Supporting Information for

Computational Modelling of Atomic Layer Etching of Chlorinated Germanium Surfaces by Argon

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1. Tersoff force field training

1.1. Discussion on the choice of the force field

Tersoff force field has been selected to describe the Ge-Cl interaction, because this bond order potential was originally calibrated for covalent elements including C, Si and Ge,[1-3] which have similar structural and chemical properties. Improved versions of Tersoff have been developed and used widely in C and Si reaction studies,[4-7] however we stick to the original version here for several reasons. First, some improvements are to achieve a better description for double and conjugation bond, such as the Brenner's correction terms in REBO potential.[5] This is important for carbon system. However, for either Si or Ge, due to their increased metallicity, double and conjugation bonds rarely form, and such corrections can be unnecessary. Second, previous studies noticed the Si-F bond energy trend has an abnormal value in SiF_3 structure[4] similar to our $GeCl_3$ case due to hybridization states(shown in section 1.3). A correction term in bond order b_{ij} can be added for better fitting the bond energies.[4, 8] However, due to our limited training data, the addition of such correction term leads to an overfitting problem, such that the

bond energy change can be fit accurately, while the fitting accuracy of bond length and bond force constant both decrease. Since each property weighs differently based on the purpose of a simulation study, here we choose to lower the total fitting error (eq.1 in Fig. S1) instead of the bond energy term only. Further optimizations can be certainly made with more training data, and a different weighing on the target terms.

1.2. The format

We used the following format as implemented in LAMMPS:

$$E = \frac{1}{2}\sum_{i}\sum_{j \neq i} V_{ij}$$

$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

$$f_C(r) = \begin{Bmatrix} 1 : r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi r - R}{2\ D}\right) : R - D < r < R + D \\ 0 : r > R + D \end{Bmatrix}$$

$$f_R(r) = Aexp(-\lambda_1 r)$$

$$f_A(r) = -Bexp(-\lambda_2 r)$$

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{2n}}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk}) exp[\lambda_3^m (r_{ij} - r_{ik})^m]$$

$$g(\theta) = \gamma_{ijk}\left(1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (cos\theta - cos\theta_0)^2]}\right)$$

where f_R is a two-body repulsion term and f_A the attraction term. The bond order term b_{ij} is a three-body term added to the attraction part, which includes all neighbors j and k of atom i. f_C is the interaction cutoff function to smoothly transit full interaction to zero. R-D and R+D is the inner and outer cutoff distance.

1.3. Training the parameters

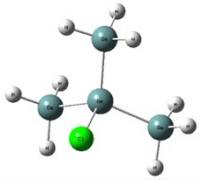
Interaction parameters for Ge-Ge and Cl-Cl atom pairs are available from previous literature.[2, 4] So only Ge-Cl interaction terms need to be trained. To do this, two-body parameters A, λ_1, B and λ_2 are first optimized against bond energy, force and force constant of several $GeCl_n$ species

(Table S1 and S2) from DFT calculation using the annealing algorithm similar to previous studies, as shown in Fig. S1 and S2.

Table S1 Training data for Cl-Ge-Cl configurations.

Species	Cl-Ge-Cl angle ($^{\circ}$)	Ge-Cl bond distance (Å)	Ge-Cl bond energy (eV)	Force constant (N/m)
Ge_2Cl_6	109.47	2.23	4.21	117.72
$GeCl_4$	109.47	2.22	4.23	163.41
$GeCl_3$	108.69	2.27	1.47	109.00
$GeCl_2$	101.09	2.30	4.16	141.26
GeCl	N/A	2.31	3.28	122.60
Ge_4H_9Cl	N/A	2.32	4.08	131.67

Table S2 Training data for Ge-Ge-Cl configurations.

Species	Ge-Ge-Cl angle ($^{\circ}$)	Ge-Ge bond distance (Å)	Ge-Ge bond energy (eV)
Ge_2Cl_6	109.78	2.50	2.91
Ge_4H_9Cl 	104.21	2.49	/

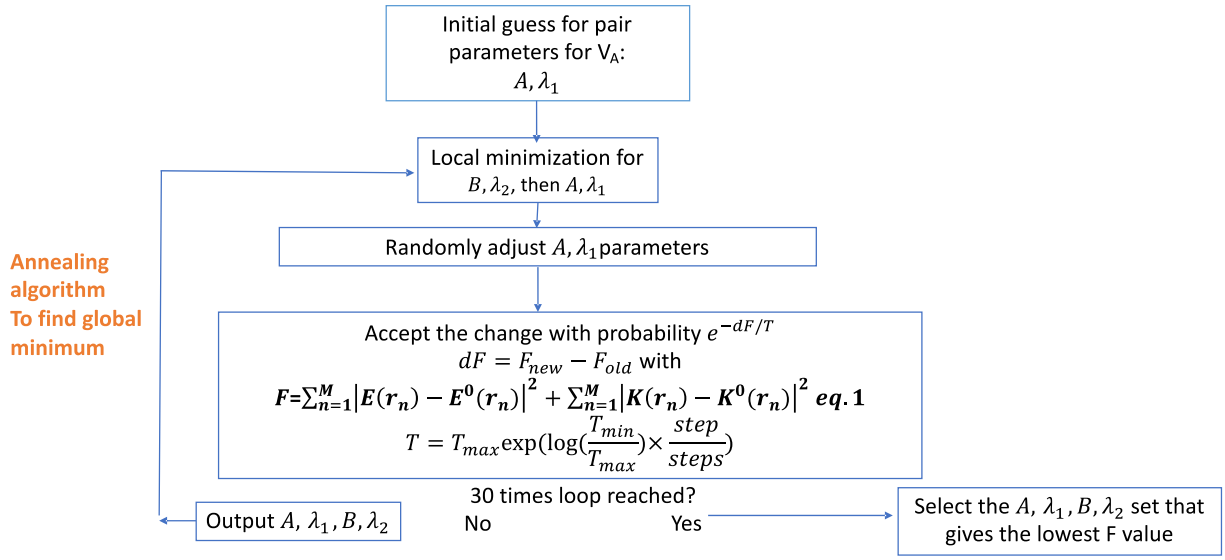


Figure S1 Annealing algorithm training scheme for two-body parameters.

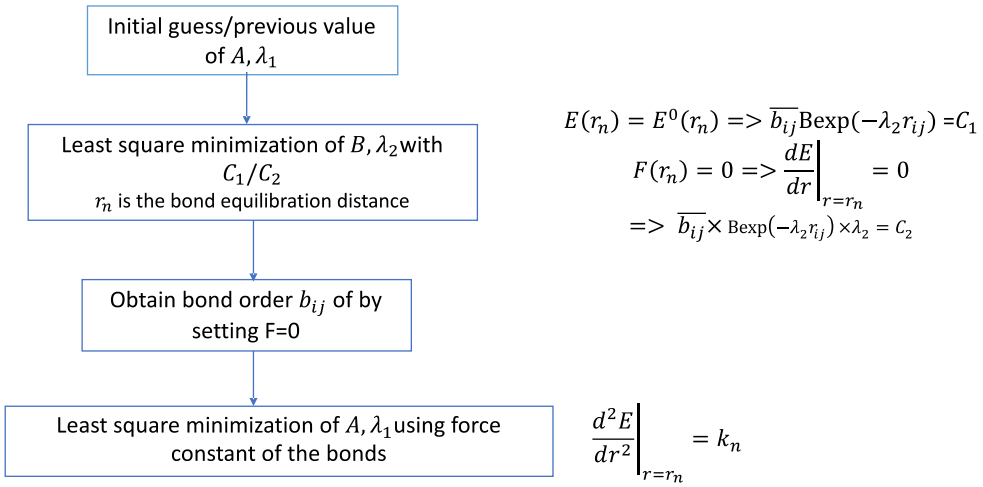


Figure S2 Local minimization scheme as mentioned in the annealing algorithm.

Eq.1 in Fig. S1 is our error function, which tries to minimize the difference in bond energy (E), force (which=0 as we require it to be during local minimization) and force constant (K) in multiple structures at their bond length (DFT value). The fitted results for the two-body parameters are shown in Table S3.

Table S3 Fitted two-body parameters using annealing algorithm. R_{min}=R-D and R_{max}=R+D are set to be the average value from Ge-Ge and Cl-Cl cutoff distances.

Fitted Parameters	**Ge-Cl**
A (eV)	521.8338
B (eV)	62.9673
$\lambda_1(\text{Å}^{-1})$	2.3248
$\lambda_2(\text{Å}^{-1})$	0.9857
$r_{min}(\text{Å})$	2.53
$r_{max}(\text{Å})$	2.83

Bond energy and force constant calculated using the above fitted value are shown in Fig. S3 and Fig. S4. Notice in Fig. S3, $GeCl_3$ (bond length 2.27 Å) has an abnormal shallow bond strength comparing to other $GeCl_n$ case, which is hard to capture with the basic Tersoff formalism. Its low bond energy indicates its instability, as this product also seems hard to detect in reality. So one

consequence of our current fitting is we overestimated the bond energy of $GeCl_3$ and will make it one of the possible etching products.

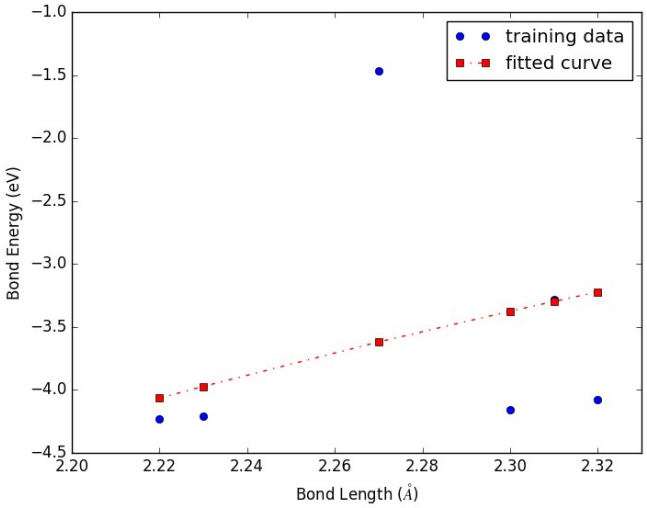


Figure S3 Bond energy fitting curve.

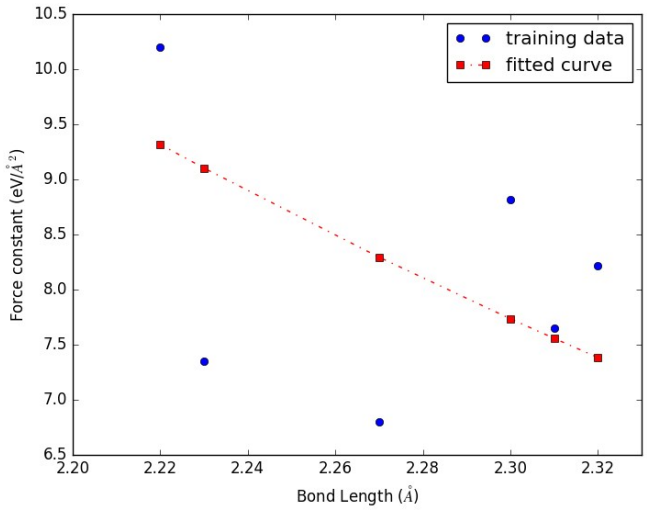


Figure S4 Force constant fitting curve.

Once these two-body term parameters are fixed, the bond order value b_{ij} can be calculated (by setting force F=0) and used to train its parameters. Following previous literatures,[6] i-j-k atom type combinations can be categorized in the way shown in Table S4.

Table S4 Data set for different i-j-k atom type combinations.

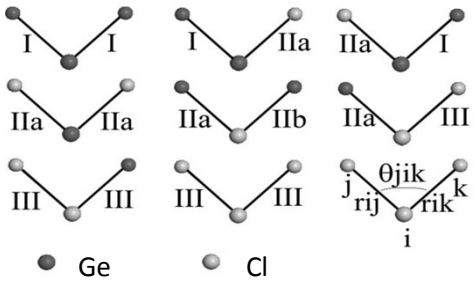
j	**i**	**k**	**n,** β	**g(**θ**), m,** λ_3

Ge	Ge	Ge	GeTersoff[a]	GeTersoff[a]
Ge	Ge	Cl	GeTersoff[a]	GeTersoff[a]
Cl	Cl	Cl or Ge	Cl with others & Cl-ClDavid[b]	Cl with others & Cl-ClDavid[b]
Cl	Ge	Cl	Fitting data	GeTersoff[a]
Cl	Ge	Ge	Fitting data	GeTersoff[a]
Ge	Cl	Ge	Fitting data	Cl with others & Cl-ClDavid[b]
Ge	Cl	Cl	Fitting data	Cl with others & Cl-ClDavid[b]

[a] Tersoff, PRB, 39.8 (1989):5566-5568

[b] David Humbird and David B. Graves, JCP, 120, 2405 (2004)

* The three-body term parameters in g(θ), along with m and λ_3, are approximated to the values in either Ge-Ge-Ge or Cl-Cl-Cl case, depending on the central atom type, since their angles are within 10 ° difference and bij values within 0.2 difference. Also, the number of training data is far less than the number of parameters, so some of the parameters need be fixed and this is a reasonable approximation.



Least square optimization is used to fit the different parameter sets. Training results are shown in the following.

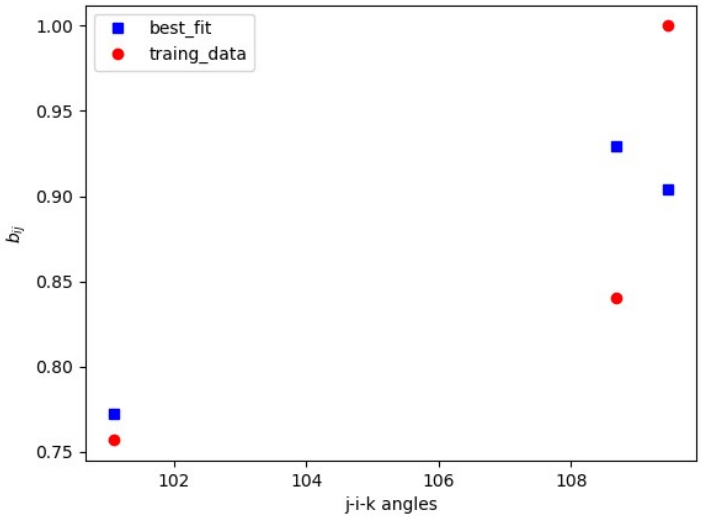


Figure S5 Training results for Cl-Ge-Cl case.

- Training results for Ge-Ge-Cl case

  Target b_{ij}: 0.9507, trained b_{ij}:0.9879

- Training results for Cl-Ge-Ge case

  Target b_{ij}: 0.8188, trained b_{ij}: 0.7978

Table S5 Fitted parameters in bond order bij term.

j-i-k Parameters	**Cl-Ge-Cl**	**Cl-Ge-Ge**	**Ge-Cl-Ge**	**Ge-Cl-Cl**	**Ge-Ge-Cl**
m	3.0	3.0	1.0	1.0	3.0
γ_{ijk}	1.0	1.0	4.0	4.0	1.0
λ_3	0.0	0.0	6.0	6.0	0.0
c	1.0643e5	1.0643e5	0.0	0.0	1.0643e5
d	15.652	15.652	1	1	15.652
$cos\theta_0$	-0.43884	-0.43884	1	1	-0.43884
n	2.23669	0.67543	1	1	0.75627
β	1.234e-4	1.0273e-5	1	1	9.02e-7

2. Ge surface relaxation at room temperature

The Ge surface was equilibrated under NPT condition (T=300 K, anisotropic zero pressure in x and y direction (the surface plane)). As shown in Fig. S6 a) and b), the original minimization

leads to a Ge lattice constant of 5.657 Å (exp: 5.652 Å,[9] DFT: 5.668 Å). At 300 K, some surface dimers appear to form (2x1) reconstruction (Fig. S6 c) and d)), consistent to experimental observations.[10] The simulated average dimer bond length is 2.53 Å (averaged over 15 dimers, with standard deviation=0.077 Å), fits well to the DFT value of 2.53 Å and experimental value between 2. 42 Å[10] and 2.55 Å[11]

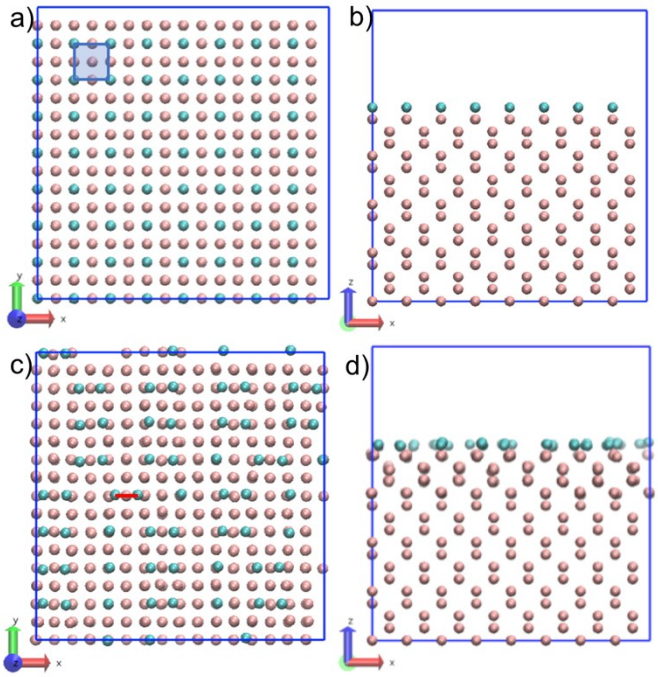


Figure S6 Ge surface minimization a) top view b) side view. Ge surface equilibration at 300 K c) top view d) side view. Green atoms represent top Ge surface layer, red is for other layer Ge. x: [110], y:[-110], z:[001].

3. Other characterizations in chlorination and bombardment process

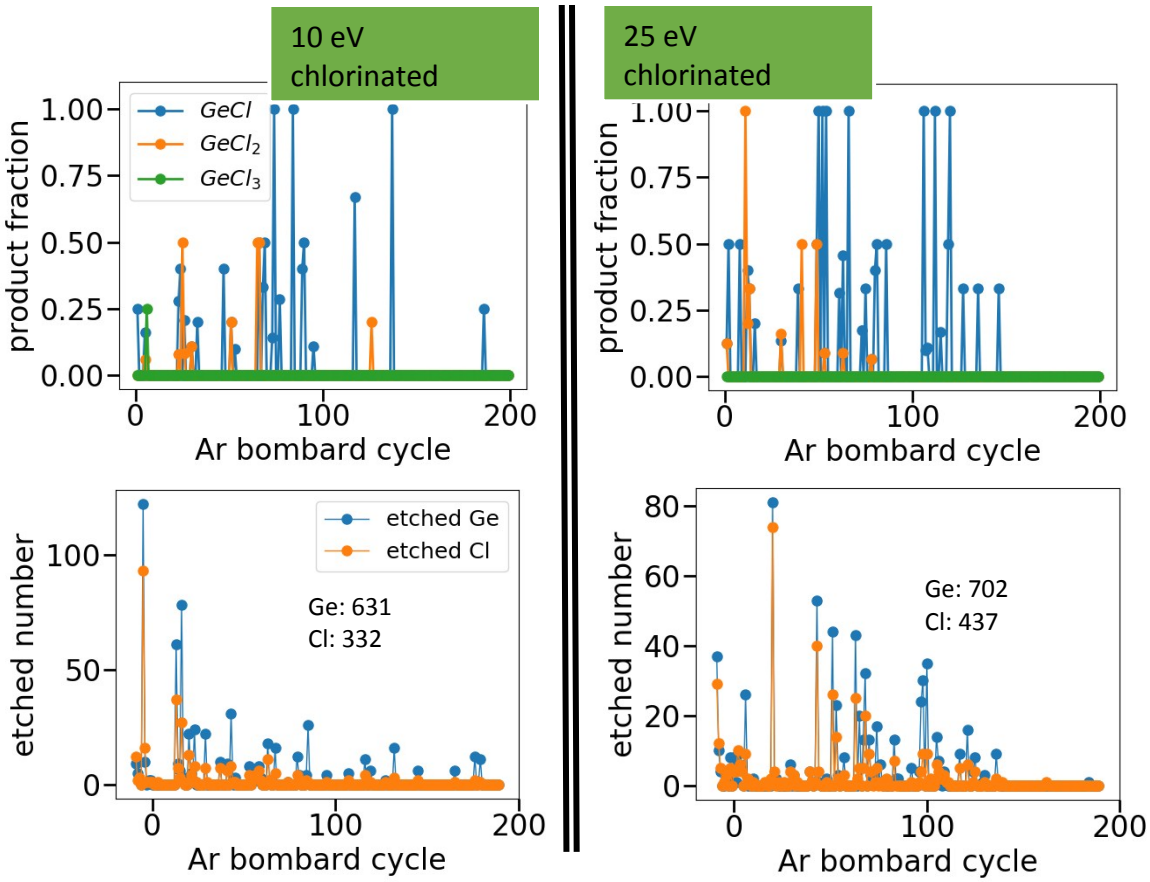


Figure S7 Etched products percentage (GeCl, $GeCl_2$ and $GeCl_3$) and element etched number change with Ar bombardment cycle for 10 eV and 25 eV chlorinated surface. The insets number on etched number graph shows the total etched Ge and Cl number. Sample 1 is used as an example here.

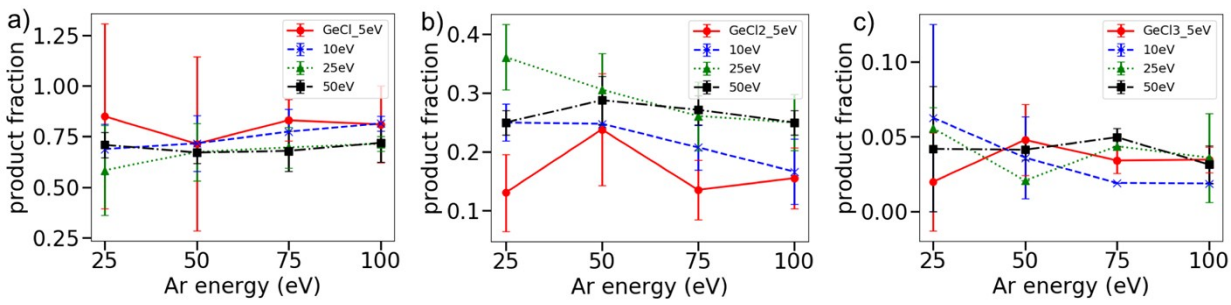


Figure S8 Product fraction (only consider $GeCl_n$ products) of a) GeCl, b) $GeCl_2$ and c) $GeCl_3$, averaged from 3 samples with error bars added.

Table S6 Total etched product numbers after 200 Ar bombardment cycles under each condition

5 eV chlorination	**Ar 25 eV**	**Ar 50 eV**	**Ar 75 eV**	**Ar 100 eV**
GeCl	13 ± 7	15 ± 9	49 ± 6	47 ± 11
$GeCl_2$	2 ± 1	5 ± 2	8 ± 3	9 ± 3
$GeCl_3$	0.3 ± 0.5	1 ± 0.5	2 ± 0.5	2 ± 0.5
10 eV chlorination				
GeCl	11 ± 2	26 ± 5	41 ± 6	44 ± 2
$GeCl_2$	4 ± 0.5	9 ± 0	11 ± 2	9 ± 3
$GeCl_3$	1 ± 1	1.3 ± 1	1 ± 0	1 ± 0
25 eV chlorination				
GeCl	21 ± 8	33 ± 7	48 ± 7	60 ± 3
$GeCl_2$	13 ± 2	15 ± 3	18 ± 4	21 ± 4
$GeCl_3$	2 ± 0.5	1 ± 0	3 ± 0	3 ± 2.5
50 eV chlorination				
GeCl	34 ± 3	49 ± 4	55 ± 8	69 ± 9
$GeCl_2$	12 ± 1	21 ± 3	22 ± 2	24 ± 2
$GeCl_3$	2 ± 1.6	3 ± 0.5	4 ± 0.5	3 ± 1.2

(averaged from 3 samples with standard deviation).

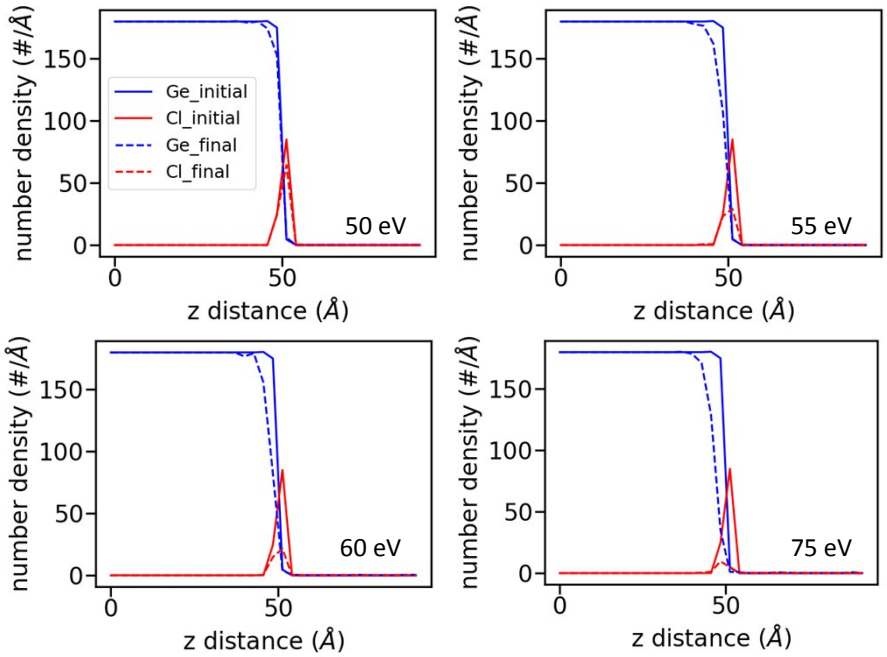


Figure S9 Density profile of Ge and Cl element evolution under different Ar bombardment energy on 5 eV chlorinated surface.

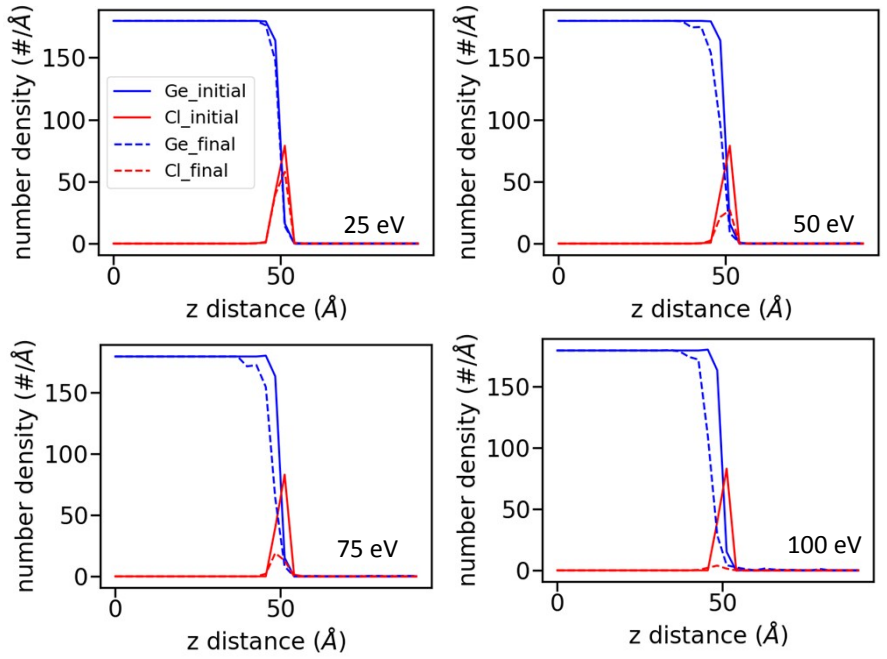


Figure S10 Density profile of Ge and Cl element evolution under different Ar bombardment energy on 10 eV chlorinated surface.

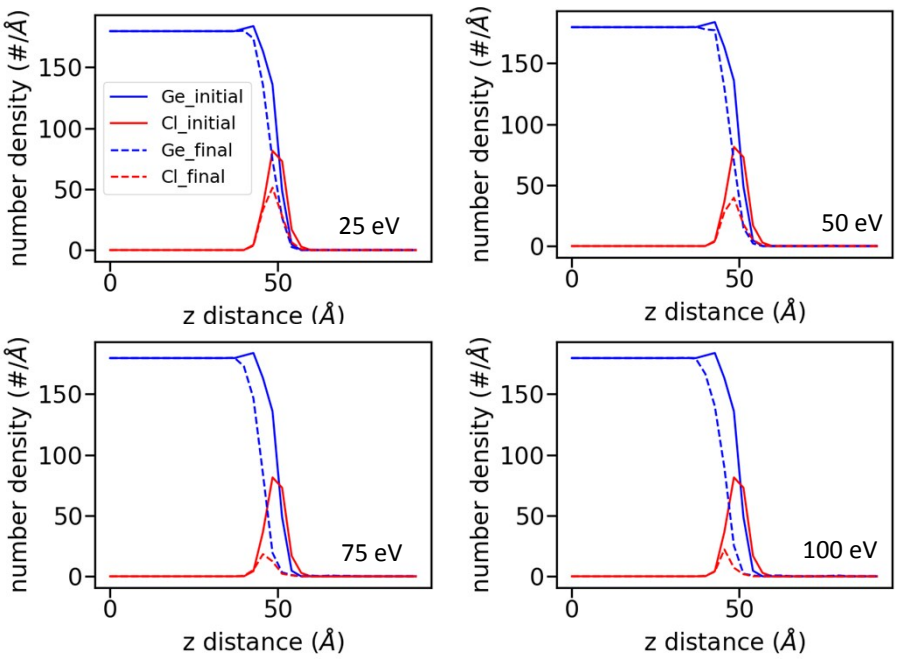


Figure S11 Density profile of Ge and Cl element evolution under different Ar bombardment energy on 50 eV chlorinated surface. Sample 1 is used.

References

1. J. Tersoff, *Physical Review B*, 1988, **37**, 6991.
2. J. Tersoff, *Physical Review B*, 1989, **39**, 5566-5568.
3. P. C. Kelires and J. Tersoff, *Physical Review Letters*, 1989, **63**, 1164-1167.
4. D. Humbird and D. B. Graves, *The Journal of Chemical Physics*, 2004, **120**, 2405-2412.
5. W. B. Donald, A. S. Olga, A. H. Judith, J. S. Steven, N. Boris and B. S. Susan, *Journal of Physics: Condensed Matter*, 2002, **14**, 783.
6. C. F. Abrams and D. B. Graves, *Journal of Applied Physics*, 1999, **86**, 5938-5948.
7. M. V. Ramana Murty and H. A. Atwater, *Physical Review B*, 1995, **51**, 4889-4893.
8. S. P. Walch, *Surface Science*, 2002, **496**, 271-286.
9. M. T. Yin and M. L. Cohen, *Physical Review B*, 1982, **26**, 5668-5687.
10. S. Pflanz, R. Buchtler, W. Moritz and H. Over, *Physical Review B*, 1996, **54**, R8313-R8316.
11. X. Torrelles, H. A. van der Vegt, V. H. Etgens, P. Fajardo, J. Alvarez and S. Ferrer, *Surface Science*, 1996, **364**, 242-252.