

Mass Spectrums of Sputtered Clusters from Ice Films, Covered Surface Au(111)

K. U. Otabaeva, M. K. Karimov*, U. O. Kutliev

Department of Physics, Urgench State University, Kh. Alimdjan str. 14, Urgench City, 220100, Uzbekistan

Received: 21 Mar. 2024, Revised: 24 May 2024, Accepted: 19 Jun. 2024.

Published online: 1 Sep. 2024.

Abstract: This paper presents the calculated mass spectra of sputtered Au(111) particles coated with ice films upon bombardment with low-energy Ar⁺ ions. It is shown that the introduction of ions into the ice film formed molecular clusters, water molecules, and clusters of water molecules and clusters consisting of water molecules and Au atoms at the ion bombardment. These clusters formed the corresponding intense peaks in the mass spectra. It has been established that the largest cluster is formed due to the implanted ion on ice films. The sputtering coefficient of ion clusters is also calculated.

Keywords: films, sputter, ion bombardment, mass spectrum, cluster, computer simulation.

1. Introduction

Currently, one of the important and open problems of sputtering physics is still the presence of emission sputtering products of multimolecular clusters [1-3]. The very nature of the processes underlying the formation of clusters during sputtering remains largely unclear. This moment the collision cascade model during sputtering is one of the main models explaining this process. However, how and how the clusters leave the surface can be different. These differences led to the discovery of two models of cluster formation. One of them is the recombination model. In this model, a cluster is formed as a result of the union of sputtered atoms above the surface, if the moments of emission times differ insignificantly. In addition, the relative kinetic energy does not exceed the cluster dissociation energy [4]. The second model of direct emission considers clusters as a whole. The cluster leaves the surface as a result of energy transfer to a group of surface atoms, and these atoms leave the surface without breaking the bond between them [5-7]. Due to the complexity of the analytical description of cluster emission during ion sputtering of solid surfaces, considerable attention has been paid to computer simulation of cluster formation under the action of ion bombardment. Such a method makes it possible not only to describe the process of formation and emission of clusters from the surface, but also makes it possible to explain the presence of a high energy of vibrational excitation in them and to take into account the processes of fragmentation of metastable particles. The work carried out in the 1970s-1990s was devoted to studying the formation of clusters during sputtering by atomic ions. The results of computer simulation show both a good degree of agreement with experiments and evidence of a significant similarity

between the results of different research groups. Therefore, we can talk about a certain general picture of the processes of formation and emission of cluster particles under the action of ion bombardment, obtained using this method. The most detailed description of computer simulation of cluster formation processes during sputtering of a solid body surface using molecular dynamics simulation was studied the emission of clusters for the case of ion bombardment of solid bodies. The emission of sputtered atoms and the development of a cascade of collisions lasted up to 1 ps, which is much longer than the sputtering time of particles. Based on the fact that emitted clusters are excited and decay into smaller particles due to monomolecular decay, 100 ps is sufficient for all emitted particles to decay. In this case, however, two different types of processes can be distinguished, leading to the emission of clusters under the action of ion bombardment. The first type causes the emission of small clusters, which are emitted through collective motion during the development of the collision cascade in the first few picoseconds after the collision. Thus, the emission times of such clusters are consistent with the emission times of atoms during sputtering. The release of energy by an incident ion, which causes the development of a cascade of collisions, can lead to the emission of neighboring surface atoms, which eventually form a cluster. This type of process can be considered if, for example, energy recoil atoms cause the development of subcascades several layers below the surface. In such an event, the energy transferred to the surface is strictly directed and can lead to the simultaneous emission of a group of neighboring surface atoms, which in some cases remain bound and form a cluster after emission, if the conditions of simultaneous emission and almost parallel pulses are satisfied. Typically, clusters emitted through this mechanism consist of atoms that are neighboring in the

*Corresponding author E-mail: karimov_m_k@mail.ru

target and almost exclusively surface atoms, which is about 95% when the surface is bombarded by Ar^+ ions with an initial energy of 5 keV. Clusters of large size are formed in the water-metal contact region during ion bombardment. The water-metal interaction process plays an important role in many of the steps used by industries. These processes include electrochemical, wetting, corrosion, and photocatalysis [8–10]. Theoretically, a number of works have been done to study the interaction of water and solid surfaces by simulation [11–13]. Studying sputtering of a thin layer of ice is important both theoretically and practically. Therefore, right now we have some experimental and theoretical results about ice sputtering. However, the works, which carry out about sputtering ionic ice are too few. In [14], the mass spectra of sputtered particles of a frozen aqueous solution containing HCl upon bombardment by fast atoms was present. Spectra of $(\text{H}_2\text{O})_n\text{H}^+$ clusters were formed in this mass spectrum. The pattern of clusters was discussed in the light of the formation of crystalline hydrate phases in a frozen solution. Ionized molecular ice clusters have been studied experimentally and theoretically in [15–16]. However, the distribution mechanism itself is not sufficiently described. In this article, we will discuss the results of sputtering of ionized ice clusters obtained by the molecular dynamics method.

2. Method and results

We have studied the process of water film sputtering, which contains Na^+ ions in its composition. This process is a very interesting mechanism for 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 molecular components accumulate around it, or vice versa. In our simulation, we used the method of molecular dynamics. Numerical solution of Newton's equations for interacting particles is the basis of the method of molecular dynamics. This method often uses the Lennard-Jones potential. And this potential describes the dynamics of the system, as the interaction of molecules in the form of balls. In this case, the force of interaction between particles depends only on the distance between them. To obtain a more accurate estimate of the macroscopic parameters of the system, periodic boundary conditions are used, and to integrate the equations of motion, the Verlet algorithm in the velocity form is usually used. Modeling using the standard algorithm indicates its criticality to the choice of the time step, and its decrease leads to an increase in computational costs, and its increase leads to a drop-in accuracy up to the divergence of the algorithm due to the possibility of acquiring too high velocities at very small distances between colliding molecules. This problem is partially solved by programmatic checking and limiting the range of input parameters. As an alternative solution to this problem, the

possibility of automatic reduction of the sampling step is considered. In this case, if the path traveled by the atom in the set time step ΔT exceeds some critical distance Δr (set by the user), the time step is iteratively reduced until the path traveled is within the specified limits. As a result, the new time step meets the condition $\Delta t < \Delta T$, and for a molecule that has exceeded the displacement limit, $n = \Delta T / \Delta t$ cycles of parameter calculation are performed, and only then the algorithm proceeds to the next atom. Thus, the reduction of the time step occurs only where it is needed, which improves the overall efficiency of the calculations. Molecular dynamics (MD) is one of the computer simulation methods that allows one to consider the evolution of interacting particles over time and can make it possible to visually observe the behavior of a system. The main advantage of the MD method is the possibility of modeling the process for a given physical (chemical) parameter. And, therefore, get a more realistic picture of the process. Currently, MD is used in many scientific studies not only in physics, but also in chemistry, solid-state physics and others:

- almost all types of defects in crystals.
- changes in the surface structure of the crystal under external influences.
- studying the formation and decay of clusters with a different size.
- study of different biological molecules.

When studying the sputtering of an ice film, the interaction potential is important. Thus, potentials described in [17]. In the interaction $\text{H}_2\text{O}-\text{H}_2\text{O}$ water-water, the SPC potential was used, and it was successfully used in the study of the properties of various structures. This potential consists of an electrostatic component between two atoms. The Lenhard-Jones potential is used to describe the repulsive part of the potential between oxygen atoms. Calculations of the structure and dynamic properties of liquid water using variable forces changed the potentials and were in good agreement with the experimental results. The Au-Au interaction also has a potential and describes the properties of Au very well. In the interaction of Au- H_2O , we chose the Spohr potential, which was used in the water molecules adsorption on metal surfaces. It mainly consists of the Morse potential. For ion-water interaction, the Coulomb potential and the Lenhard-Jones potential were used.

In our investigation, we considered the case when the Na^+ ion is in the upper part of the film, which consists of four layers of ice on the Au(111) surface, which consists of 1980 atoms located on eight layers. The system was under observation for 25 picoseconds, and external influences were not taken into account in this case. This time is sufficient for the ion to approach the film surface and form ionic bonds with oxygen atoms. During the above time, the sodium ion is completely located on the first upper layer of the film [17]. Structural changes in the film occur mainly

only around the location of the ion. The rest of the film completely retains its original structure.

We have considered the mass spectra of sputtered particles from the Au(111) surface covered by four layers of ice, which contains the Na⁺ ion in its composition at the bombardment by Ar⁺ ions at the normal incidence. The initial energy values were chosen as E₀=400 eV and E₀=700 eV.

Figure 1 shows the mass spectrum of sputtered particles from the indicated surface upon bombardment with Ar⁺ ions with an initial energy E₀=400 eV.

This mass spectrum can be divided into 3 groups. The first group is water molecules and molecular clusters containing from two to five water molecules in their composition. It should be noted that the highest peak belongs to water molecules, while the remaining peaks belong to molecular clusters located up to 100 a.m.u.

The second group of peaks located in the range of 200-240 a.m.u refers to sputtered clusters that contain one gold atom and 1-2 water molecules.

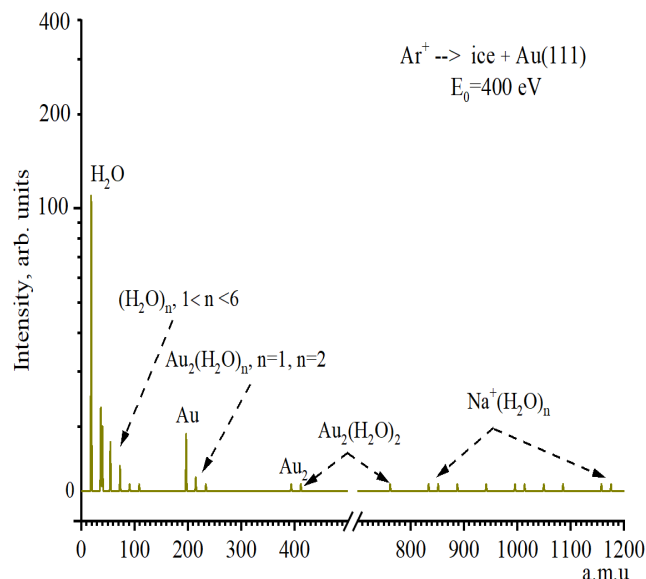


Fig. 1: Mass spectrum of sputtered particles from the surface Au(111) covered with four layers of ice film at the normal incidence of Ar⁺ ions with E₀=400 eV.

The next peaks that formed in the range of 400-800 a.m.u. belong to sputtered clusters that contain one or two water molecules with two gold atoms. Our calculations showed that gold atoms are sputtered when falling particles collide with an open part of the substrate. When the film is sputtered, these atoms capture one or two water molecules, since there is a certain interaction potential between them. The next group of peaks belongs to the ion cluster, which has a mass spectrum range from 820 to 1176 a.m.u. From the analysis of the trajectories of falling particles, it can be seen that not all trajectories form a large ion cluster, which contains the Na⁺ ion in its composition. In this case, 150

trajectories of the incident particle are considered.

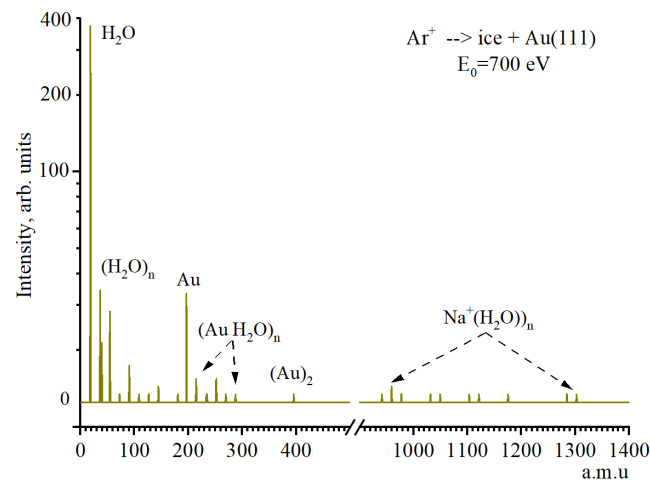


Fig. 2: Mass spectrum of sputtered particles from the surface Au(111) covered with four layers of ice film at the normal incidence of Ar⁺ ions with E₀=700 eV.

On the Figure 2 presents the mass spectrum of sputtered particles from surface of Au(111) covered with four layers of ice film at normal incidence of Ar⁺ ions and the initial energy was E₀=700 eV.

The mass spectrum shows that it differs from the mass spectrum, which is shown in Fig.1. It can be seen from the mass spectrum that the intensity of the peak attributable to Au atoms increased. Also, the Au+H₂O peak disappears, which is associated with an increase in the initial energy of the ion. Moreover, the peak «ion + ice» increased in mass, which is explained by an increase in the number of water molecules. It should be noted that almost all the peaks formed at E₀=4 keV are increased in intensity.

We have also calculated the sputtering coefficient of ionic clusters of water molecules coated on the Au(111) surface at the bombardment with Ar⁺ ions with an initial energy of E₀=400 eV. The sputtering coefficient for different types of ions is presented in Table 1. The results obtained are in good agreement with the experimental results, which are present in [15–16].

Table 1: Sputtering coefficient for different types of ions

Ions	Coefficient of sputtering
Li ⁺	0.22
Na ⁺	0.21
Cs ⁺	0.18

3. Conclusions

The process of sputtering during the bombardment of an ice film doped with Na⁺ ions, covering the surface of Au(111) by Ar⁺ ions with E₀=400 eV and 700 eV, has been studied. It has been established that sputtering of a large ion cluster is observed due to the polarity of ice during ion bombardment. It has been established that the formation of a more massive ion cluster, in the case when the doped ion

is located inside of this cluster. The mass spectra of sputtered particles were obtained during the bombardment of an ice film with doped ions, coated on the surface with Au(111) by Ar^+ ions. The mass spectrum showed peaks attributable to an ion cluster consisting of a doped ion, water molecules, clusters of gold, and a cluster consisting of “ Au^+ water molecules”. The sputtering coefficient of a positive cluster is calculated. It has been determined that the charge of a doped ion can form a bond with hydrogen (weaker bond) or oxygen (stronger bond) atoms.

References

- [1] H. W. Werner, R. P. Garten. A comparative study of methods for thin-film and surface analysis. *Reports on Progress in Physics*, **47**, 221 (1984). DOI 10.1088/0034-4885/47/3/001
- [2] T. L. Alford, L. C. Feldman, J. W. Mayer. Fundamentals of nanoscale film analysis, *Springer New York, NY*, (2007). <https://doi.org/10.1007/978-0-387-29261-8>
- [3] S. Hofmann. Sputtering: survey of observations and derived principles. *Philosophical Transactions of the Royal Society A*, **362**, 55 (2004). 2355–2366. <https://doi.org/10.1098/rsta.2003.1304>
- [4] Dzhemilev, N.K. Mechanism for the formation of molecular clusters under ion sputtering. *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, **6**, 654 (2012). <https://doi.org/10.1134/S1027451012080083>
- [5] P. A. Thiel, T. E. Madey. The interaction of water with solid surfaces: Fundamental aspects. *Surface Science Reports*, **7**, 211 (1987). [https://doi.org/10.1016/0167-5729\(87\)90001-X](https://doi.org/10.1016/0167-5729(87)90001-X)
- [6] A. Verdaguer, G. M. Sacha, H. Bluhm, and M. Salmeron. Molecular Structure of Water at Interfaces: Wetting at the Nanometer Scale. *Chemical Reviews*, **106**, 1478 (2006). <https://doi.org/10.1021/cr040376l>
- [7] A. Michaelides. Density functional theory simulations of water–metal interfaces: waltzing waters, a novel 2D ice phase, and more, *Applied Physics A*. **85**, 415 (2006). <https://doi.org/10.1007/s00339-006-3695-9>
- [8] M. C. B. Funel, A. Hassanali, M. Havenith, R. Henchman, P. Pohl, F. Sterpone, D. van der Spoel, Y. Xu, and A. E Garcia. Water determines the structure and dynamics of proteins. *Chemical Reviews*, **116**, 7673 (2016). <https://doi.org/10.1021/acs.chemrev.5b00664>
- [9] A. Nilsson, L. G. M. Pettersson. The structural origin of anomalous properties of liquid water. *Nature communications*, **6**, 8998 (2015). doi: 10.1038/ncomms9998
- [10] R. Shi, H. J. Tanaka. Microscopic structural descriptor of liquid water. *The Journal of chemical physics*, **148**, 124503 (2018). <https://doi.org/10.1063/1.5024565>
- [11] A. Hodgson, S. Haq. Water adsorption and the wetting of metal surfaces. *Surface science reports*, **64**, 381 (2009). <https://doi.org/10.1016/j.surfrep.2009.07.001>
- [12] Y. B.Tu, M.L.Tao, K.Sun, J.Z.Wang. Effects of an electric field on the adsorption of water molecules on the Cd (0001) surface. *Surface Science*, **668**, 1 (2018). <https://doi.org/10.1016/j.susc.2017.10.012>
- [13] S. Meng, E. G. Wang, S. Gao. Water adsorption on metal surfaces: A general picture from density functional theory studies. *Physical Review B*. **69**, 1 (2004). <https://doi.org/10.1103/PhysRevB.69.195404>
- [14] O. A. Boryak, M. V. Kosevich, I. Stepanov, V. Shelkovsky. Low temperature fast atom bombardment mass spectra of HCl water solution. *International Journal of Mass Spectrometry*, **189**, L1 (1999). [https://doi.org/10.1016/S1387-3806\(99\)00128-1](https://doi.org/10.1016/S1387-3806(99)00128-1)
- [15] O. A. Boryak, M. V. Kosevich, V. S. Shelkovsky, V. V. Orlov. Production of doubly charged clusters (H_2O) $n \cdot \text{Ba}_2^+$ and (H_2O) $n \cdot \text{Ca}_2^+$ under low temperature fast atom bombardment conditions. *Journal of Mass Spectrometry*, **194**, 49 (2000). [https://doi.org/10.1016/S1387-3806\(99\)00157-8](https://doi.org/10.1016/S1387-3806(99)00157-8)
- [16] L. Wang. Clusters of Hydrated Methane Sulfonic Acid $\text{CH}_3\text{SO}_3\text{H} \cdot (\text{H}_2\text{O})_n$ ($n=1-5$): A Theoretical Study. *The Journal of Physical Chemistry A*, **111**, 3642 (2007). <https://doi.org/10.1021/jp067893n>
- [17] U. Kutliev, K. Otabaeva, M. Karimov, I. Woiciechowski. Computer simulation of ice film sputtering from Au (111) surface. *Journal of Physics: Conference Series*, **2388**, 012012 (2022).