

## **Formation of Ion Cluster During Bombardment of Ice Surface by Low-Energy Ar<sup>+</sup> Ions**

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**Abstract:** The process of sputtering of ice film with doped Na<sup>+</sup> ions covering the Au (111) surface was studied. It was found that sputtering of a large ion cluster is observed due to the polarity of ice during ion bombardment. The size of the sputtered ion cluster depends on the polarization of water molecules. At the bombardment by Ar<sup>+</sup> ions, it was found that in the presence of a Na<sup>+</sup> ion, an ice cluster consisting of several water molecules is formed on the ice surface. The results obtained are of great interest when cleaning metal surfaces from various types of films.

**Keywords:** Sputtering, thin films, computer modeling, cluster.

### **Introduction**

The possibilities of obtaining information about the composition of the outer atomic layer of a solid have been greatly expanded by the development and improvement of secondary ion mass spectrometry (SIMS) and other methods. Most of these methods are close to analyzing the surface itself, since the main information about the composition of the material comes from its near-surface region, and the sensitivity of all such methods is sufficient to detect small fractions of the monoatomic layer of most elements.

The interaction of fast ions with a solid body results in the knocking out of atoms and molecules of the material, both in neutral and charged states. The SIMS method is based on this phenomenon of comparatively effective formation of charged particles (secondary ions) and on the principle of highly sensitive mass spectrometric measurements [1,2].

The most important value in the question of the capabilities of SIMS as a method for surface analysis is the relationship between the parameters of the primary ion beam, the surface sputtering rate, and the sensitivity threshold for elements [3]. Recently, there has been interest in studying the sputtering of thin films, including ice films. Ionized molecular water clusters have been studied experimentally and theoretically in [4-7]. It took about 100 years until the physical processes involved in sputtering and about another 20 years until a quantitative description of the sputtering process for keV ions had been developed. For energies in the 100 eV to the keV range sputtering is caused by atomic collisions between the incoming particles and the atoms in the surface layers of a solid, i.e. the incident particles initiate a collision cascade between the lattice atoms in the solid. In this paper, we will discuss the sputtering of ice film, covered on Au(111) under bombardment by Ar<sup>+</sup> ions by low energy. We will study some snapshots of sputtering process.

## Method of investigation

In this paper we will discuss the results of sputtering ionized water clusters obtained by the molecular dynamics method. Molecular dynamics (MD) is a computer simulation technique that allows one to trace the evolution of a system of interacting atoms over time by integrating the equations of motion. An undoubted advantage of the MD method is the ability to simulate a system at a given temperature or at given velocities of atoms (ions) with a sufficiently high calculation speed [8-10].

Currently, MD is used in quantum chemistry and solid-state physics for: - studying defects in crystals, ranging from point to linear and flat; - reconstructing the surface of a crystal, associated with the rearrangement of the coordinates of many atoms on the surface. It can be described using MD, and it is possible to track the change in the surface depending on the temperature; - studying clusters, the size of which varies from several atoms to several thousand, MD is mainly used for the procedure of numerical annealing during geometry optimization.

To describe the water-water interaction in our work, we chose the SPC [11] potential. This potential has been successfully used in studying the properties of water in solid, liquid and gaseous states.

In the SPC model, the interaction potential consists of an electrostatic component between two atoms. The Lenhardt-Jones potential was chosen to describe the repulsive part of the potential between the oxygen atoms. The total potential of water looks like this:

$$U_{\text{inter}} = U_{\text{LJ}} + U_{\text{electrostatic}} = 4 \zeta_0 \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{i=1}^3 \sum_{k=1}^3 \frac{q_{ik} q_{jl}}{4\pi\sigma_{kl}}$$

where  $r_{ij}$  are the distances between oxygen atoms.

Electrostatic interactions of water are used to create a pure dipole-dipole interaction of repelling and attracting parts of ions. Therefore, corrections due to the force setting have the appearance of repulsion. Calculations of the structure and dynamic properties of liquid water using variable forces changed potentials and had good agreement with the experimental results.

**Au-Au interaction** The corrected potential of the MD/MONTE CARLO function is presented. i.e. fcc of metals [12]. This potential describes the properties of Au very well. It should be noted that with the help of this potential it is possible to show the nature of the surface energy of Au atoms more realistically. Also with the help of this potential the thermal properties of Au were studied [13]. This potential was used in the study of monolayers on a gold substrate [14].

To describe the Au - H<sub>2</sub>O interaction, we chose the Spohr potential [15], which was used for the adsorption of water molecules on the Ni (100) surface.

In our calculations, we considered the case where the Na<sup>+</sup> ion is located at the top of a film consisting of four layers of ice on the Au (111) surface, which consists of 1980 atoms located on eight layers. The system was observed for 25 picoseconds, and external influences were not taken into account in this case. This time is enough for the ion to approach the surface of the film and form ionic bonds with oxygen atoms. During the above-mentioned time, the sodium ion is completely located on the first upper layer of the film.

Structural changes in the film occur mainly only around the location of the ion. The rest of the film completely retains its original structure.

## Results and discussion

We have investigated the process of sputtering a water film containing an implanted Na<sup>+</sup> ion. This process is a very interesting mechanism of sputtering molecules and atoms in the form of large clusters. The sodium ion located inside the film forms ionic bonds with its molecules.

These bonds primarily depend on the charge of the ion. i.e., if the ion is positive, then negative components of the molecules accumulate around it or vice versa.

Figures 1-2 show the sputtering pattern of the Au (111) surface covered with a water film under bombardment with  $\text{Ar}^+$  ions with an initial energy of  $E_0 = 400$  eV. The interaction process of the target with the incident particle lasted for a time of  $t=4$  picoseconds. The case under consideration differs from the previous one in that we use boundary conditions and the sodium ion is located on the upper layers of the film.

Fig. 1a shows the state of the target before bombardment. Here it is clearly seen that the sodium ion located on the upper layer already has ionic bonds with oxygen atoms. This explains the changes in the film structure associated with the sodium ion.

Fig. 1b shows the state of the target at a bombardment time of  $t = 0.4$  picoseconds. The figure clearly shows that the incident particle is repelled from the surface of the film after interaction. This is due to the fact that the initial energy of the incident particle is not sufficient to penetrate deeper into the target. During the specified time of interaction of the ion with the target, significant changes mainly occur in the upper two layers of the film. It should be noted that at this time, due to the energy of the falling particle, the film molecules are sprayed on the surface.

Figure 1c shows the change in the surface at a bombardment time of  $t = 0.8$  picoseconds. It is clearly seen that at this time the sputtering process is already observed in a large volume. By this time the sodium ion, surrounded on all sides by water molecules, begins to leave the surface. It should also be noted that the substrate atoms mainly perform vertical oscillatory movements near the collision point on the upper seven layers of the substrate. Some of these gold atoms are located between the film and the substrate, which leads to intense sputtering of the film molecules.

Further development of the interaction process showed that due to the vibration of gold atoms near the film, the film molecules begin to sputter in the entire surface volume, including all layers of the film. This occurs at a bombardment time of  $t = 1.2$  picoseconds (Fig. 1d). From this figure it is evident that the film structure is completely destroyed, the concentration of molecules increases on both its parts, while in the middle of the target it decreases, and at the same time, molecules begin to accumulate around the sodium ion.

The vibrational movements of gold atoms in the top layer of the substrate act on the sputtering process, pushing the film molecules towards the vacuum.

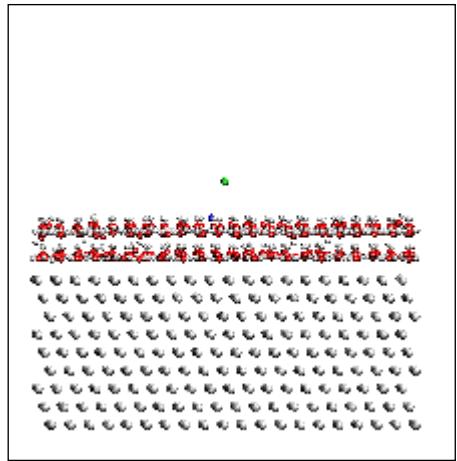
When the interaction time reaches  $t = 1.6$  picoseconds (Fig. 2a), the sodium ion together with the water molecules begins to move away from the film surface, while the molecules around it form a large spherical cluster due to the forces of attraction. At the same time, a spray of small molecular clusters consisting of 2-7 molecules is observed around this cluster. An accumulation of water molecules not participating in the spray is also observed on the film surface itself, which is explained by the superiority of the bond energy between the surface molecules compared to the kinetic energy of these molecules.

By this time of bombardment, the oscillations of the substrate atoms continue, but with the smallest amplitude values. Our calculations showed that these oscillations continued for 4 picoseconds. Therefore, when describing the following states of the target, we will not dwell on these insignificant oscillations of gold atoms. which has managed to separate from the film surface. It should be noted that this cluster appears to be quite unstable, since some molecules can leave it.

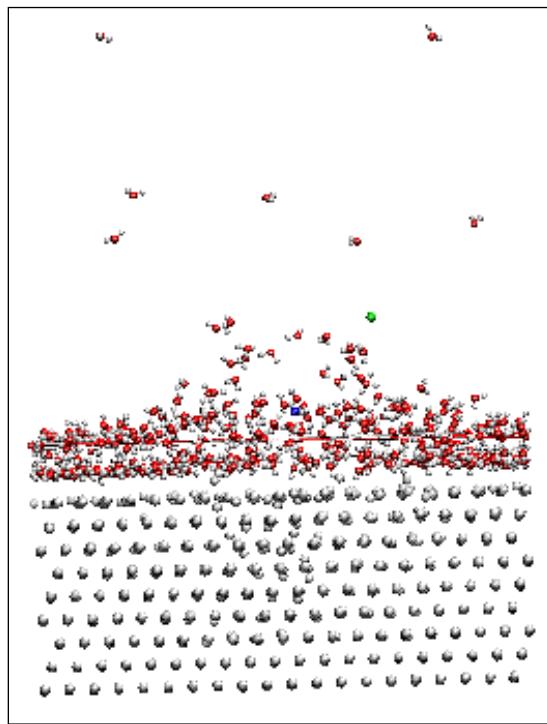
After the ion cluster is removed from the film, surface movements and sputtering of film molecules are observed (Fig. 2c-d). This occurs due to the continuing distribution of energy received from the incident particle between water molecules and gold atoms on the target.

At a bombardment time of  $t = 2.8$  picoseconds (Fig. 2d), the ion cluster acquires a shape close to a sphere. Our calculations showed that the ion cluster acquires a final, uniform shape at a bombardment time of 4.5 picoseconds. In our calculations, we considered the state of the ion cluster for a time of 25 picoseconds without the influence of the target. From the calculations it is clear that during this time the cluster did not undergo significant changes, which indicates the stability of its structure.

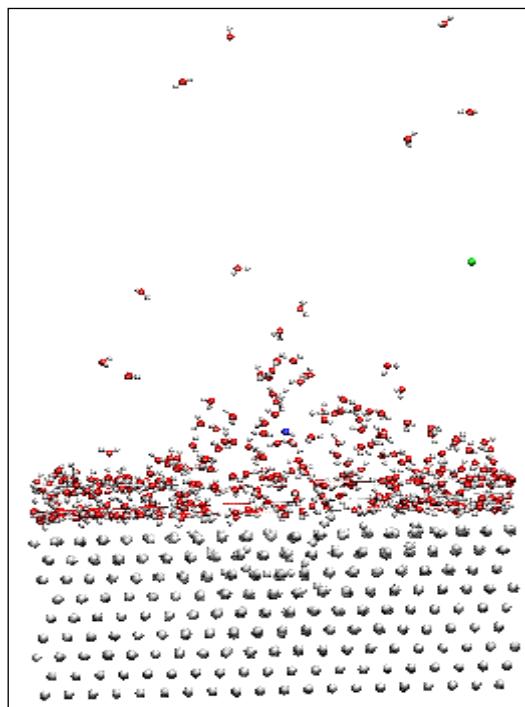
a (  $t = 0$  picoseconds)



b (  $t = 0.4$  picoseconds)



c (  $t = 0.8$  picoseconds)



d (  $t = 1.2$  picoseconds)

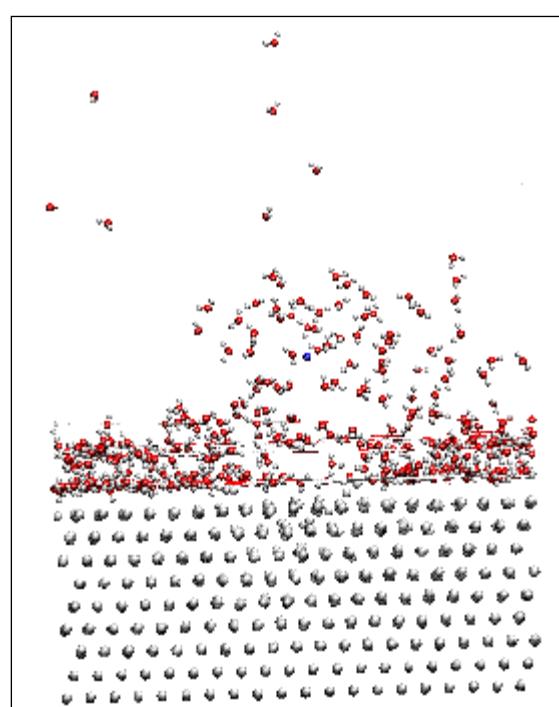
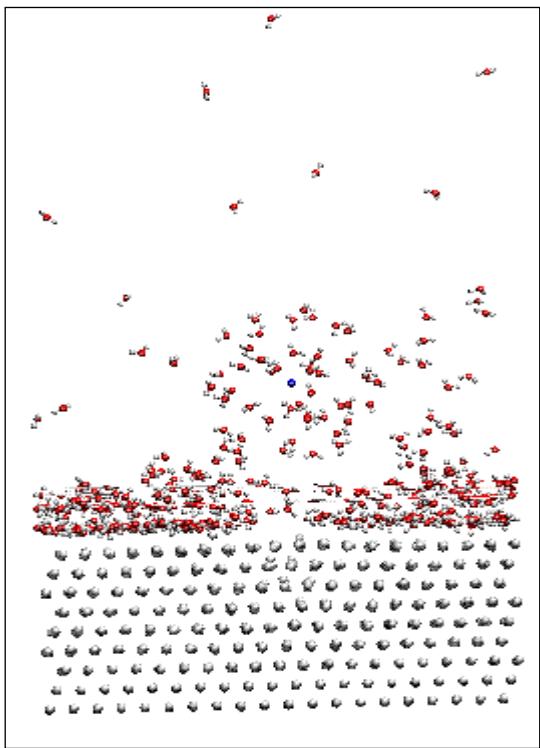
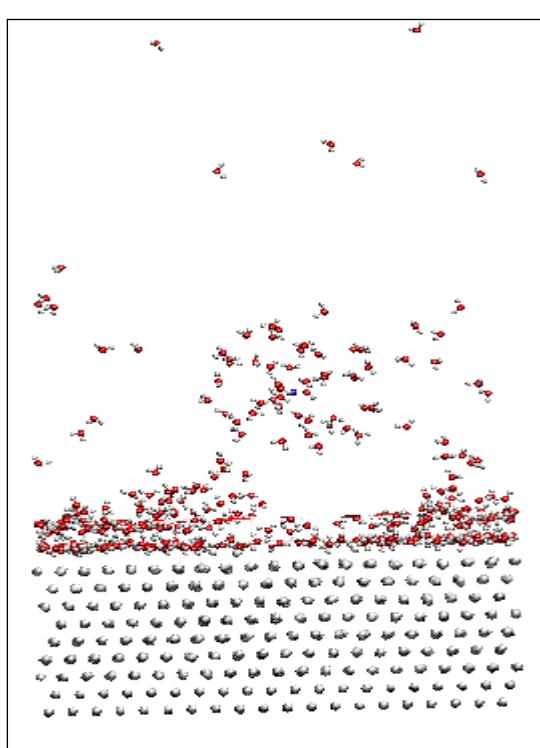


Fig. 6.1. Sputtering process up to 1.2 pcsec during bombardment with  $\text{Ar}^+$  ions with  $E_0 = 400$  eV of an ice film with an implanted  $\text{Na}^+$  ion (ion on top of the film), covered on the surface of gold

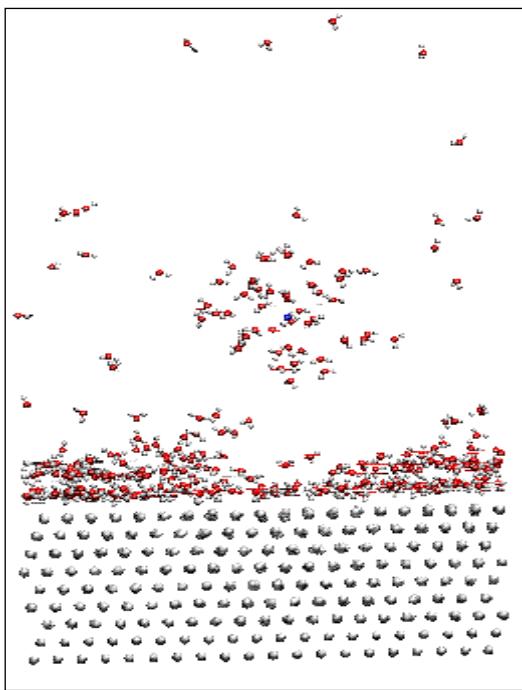
a (  $t = 1.6$  picoseconds)



b (  $t = 2$  picoseconds)



c (  $t = 2.4$  picoseconds)



d (  $t = 2.8$  picoseconds)

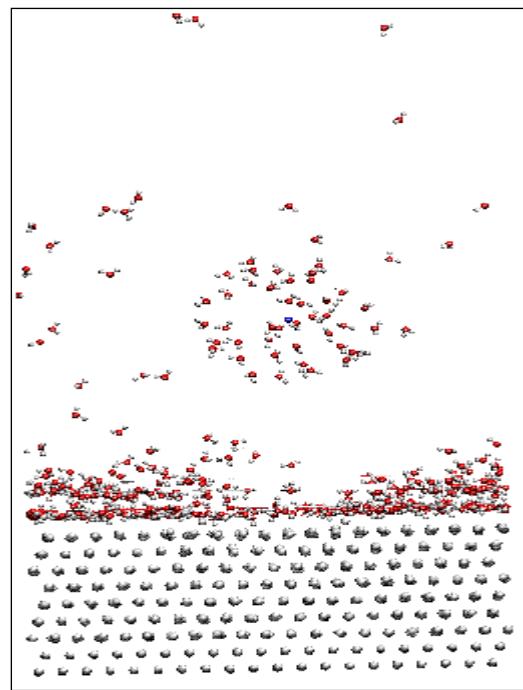


Fig.2. Sputtering process from 1.6 px sec to 2.8 pcsec during bombardment with  $\text{Ar}^+$  ions with  $E_0 = 400$  eV of an ice film with an implanted  $\text{Na}^+$  ion (ion on top of the film), covered on the surface of gold

Fig. 2b shows the state of the target at an interaction time of  $t = 2$  picoseconds. It is evident that by this time the formation of a molecular ion cluster is observed.

## Conclusion

Using the molecular dynamics method, we have studied the process of sputtering an ionized ice film covering a metal surface. In our calculations, we considered the case when the  $\text{Na}^+$  ion is located in the upper part of the film consisting of four layers of ice on the Au (111) surface, which consists of 1980 atoms located on eight layers. Structural changes in the film occur mainly only around the location of the ion. The rest of the film completely retained its original structure. When bombarding an ice film with an implanted  $\text{Na}^+$  ion with  $\text{Ar}^+$  ions with  $E_0 = 400$  eV, sputtering of ice molecules and a large ionized cluster of molecules were observed. The results obtained are useful in studying the process of cleaning metal surfaces from different types of films.

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