputtering of single Si atoms is observed. The Si sputtering yield is slightly reduced by the addition of a Cl layer on the surface. The low Si sputter yield is consistent with the low sputter yield of clean Si as the configuration with Cl has the same openness as the clean surface. The molecules escaped between 350–800 fs after the impact of the incident ion. It appears from an analysis of the molecule ejection event that it takes some time before all the atoms of the molecule have sufficient kinetic energy to let the structural rearrangement, necessary to escape from the surface as a molecule, take place. In these three sputtered molecules, the Si atoms originate from a position in the first Si layer below the monolayer of Cl. The Cl atom of the sputtered SiCl molecule is on top of the Si atom. Of the two Cl atoms of the sputtered $SiCl_2$ molecules, one is on top of the Si atom, while the second originates from a position on top of a neighboring Si atom.

It has been suggested by Mayer *et al.*[9,10] and by Dieleman *et al.*[12] that etching of silicon in a Cl_2 atmosphere may be strongly enhanced by the presence of mixing. In the simulation described in this section the impact of a 200 eV Ar^+ ion on a perfect Cl passivated Si(111) surface, the Cl neither mixes into the first surface layers, nor enhances the etch yield.

C. High-dose Si(Cl)

In order to study the effect of a higher ion dose, the crystallite is bombarded continuously with 200 eV Ar^+ ions without refreshing the lattice. In Fig. 1 the surface of the crystallite is shown after no more than 12 impacts. A very rough surface with tower-like structures of Si atoms with all the Si bonds passivated with Cl atoms has been produced. Some of the Si atoms even have three chemical bonds with Cl atoms. Because of the fact that the impact points are chosen randomly, the dose needed to create such an amount of roughness cannot exactly be predicted, but evidently this dose is as low as about one ion impact per five surface atoms. With this amount of roughness the

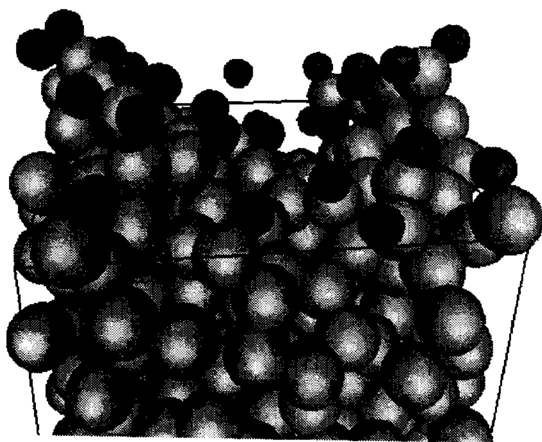

FIG. 1. Rough Cl covered Si surface after 12 impacts. Large light spheres represent Si atoms, smaller dark spheres represent Cl atoms. Also shown are the boundaries of the simulation box.

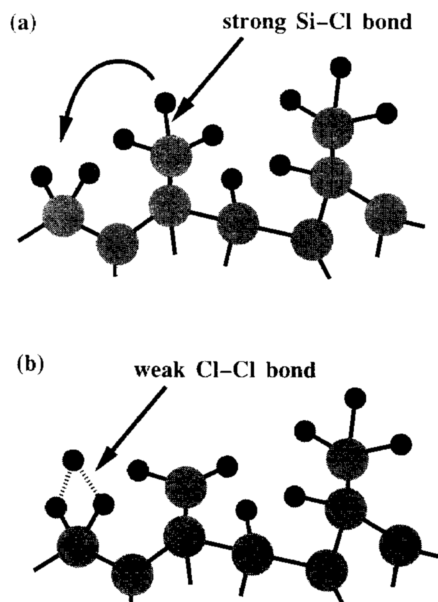

FIG. 2. Surface diffusion of Cl atoms involves breaking of a strong Si—Cl bond (a) and the formation of a weak Cl—Cl bond at a neighboring site (b). Large light spheres represent Si atoms, smaller dark spheres represent Cl atoms.

sputtering of a $SiCl_3$ molecule has been observed for the first time. Similar tower-like structures are also observed in simulations for the Si-F system by Schoolcraft and Garrison[27] although the amount of roughness in the present case appears to be larger due to the much larger kinetic energy of the projectiles.

Before discussing the sputtering properties of the crystallite with this rough surface, (i) the process of roughness formation and (ii) the observation that genuine mixing of Cl atoms in the top layers does not occur will be treated first. Observation of the development of the collision cascades shows that the formation of the surface roughness is caused by recoil atoms moving towards the surface and pushing surface atoms upwards. This happens during any sputtering process but as such cannot explain the amount of roughness observed in the simulations of the bombardment of the Cl-passivated surface. In sputtering of pure Si this tower formation is not observed. The essential difference with the sputtering processes of pure Si lies in the passivation of the surface with Cl. The major process causing flattening of a surface is diffusion of surface atoms on the surface. On a Cl-passivated surface most Si dangling bonds are tied up to Cl and all surface atoms are Cl atoms. These Cl atoms form a chemical bond to a Si atom with a bond strength of about 4 eV. In order to let surface diffusion take place, the Si—Cl bond must be broken and the Cl surface atom must move to a neighboring site. As the Si surface is largely passivated, there are no other dangling bonds available and the Cl atom would have to hop onto another Cl atom that already has a chemical bond with the underlying substrate. The shifted Cl atom is then at best bonded by weak van der Waals forces (see Fig. 2). This simply means that the surface diffusion process has a large activation barrier, i.e., at least the Si—Cl bond strength of about 4 eV. This is the reason why the created roughness does not disappear even when the surface is highly excited during subsequent impacts of Ar^+ ions. It also means that it is unlikely that a flattening of the surface will occur on the time scale used in the experiments, in which the surface is at room temperature during about one second between two successive, very short, impact events.

It has been suggested that Cl might be mixed into the Si lattice by the ion bombardment.[9,10,12] In the simulation however, such a mixing is not observed. Even when a Cl atom is recoiled downwards by an incident Ar^+ ion, the high excitation density in this region appears to enable the Cl atom to diffuse again to the surface within the duration of this hot spot. In addition, the Cl atom can form just one chemical bond with a Si atom and the energy gain from this bond formation is insufficient to compensate for the potential energy loss due to the disturbance of the bulk Si lattice and the breaking of the surface Si—Cl bond. The latter result is somewhat similar to the results of the calculations of van den Hoek *et al.*[28] where the configuration with a subsurface Cl atom appears to have a large energy. Van den Hoek suggested that the presence of such subsurface Cl atoms might explain the experimentally observed low binding energies of SiCl and $SiCl_2$ product molecules. It was argued that one ion impact might produce such subsurface Cl atoms. The relaxation of these subsurface atoms during removal of SiCl or $SiCl_2$ molecules from the surface by a subsequent ion impact would lower the net amount of energy needed to remove these molecules. However, the present simulations show that this relaxation of subsurface Cl already occurs during the hot spot period of the ion impact that produced the subsurface Cl atoms. So, the increased density of Cl atoms observed in the surface region as a result of simultaneous Ar^+ bombardment and Cl_2 exposure[9,10] is due to the roughness at the surface and thus to an increased number of bonding positions for Cl atoms at this rough surface. Conventional ion bombardment-induced mixing does not play a role in this particular case.

TABLE II. Sputtering yield for the rough Cl-covered surface (500 trajectories).

	Ar	Cl	SiCl	$SiCl_2$	$SiCl_3$	Cl_2	Si	Si_xCl_y
Yield	0.95	1.05	0.14	0.12	0.08	0.09	0.05	0.02

In order to investigate if the sputtering yield is enhanced in the case of the rough Cl-covered surface, the development of 500 trajectories of impacts of 200 eV Ar^+ ions at normal incidence is studied. The impact points are chosen randomly on the total surface. For every new trajectory, the rough surface shown in Fig. 1 is chosen as the starting situation for bombardment with the ion. The sputtering yield of the different products is shown in Table II.

The total sputtering yield of Si is 0.43. This is a considerable enhancement compared to the sputtering yield of the fresh Si(111) surface with or without coverage of Cl atoms where $Y_{Si} \sim 0.07$. This large enhancement agrees quite well with the enhancement of about 5–7 times found experimentally.[8] However, for this particular case the absolute value of the Si sputtering yield is about a factor of 2 lower than the only experimental value available.[8] Earlier experimental studies[29] suggest that an ion dose of about two orders of magnitude higher than used in the present MD simulations is required to reach the high steady-state yield. So, this low yield may be due to the fact that the 12 impacts used here are not yet sufficient to reach this final steady state. Future MD simulations studies have to shed more light on this point. A further very gratifying result is that, except for Cl_2 (and some Si_xCl_y), all main products correspond to the main products observed experimentally.[11,12,15] Unfortunately, a quantitative comparison of the contributions of the various products is not possible, as the estimates of the experimentally determined values are based on the assumption of equal electron impact ionization cross sections (at equal velocities) in the ionization chamber of the mass spectrometer,[11,12,15] and because steady state may not have been reached in the MD simulations.

It is not possible to identify one single desorption or sputtering mechanism for all of the products. The emission mechanism of Ar atoms was explained recently by Feil *et al.*[30] At low incident Ar^+ energies, the Ar is trapped in the first atomic layers for a time short compared to the duration of the hot spot created by its impact. After just a few collisions Ar is then reemitted, peaked along the surface normal. This process differs from a pure linear collision cascade-like desorption process. The Si atoms are sputtered within about 200 fs after the impact of the incident ion and the peak of the kinetic energy distribution is at a few eV indicating a collision-cascade sputtering mechanism. The escape time distribution of the $SiCl_x$ products is much wider but most of the higher chlorinated products have left the surface after the time that the energy of the incident ion is distributed among most of the atoms in the crystallite. It cannot be concluded from the MD simulations that the particles are formed and desorbed during the same collision cascade[31] because it appears that sometimes the sputtered molecule is already present at the surface and rather weakly bound with one Si—Si bond. The excitation density in the impact region during the hot spot is often so high that radicals and other reactive intermediates are relatively weakly bound to the surface at this "high temperature" and desorb into the gas phase.

In the example discussed above the peak in the kinetic energy distribution of the $SiCl_x$ molecules is at about 1 eV. This is about half the energy it takes to break a Si—Si bond in the simulations (2.2 eV). When sputtering takes place via a collision cascade mechanism, the peak in the kinetic energy distribution is at half the binding energy. However, the statistics are not yet sufficiently good to determine a sputtering mechanism from a fit to the kinetic energy distributions. Moreover, a detailed analysis of the ejection events does not lead to identification of one single mechanism. The peak in the kinetic energy distributions is at higher kinetic energies than observed in experiments.[11,12,15] One reason may be that the surface has not yet reached steady-state roughness.

Further work is in progress to obtain simulations with a steady-state surface roughness that might be even considerably higher than that of the surface in the present simulation. Surface roughening and a corresponding yield enhancement are not typical for bombardment with 200 eV Ar^+ ions. Preliminary MD simulations with 50 eV Ar^+ give similar results. It only takes more impacts to reach a certain roughness and yield enhancement.

D. High-dose, clean Si

To check the observation that formation of surface roughness is the major ingredient for chemical sputtering, sputter simulations have also been performed on clean Si surfaces, without Cl atoms. Some roughness formation is observed during the first few impacts. However the excitation of the surface layers during subsequent impacts of Ar^+ ions causes a counteracting flattening of the surface as expected (see Fig. 3). This flattening is mainly due to the relatively large mobility of surface atoms as compared to the Cl-passivated surface. Tower-like structures are not observed on this surface. The sputtering yield is enhanced ($Y_{Si} \sim 0.12$) compared to the perfect Si surface but is still much smaller than that of the high-dose Cl-passivated surface.

IV. CONCLUSIONS

Molecular dynamic simulations of the synergistic effects of simultaneous exposure of Si surfaces to bombardment with 200 eV Ar^+ ions incident along the surface normal and to thermal energy Cl_2 molecules at Cl_2/Ar^+ flux ratios sufficiently high to keep the Si surface passivated by

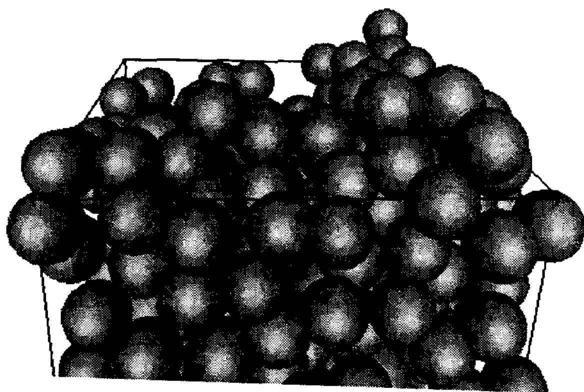

FIG. 3. Si surface after about 10 impacts without Cl. Some roughness is observed. Note the absence of tower-like structures.

Cl, have produced results that are consistent with these obtained from experimental studies on these effects using time-of-flight measurements in combination with mass spectrometry.[11,12,15] In addition, new insight is gained about the mechanisms of the sputtering yield enhancement and the mechanisms of formation and desorption of products.

The yield increase with respect to that of physical sputtering of Si by Ar^+ agrees well with the experimental value, but the absolute value is about a factor of 2 smaller. This might be due to the fact that steady-state etching with its higher yield requires much higher doses than used in the present simulations. Products appear to be ejected by several mechanisms: (i) Si and Cl atoms desorb within about 200 fs after the ion impact with an average kinetic energy higher than 1 eV, suggesting a linear collision-cascade mechanism, (ii) Ar and also the molecular products escape during the period where most of the energy of the incident ion is distributed among most of the atoms of the crystallite. The average kinetic energies for the $SiCl_x$ molecules are clearly lower than those observed for the atoms but still about 1 eV.

The MD simulations show the rapid roughening of the Cl passivated surface with increasing ion dose and the correspondence of this roughening to an increased etching yield. Ion doses as low as about one ion per five surface atoms cause surface roughening of the Cl-passivated surface depths of several atomic layers. The conservation of surface roughness is explained by the very low mobility of the Cl surface atoms. In addition it is observed that Cl is not mixed permanently into Si. The increased Cl content of the Si surface is explained by the increase of the number of bonding sites on a corrugated Si surface.

This result could be checked by, e.g., by scanning tunneling or force microscopy. If experiment confirms the existence of the roughening, such a roughening effect prohibits flat atomic layer etching and, depending on the depth, could pose a problem in advanced ultralarge scale integrated circuit technology.

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