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Fundamental studies of the cluster ion bombardment of water ice

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Abstract

The fundamental sputtering properties of water ice are of interest for molecular depth profiling of biological samples in their native environment. We report on a method of studying amorphous water ice films of precise thicknesses in which pure water vapor is condensed onto a pre-cooled, silver-coated quartz crystal microbalance (QCM). This scheme allows for the determination of water ice sputter yields for any primary projectile as well as providing a means for studying escape depths of atoms and molecules beneath the deposited water ice layer. Specifically, we find a removal of approximately 2500 water molecule equivalents/20 keV C_{60}^{+} projectile with an underlying silver ion escape depth of 7.0 Å.
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1. Introduction

Polyatomic primary projectiles such as C_{60}^{+}, SF_5^{+}, Au_n^{+}, and Bi_n^{+} have become commonplace for a variety of SIMS analyses. The different sputtering properties of cluster ions from their atomic counterparts have been extensively reported in recent literature [1–6], leading to new avenues for SIMS studies. Of particular interest has been the increased interest in studying systems related to medicine, molecular biology, and biochemistry. The ability to use molecular depth profiling has opened up possibilities for three-dimensional imaging applications in cellular processes such as exocytosis—providing chemical information that will help in understanding physiological processes.

Since a popular method for looking at biological cells and materials involves freeze–fracturing samples in a frozen aqueous environment, it is imperative to understand the sputtering properties of water ice if molecular depth profiling through biological materials is to ensue. With new applications of cluster ion mass spectrometry, it is a logical extension that new tools for characterizing the interactions of the ion–solid relationship must be developed. Here, we report on a method of studying the sputtering properties of water ice, including the yields of sputtered water molecule equivalents for different primary projectiles, and the escape depths of silver ions from an underlying sample layer. A similar approach was first used [7] to study the yields of water ice by atomic ion bombardment, but in comparison, the current methodology improves the accuracy of the reported water ice film thickness measurement by two orders of magnitude.

2. Experimental

2.1. Sample preparation

Ice samples were prepared on an Ag-coated, modified quartz crystal microbalance (QCM) assembly from Maxtek, Inc., as illustrated in Fig. 1. Briefly, a polished standard 6 MHz AT-cut quartz crystal of 13 mm diameter is coated in gold, and 50 nm of Cr and 500 nm of Ag are vapor-deposited, respectively. The Cr acts as a buffer layer between the Ag and Au to prevent alloy formation. The crystal is mounted in such a way as to expose only the mass-sensitive area of the top crystal (the center 6.6 mm diameter, or the size of the bottom electrode superimposed upwards) to the vacuum chamber. Before ice deposition, the sample device is cooled to about 100 K by liquid nitrogen and allowed to equilibrate since temperature fluctuations cause drifts in QCM measurements. In this experiment, we take advantage of the intrinsic property of the AT-cut quartz having a frequency change sensitivity that is independent of the temperature of the analysis, once a constant temperature is achieved. Astrophysics experiments where water ice was

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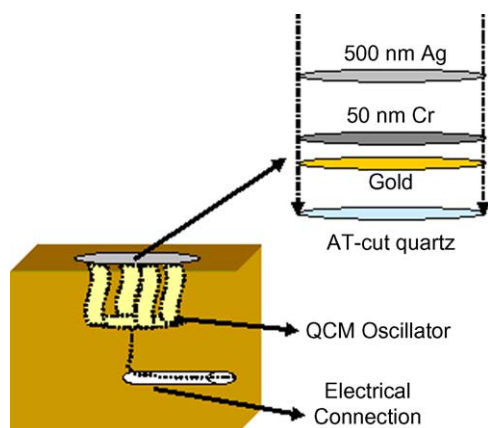E-mail address: nxw@psu.edu (N. Winograd).

Fig. 1. Schematic diagram of a modified QCM assembly. The oscillator is embedded into a copper holder with proper insulation for the electrical connection. Only the mass-sensitive area of the crystal is exposed at the top of the holder.

deposited onto a QCM apparatus revealed that between 80 and 130 K, the water ice forms in an amorphous manner, whereas above 130 K, the ice is crystalline, and below 80 K, different forms of ice begin to form [8].

Water vapor is bled into the analysis chamber with a base pressure of 1×10^{-9} Torr at any desired time using a Varian variable leak valve. The vapor is formed on the other side of the leak valve by first placing liquid water into a reservoir and cooling to liquid nitrogen temperature, pumping on the system, and finally letting the system thaw after vacuum isolation. When the valve is opened again, vapor enters a side chamber for first-stage control of pressure, and when a stable leak rate is established, the valve between the side chamber and analysis chamber is opened to achieve localized pressures of 2×10^{-6} and 2×10^{-7} Torr, respectively. A residual gas analyzer (RGA, model 100C from UTI, Sunnyvale, CA) was used to monitor the components of the vacuum before, during, and after ice deposition.

A Maxtek TM-400 thickness monitor is used to measure the amount of ice deposited onto the silver-coated QCM crystal before, during, and after the planned deposition period. The measured frequency change is related to the mass of deposited material. From the known density of amorphous ice of 0.92 g/cm^3, and knowledge about the active area of the quartz crystal, it is possible to directly measure the change in film thickness as a function of time. Details of this procedure have been reported elsewhere [2,5]. Before the deposition, no change in frequency is observed, and therefore, there is no change in the mass of species on the crystal surface. During the deposition, a rate of approximately 0.15 Å/s is measured—a value that is consistent for the pressures indicated above over the multiple iterations of water ice deposition and for values deposited ranging from 5 Å to 150 nm. After the deposition interval, the rate immediately changes to zero again. This series of observations, along with the RGA data listed above, proves that only water is being deposited and/or measured during the deposition events, meaning that all mass change on the crystal that induces a change in frequency can be attributed to water ice.

2.2. Sample analysis

A ToF-SIMS instrument with both C_{60}^+ [9,10] and Au_n^+ [11] primary ion sources from Ionoptika, Ltd. has been described in detail elsewhere [12], and was used to monitor the water and ^{107}Ag ion signals with respect to primary ion sputter time. For this study, 20 keV C_{60}^+ and 25 keV Au_n^+ primary projectiles were employed.

3. Results and discussion

The number of sputtered water molecule equivalents was calculated using the following relationship:

$$Y_{H_2O} = \frac{S_R A \rho}{I_p}, \tag{1}$$

where S_R is the sputter rate (cm/s), A the sputtered area of the sample (cm^2), ρ the molecular density of water ice (3.075×10^{22} molecules/cm^3), and I_p is the number of primary ions per second irradiating the sample.

A representative profile through the deposited ice layer to reach the ice/silver interface is shown in Fig. 2. In this particular example, C_{60}^+ primary ions were used for the analysis. After the above sputter yield analysis was performed for each projectile, the resulting removed water molecule equivalents can be compared, as shown in Table 1. There is a distinct trend of higher amounts of removed water molecules as the cluster size increases.

By depositing ice films of varying thickness and examining the attenuation of the Ag ion signal at m/z 107, it is possible to gain information about the escape depth of the Ag as it exits through the ice overlayer. We find that for all primary
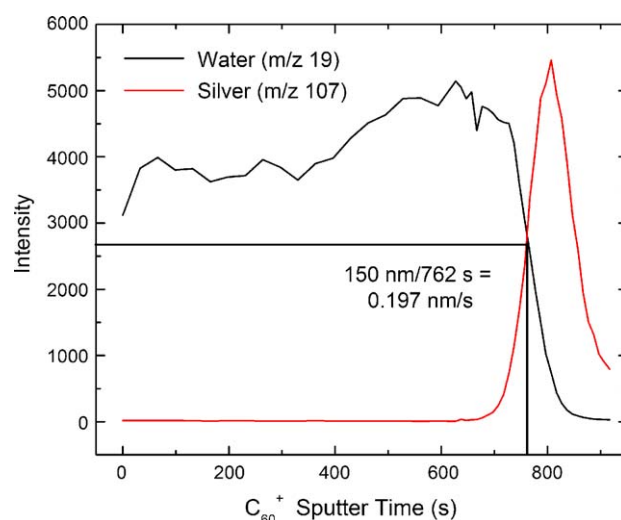

Fig. 2. C_{60}^+ profile through 150 nm of deposited ice on Ag. The bar lines represent the 50% maximum ^{107}Ag intensity, where the interface was assigned. The sputter rate of 0.197 nm/s, along with the molecular density of 3.075×10^{22} water molecules, 0.035 nA C_{60}^+ etching current, and a sputter field of 300 μm × 300 μm give approximately 2500 water molecule equivalents removed per incident 20 keV C_{60}^+ projectile, according to Eq. (1).

Table 1
Removed water equivalents and ^{107}Ag escape depths for C_{60}^+ and Au_n^+ projectiles

	Au$^+$	Au$_2^+$	Au$_3^+$	C$_{60}^+$
Removed # of water molecule equivalents[a]	94	570	1200	2500
Escape depths[b] (λ)	24	20	18	7.0

[a] Number of sputtered water molecule equivalents for the four primary projectiles in this study, as measured by the sputter time needed to profile through a 150 nm ice film on a modified QCM assembly, and to see 50% of the ^{107}Ag ion signal.

[b] Escape depths, in Å, for ^{107}Ag ions underneath the deposited ice.

projectiles, the attenuation follows an exponential decay of the form

$$I_{(d)} = I_{(0)}\, e^{-d/\lambda}, \qquad (2)$$

where $I_{(d)}$ is the Ag intensity at m/z 107 associated with an ice film of thickness d and $I_{(0)}$ is the intensity of m/z 107 before ice deposition. In practice, measurements were performed on a series of films varying in thickness from 5 to 60 Å. The resulting m/z 107 signal intensities for all thicknesses were plotted on a log scale and the linear portion of the curve was extrapolated to $d = 0$. This was done to obtain a correct intensity value for the case where no ice film is deposited, since SIMS matrix effects lead to signal fluctuations at the lowest ice film thicknesses. Results are reported in Table 1. It will be interesting to examine the reasons behind the observed trends in these data, and to speculate about the mechanisms behind the effect. For example, preliminary MD simulations suggest that the organic film is swept away in a circular area around the point of impact, allowing exposed Ag atoms to escape [3].

4. Conclusions

We report on a combination of ToF-SIMS and QCM techniques to monitor and characterize precise thicknesses of deposited amorphous ice films in ultra-high vacuum. These films allow for fundamental studies of water ice after energetic primary ion bombardment, and help to illustrate quantitatively the enhanced sputter yields and reduced ion escape depths for cluster ions. The small escape depth of an ion underneath the ice film, combined with the extraordinarily high sputter yields imply that C_{60}^+ is an excellent candidate for molecular depth profiling experiments, particularly for systems of biological interest buried within a water ice matrix.

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