

Molecular Dynamics Simulations of Energetic Ar⁺ Bombardment of Ice Thin Films

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Abstract—Secondary ion mass spectrometry (SIMS) is a wonderful technique for providing mass spectrometric information of molecules on surfaces. Theoretical studies of the ion bombardment of organic films on metallic surfaces have contributed to our understanding of the mechanisms governing these processes. Many experiments of ion bombardment, however, are performed on thin films.

Keywords—computer simulation, cluster, sputtering.

The sputtering effect of the water molecules and their clusters from the water films covered on Au(111) surface at normal incidence have been investigated by molecular dynamic simulation. The mass spectra of sputtering particles which contains of several molecules have been calculated. The simulation clearly shows that the mass spectrum contains peaks of the water molecules, water clusters and Au atoms. These results are of interest for mass spectrometry of molecules, and study of surfaces.

Introduction

The bombardment of solid and organic molecules with energetic atoms or ions leads to the release of a variety of secondary particles from the surface. Provided that each emission event is caused by a single particle impact, this process is usually called sputtering. Besides atomic species, the flux of sputtered particles contains an abundant fraction of agglomerates of two or more atoms. These species, which will in the following be called "sputtered clusters", attract special interest in analytical mass spectrometric techniques like SIMS and SNMS for mainly two reasons. First, molecular signals can create mass interferences with atomic signals and may therefore disturb the interpretation of measured mass spectra. Second, on the other hand, the

interpretation of molecular signals can be extremely useful to obtain information about the chemical state of the investigated surface, provided the mechanisms leading to the formation and/or ejection of clusters during the sputtering process are sufficiently well understood. Hence, numerous studies have been devoted to the investigation of cluster emission in sputtering, a review of which is found in [1,2,3].

Recently experimental procedure has been developed by Barros et al. [4] to measure the water molecular yield Time-of-flight mass spectra were taken during the warming up of the ice from 10 to 216 K. Up to 30 K, the cluster ion yields are approximately constant, whereas between 30 and 75 K, they decrease gradually by a factor 6.5 and remain constant until 130 K. This procedure offers a reliable method to identify structural changes of water ice, such as phase transitions.

Killelea D.R et al. [5] presents the collision-induced sputtering of water molecules into the gas-phase from the ice surface. Sputtering is strongly activated with respect to xenon translational energy, and a threshold for desorption was observed. To best understand these results, they discussed the context of other sputtering studies of molecular solids. They show that the sputtering yield is quite small; differential measurements of the energy of xenon scattered from ice surfaces show that the ice efficiently accommodates the collision energy.

In this paper we first show that at the bombardment by low energy ions we can observe the sputtering of water molecules and clusters from the ice films. By the simulation method we calculate the time dependent behavior of a molecular system.

Computational methods

Below we give our choices for the interaction potentials for the H₂O-H₂O, Au-Au, and Au-H₂O

components of the system. At the end of this section, the details of the MD simulations are described. H₂O-H₂O interaction potential employed to describe the H₂O-H₂O interaction is the simple-point-charge (SPC) water potential developed by Berendsen et al.[6] This potential has been used extensively to study the properties of H₂O as a solid[7,8]. It has been shown that the SPC potential is able to reproduce many of the properties of bulk H₂O [9]. In the SPC model, the molecular interaction potential U_{inter} consists of an electrostatic component $U_{electrostatic}$ describing the charge-charge interaction between pairs of atoms in the two molecules. In order to describe the dispersion and repulsive interactions between the two oxygen sites, a Lennard- Jones function U_{LJ} is included.

The Au-Au interactions are represented by the MD/Monte Carlo corrected effective medium (MD/MC-CEM) potential function for fcc metals [10]. For metal-water systems a potential developed by Spohr [11] has been used. The Spohr potential consists of a Morse function combined with a corrugation term defining various surface sites for the oxygen-surface interaction and a repulsive term for the hydrogen –

surface interaction. For our calculation we used a modified Spohr function. Because we need the metal atoms to move and interact the water molecules, we have modified the Spohr function so that the interactions are pair wise additive between the O and H atoms in the H₂O molecule and the metal atoms.

At the system a face centered cubic crystallite composed of 1980 Au atoms arranged in 9 layers of 220 atoms each is used in all of the simulation. The periodic boundary condition has been used in the lateral plane. Initial water films are constructed based on a hexagonal arrangement of O atoms as in the Ih ice structure. The molecules in the first layer, just above the Au(111) surface, are oriented so that the angles between the surface normal and both OH bonds are about 109° (Fig.1.). The H₂O molecules in the second layer are arranged as if each molecule has one H atom oriented to form a hydrogen bond with the O atom in the first layer and one H atom oriented to form a hydrogen bond with the O atom in the second layer. The water layer molecules in subsequent pairs of layers repeat the orientation patterns of those in the first and second layers.

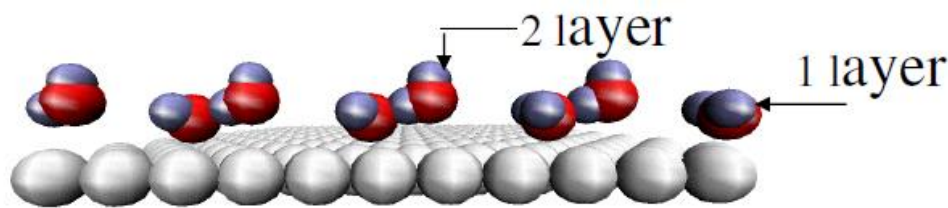


Fig.1. The structure of water molecules on the Au(111) surface. The water molecules in subsequent pairs of layers repeat the orientation patterns of those in the first and second layers.

The MD approach involves integrating the classical equations of motion for all the particles in the solid[12,13]. The results of the simulation provide the positions and velocities of all the atoms in the system as a function of time. From the final velocities, measurable quantities such as energy, angular distributions and mass spectrum can be calculated. From the time development of the atomic positions, a microscopic picture of some specific motions can be visualized. In addition, the microscopic mechanisms can be identified with specific quantities that can be measured. The MD approach needs as input a force field or interaction potential among the atoms. A great advance in the past decade has been the development of many-body potentials for describing extended systems[14].

Computational results and discussion

In this section we present the computational results of sputtering of water molecules from Au(111) surface. In our calculations we choose that the water molecules are not dissociated. In the Fig.2 the mass spectra of water molecules and Au atoms sputtered from water overlayers on Au(111) at the bombardment by Ar⁺ with E₀=0.3 keV and 0.7 keV at the normal

incidence are presented. For each incidence particle, 1000 trajectories were performed.

The computational results show that in the mass spectra a few intensive peaks are observed. In case E₀=0.3 keV at the mass spectrum a very intensive peak corresponding to H₂O has been observed (Fig.2a). In addition to this peak the peaks corresponding to the water cluster and Au atoms are observed. These clusters formed by only 2 water molecules, which no dissociated during emission.

In this case of E₀= 0.7 keV(Fig.2b) the mass spectra consists some another peaks performed by 2-8 molecules of water. It is seen that the intensity of Au peak the higher than one in the Fig.2a.

Actually, we would like to understand the fundamental events that give rise to the spectrum shown in Fig.2, especially if such an understanding would help interpret spectra. Actually, we would like to understand the fundamental events that give rise to the spectrum shown in Figure 2, especially if such an understanding would help interpret spectra. A fundamental understanding allows one to think about possible new applications as well as limitations of the technique. One often hears the phrase that the

primary ion establishes a collision cascade in the solid. To us a collision cascade implies a sophisticated pool game as shown in Figure 3 for an

Ar atom striking a film of ice adsorbed on a Au surface.

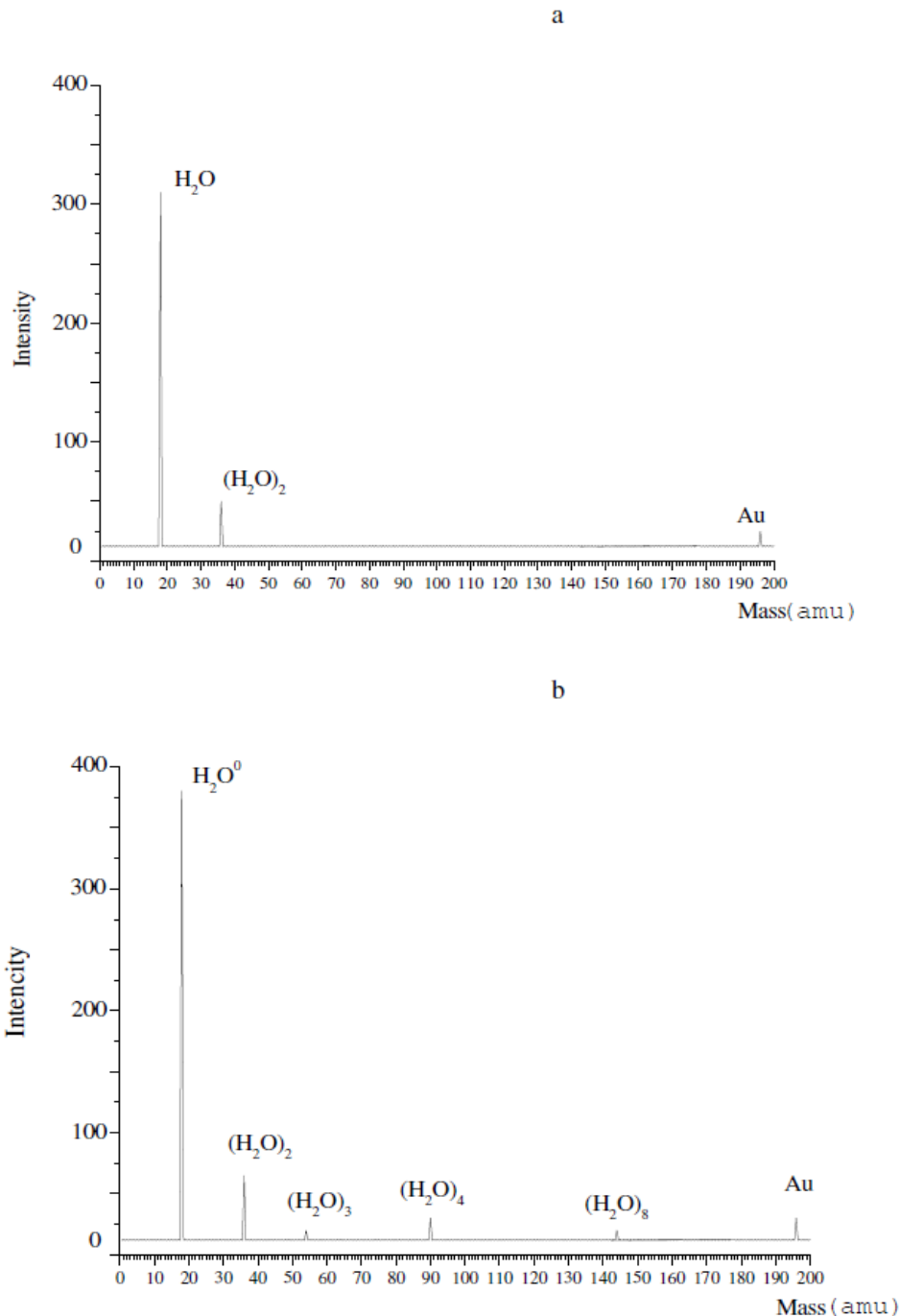


Fig.2. Mass spectra both water molecules and water clusters sputtered from water overlayers on the Au(111) of the bombardment by Ar^+ ions by $E_0=0,3$ keV(a) and $E_0=0,7$ keV(b)

The Fig. 3 presents the snapshots of the behavior of system at the bombardment by Ar ions with initial energy of $E_0=0.3$ keV. The visualization in Fig. 3 has been generated from classical molecular dynamics computer simulations. In Figure 3a the initial state of system ($t=0$ fs) is shown. The green particle is Ar ion. The next picture presents the behavior of system after 200 fs(Fig.3b). At this moment distractions of the surface of water film starts. As shown in this picture, near by surface of water film a “small iceberg” of water

molecules has been formed. Figure 3c presents this system after 1.5 ps. In this picture a separate cluster which consists of 2 molecules of water are observed. At this moment the “small iceberg” (1) of water molecules are also observed. Incidence particle is still inside of surface film and continues an interaction with the system. It destroys all come cross water-water and water – gold bonds. And last picture presents the behavior of system after 2 ps (Fig.3d). We can observe from this picture that the water molecule

clusters and Au atoms lifted from the target. At this moment the “small iceberg” (1) of water molecules moved to the lateral part of the system. Therefore we can not register a peak of “small iceberg” in the mass spectra. After this time the Ar^+ ion also finished its interaction with the surface and leaves of the surface.

Conclusions

The process of water molecules sputtering from the metal surface have been investigated by computer simulation. For the 2 layers of water molecules on the Au(111) the mass spectra secondary particles have been obtained. The mass spectra consists peaks corresponding to the both water molecules and clusters. In the mass spectra the peaks of gold atoms also are observed.

The visualization has been generated from classical molecular dynamics (MD) computer simulations. From this animation and many more animations with different initial position of Ar^+ hits, a visual picture of the process begins to emerge. In this case, the primary Ar particle strikes the ice film, first creating ice molecules. These species then damage the film while the Ar particle hits the metal substrate. Further action within the metal substrate creates an uplifting motion that induces the lift-off of entire ice molecules. The visual snapshots also allowed at the bombardment to observe “small iceberg” which can not be registered by mass detectors. These results are of interest for mass spectrometry of molecules and study of surfaces coverage’s.

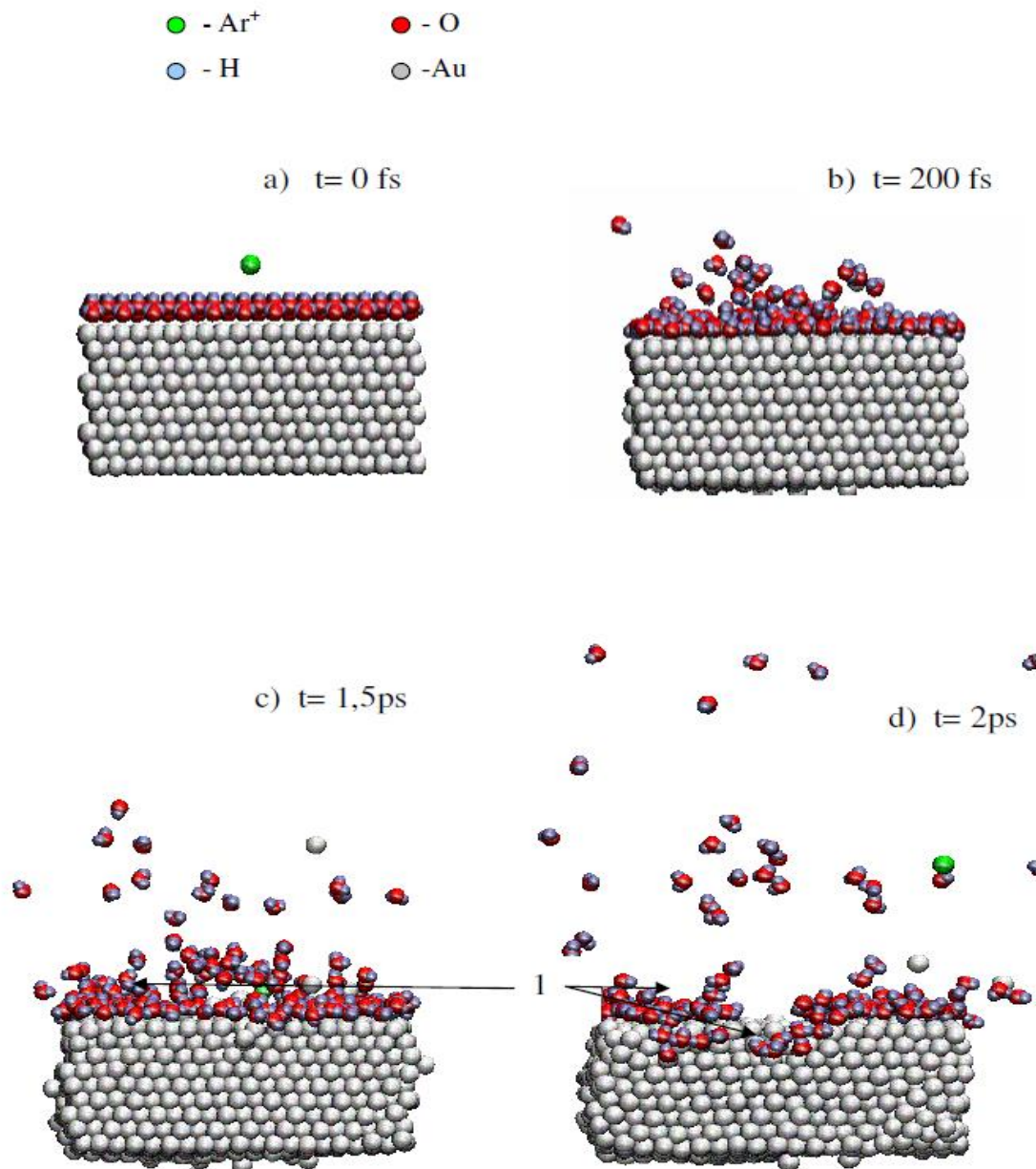


Fig.3. The visual picture receiving after time steps at the at the bombardment water layers on the Au(111) surface by the Ar^+ ions: a) $t=0$ fs, b) $t=200$ fs, c) $t= 1,5$ ps, d) $t=2$ ps

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