



Desorption of chemisorbed Carbon on Mo(1 0 0) by noble gas ion sputtering: Validation of ground test measurements of ion engine lifetimes

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Abstract

We report desorption cross section measurements for one monolayer of chemisorbed carbon on a Mo(1 0 0) surface induced by sputtering with noble gas ions (Ne⁺, Ar⁺, Xe⁺) at different incident angles, ion energies, and substrate temperatures. Desorption cross sections were determined by using low-energy ion scattering (LEIS) to monitor the increase of the signal from the Mo substrate. A monolayer of p(1 × 1) carbon adatoms on the Mo(1 0 0) surface was created by dosing ethylene (C₂H₄) to the substrate at 800 K, and characterized by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). We find that the carbon desorption cross section increases with increasing mass and energy of the impinging ions, and there is a maximum value for the desorption cross section at an incident angle for the ions of 30° from the surface plane. The desorption cross section also increases up to a substrate temperature of 300 °C. Values for the carbon desorption cross section for carbon adatoms on Mo(1 0 0) by 400-eV Xe⁺ ion sputtering are about 2 × 10⁻¹⁵ cm², which is one order of magnitude higher than those for bulk carbon samples. This information is particularly important for evaluation of ion-engine lifetimes from ground-test measurements in which contaminant carbon is deposited on Mo accelerator grids, potentially altering the sputtering rate of the Mo. Our measurements show that monolayer amounts of carbon on Mo have desorption cross sections that are two orders of magnitude higher than estimates of what would be required to reduce the Mo erosion rate, and thus ground-test measurements can be used with confidence to predict ion-engine wear in space, from this perspective.

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1. Introduction

Noble-gas ion sputtering is a widely used technique for surface cleaning and depth profiling, and the sputtering of adsorbed carbon is a particularly important process because carbon is one of the most common contaminants present at surfaces. Accurate knowledge of ion-induced desorption, or sputtering, cross-sections for carbon is helpful in these and other applications. We are particularly interested in measuring such sputtering cross-sections for chemisorbed monolayers present at interfaces where chemical bonding interactions and mass changes may alter those values tabulated for bulk materials.

Ion-induced desorption cross-sections for carbon, and the potential importance of cross-section changes at an interface, play a role in the evaluation of lifetimes in ground tests of ion thrusters used for space applications [1]. During long-duration, ion-engine ground testing, sputtering of carbon from beam targets used in these tests deposits contaminant material (carbon) onto ion thruster grids made of Mo. Thus, the Mo accelerator grid and accumulated contaminant carbon is simultaneously sputtered by Xe^+ ions during testing. Xenon is used as the ion source in ion engines because of its beneficial properties of high atomic number, inertness, and easy ionization, and it is non-radioactive and non-toxic. In order to avoid overestimating the Mo-grid lifetime in ion engine ground testing, it is therefore important to understand the effects of carbon deposition onto the Mo grids, and whether deposited carbon forms a protective coating to artificially reduce the Mo-accelerator grid erosion rate [1]. To make this evaluation, information is needed on the sputtering cross sections of interfacial, possibly monolayer amounts of carbon at Mo surfaces, in addition to information on the sputtering of bulk carbon relevant for thick contaminant films. No Xe^+ -ion cross sections for interfacial carbon monolayers are currently available.

We report herein desorption cross section measurements for one monolayer of chemisorbed carbon on a Mo(1 0 0) surface induced by sputtering with noble gas ions (Ne^+ , Ar^+ , Xe^+) at different incident angles, ion energies, and substrate temperatures. These cross sections were determined by using low-energy ion scattering (LEIS).

2. Experimental methods

The experiments were carried out in a two-level ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. Schematic diagrams of the apparatus are shown in Fig. 1. The upper level of the vacuum chamber is equipped with a 4-grid low energy electron diffraction (LEED) optics and quadrupole mass spectrometer (QMS). The lower level contains a Colutron[®] ion gun that provides collimated and monoenergetic ions ($\Delta E/E = 0.25\%$). The energy analyzer used for LEIS in these measurements was a Perkin-Elmer Model 10–360 spherical capacitor analyzer (SCA) located at a fixed scattering angle from the incident ion beam of 144° . The analyzer was equipped with a multichannel detector (MCD) that utilizes dual multichannel plates configured to act as 16 discrete detectors and provide high count rates. The lower level of the chamber also contains instrumentation for Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), a rotatable Comstock[®] energy analyzer, and another ion sputtering gun.

The Mo(1 0 0) single-crystal sample (Atomerigic Chemetals Corp.) was 10 mm in diameter and 1.5-mm thick, and oriented to within $\pm 0.5^\circ$. The crystal was mounted onto the sample holder by two 0.015-in. W wires clamped to slots along the sample edge. The sample temperature was measured by a W–5%Re/W–26%Re thermocouple that was spot-welded to the edge of the crystal. The crystal was cleaned by Ar^+ -ion sputtering at room temperature, along with repeated cycles of oxygen treatments (1×10^{-7} Torr O_2 , 2 min) with the sample at 800 K to oxidize surface carbon and heating to 1700 K in UHV to desorb oxygen [2,3]. The sample could be heated either resistively or by electron-beam bombardment.

A $p(1 \times 1)$ carbon monolayer on the Mo(1 0 0) surface was synthesized by dosing 20-L (1×10^{-7} Torr, 200 s) ethylene (C_2H_4 , Matheson, 99.99%) onto the surface at 800 K to decompose the hydrocarbon and remove hydrogen [4,5]. The carbon adlayer was characterized by a $\text{C}_{271}/\text{Mo}_{221}$ peak-to-peak height ratio in AES of 0.36 ± 0.01 [5,6]. The sharp $p(1 \times 1)$ LEED pattern confirmed that one monolayer of carbon was accurately established on the Mo(1 0 0) surface [5,7,8]. These C adatoms adsorb in four-fold hollow sites, thus occupying deep holes between four Mo atoms [7,8].

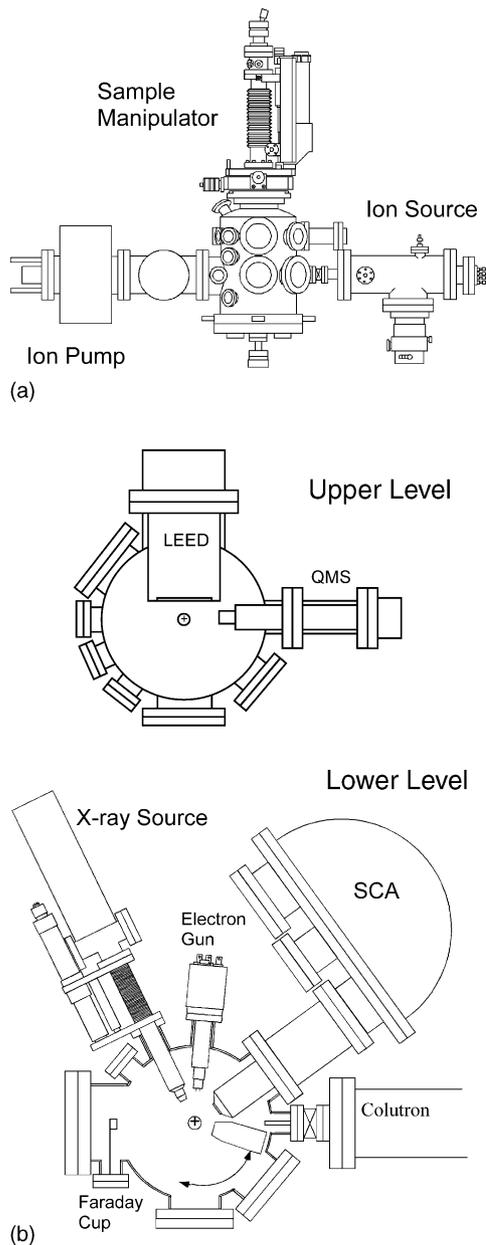


Fig. 1. Schematic drawings of the (a) UHV apparatus overall, and (b) layout of instrumentation in the upper and lower levels of the UHV chamber.

Determination of sputtering yields has been well-described since noble gas ion sputtering is a widely applied technique. The sputtering yield Y (atoms/ion) is a parameter used to characterize how efficiently atoms are removed from the substrate surface. In the

case of adsorbed atoms or species, the ion-induced desorption cross section can be deduced by monitoring the decrease of the signal from the adsorbate or the increase of the signal from the substrate, according to the following equations [9] for monitoring the adsorbate signal:

$$\ln \left[\frac{I_a(t)}{I_a(0)} \right] = -\sigma_D i_0 t \quad (1)$$

and for monitoring the substrate signal:

$$\ln \left[1 - \frac{I_s(t)}{I_s(\infty)} \right] = -\sigma_D i_0 t + \text{constant} \quad (2)$$

The ion-induced desorption cross section σ_D (cm^2/ion) is simply related to the sputtering yield Y by

$$Y = \sigma_D N_{\text{ML}} \quad (3)$$

where N_{ML} is the surface atom density at monolayer coverage (atoms/cm^2). For the particular case of one monolayer of carbon chemisorbed on Mo(1 0 0), the carbon coverage can be defined as $\Theta_C = 1$, which corresponds to a C coverage equal to the Mo(1 0 0) surface atom density, $N_{\text{ML}} = 1.10 \times 10^{15} \text{ atoms}/\text{cm}^2$.

In these studies, we followed the surface concentration by utilizing LEIS. This is a highly surface sensitive, elemental analysis technique [10,11]. The basis for this technique is shown in Fig. 2. An incident projectile ion with mass m_1 and energy E_0 is scattered through an angle θ by collision with a surface atom with mass m_2 . Backscattered ions can be detected by

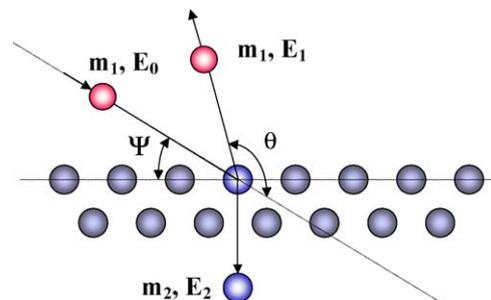


Fig. 2. Schematic diagram for the scattering of an incoming ion with mass m_1 and energy E_0 at an incident angle Ψ from the surface plane with a surface atom with mass m_2 . The incident ion is detected at energy E_1 after scattering through an angle θ , and the target atom recoils into the solid with energy E_2 .

an energy analyzer with energy E_1 which is given by energy and momentum conservation, according to

$$\frac{E_1}{E_0} = \left(\frac{\cos\theta + \sqrt{m_2^2/m_1^2 - \sin^2\theta}}{1 + (m_2/m_1)} \right)^2 \quad (4)$$

which depends only on the lab scattering angle θ and mass ratio m_2/m_1 .

The LEIS spectrum was collected in a back-scattering geometry because the scattering angle θ is fixed at 144° when using the large SCA. There is no back-scattering signal from carbon because it has a lighter mass than that of any of the incident ion beams (Ne^+ , Ar^+ , and Xe^+). (In other experiments, the signal from adsorbed carbon could be detected in forward-scattering geometries, but was not used here.) Monitoring the signal from the substrate to deduce the ion-induced desorption cross sections must be used in many cases compared to detecting the signal from an adsorbate, because it often has a lighter mass than that of the incident ions [12]. Therefore, the desorption cross sections of carbon on Mo(1 0 0) induced by bombardment with Ne^+ , Ar^+ , and Xe^+ ions were measured by monitoring the increase in the Mo-substrate signal, according to Eq. (2). This is straight forward in $\text{Ne}^+ \rightarrow \text{C}/\text{Mo}(1\ 0\ 0)$ and $\text{Ar}^+ \rightarrow \text{C}/\text{Mo}(1\ 0\ 0)$ experiments. However, because the mass of Xe^+ ion is heavier than that of the Mo atoms, there is no back-scattering signal from Mo when using Xe^+ ions. In this case, we produced a discharge in a Xe and Ar mixture and then adjusted the velocity filter magnet to periodically select different mass ions for sputtering and analysis. In the case of $\text{Xe}^+ \rightarrow \text{C}/\text{Mo}(1\ 0\ 0)$ measurements, Xe^+ ions were selected for sputtering carbon from the Mo(1 0 0) surface and Ar^+ ions were selected for analysis of the surface. A small correction was applied for the amount of sputtering by Ar^+ ions during LEIS by using the desorption cross section values directly measured in $\text{Ar}^+ \rightarrow \text{C}/\text{Mo}(1\ 0\ 0)$ experiments that utilized Ar^+ ions for both sputtering and analysis.

The ion beam current incident on the sample was measured by recording the sample current to ground caused by the incident ion beam current. The sample was biased by +80 V during this measurement in order to suppress secondary electron emission from the sample that is caused by ion bombardment, which

would otherwise artificially increase the measured incident ion current. A Faraday cup with a 1-mm² aperture that was located 6 in. behind the sample was also used to routinely monitor the ion beam current. A factor of 0.94 was used to convert the current density measured by the unbiased Faraday cup to the sample beam current density. The ion beam size at the sample location was determined by calculating the beam current density assuming no divergence of the incident ion beam and using the cross-sectional area (2 mm²) of the ion beam entrance tube as the spot size on the crystal, measuring the beam current density at the Faraday cup obtained with a biased collector, and interpolating the beam current density using a $1/r^2$ dependence. We find that the beam diverges little and had a size of 2.04 mm² at the sample location, and this value has been used in our calculations of ion beam density and ion yield.

The angle ψ for incident ions was 90° in all experiments except where specified to be different. This decision was made to better model the situation in ion-engine ground tests where deposited C is sputtered by Xe^+ ions incident along the surface normal of the Mo accelerator grids. One monolayer C-covered Mo(1 0 0) surfaces were investigated rather than multilayer covered surfaces. Thick multilayer adsorbate cross sections are likely to be represented well by cross sections obtained for bulk materials. Also, multilayers may exhibit a higher desorption cross section than that for monolayer or submonolayer amounts of adsorbate, because monolayers typically have a higher surface binding energy which leads to a lower desorption cross section [13,14]. Thus, to avoid possibly underestimating the protection effect of C on Mo by using higher C desorption cross section from bulk C values, we carried out measurements on one monolayer of C deposited on Mo.

3. Results and discussion

Energy scans in LEIS for 500-eV Ar^+ ions scattered from Mo atoms at the p(1 × 1)-C/Mo(1 0 0) surface at room temperature after increasing sputtering time are shown in Fig. 3. The spectra were obtained at an incident polar angle of 90° . There were no other features in the LEIS spectrum, and specifically there was no back-scattering signal from C because the

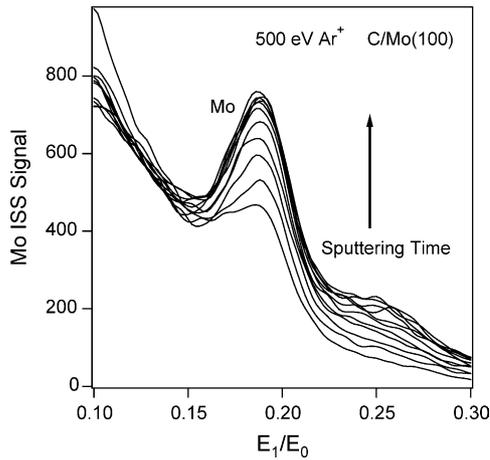


Fig. 3. Ar^+ ion scattering peaks from an initially prepared $p(1 \times 1)$ -carbon monolayer on a $\text{Mo}(1\ 0\ 0)$ surface at room temperature after various sputtering times. The ions were incident along the surface normal, i.e., the incident angle ψ was 90° from the substrate surface plane.

mass of C is lighter than that of Ar. The Mo peak intensity increases with increasing sputtering time and approaches a constant value.

The desorption cross section σ_D for C at this interface was determined by fitting the measured data to Eq. (2). Fig. 4 shows the results of this fit to

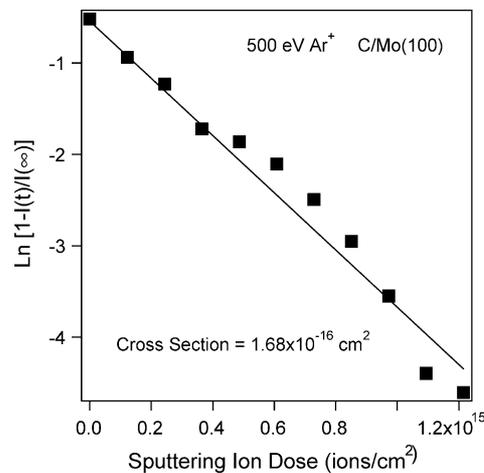


Fig. 4. Desorption of C adatoms from the $p(1 \times 1)$ -C/ $\text{Mo}(1\ 0\ 0)$ surface at room temperature by Ar^+ ion sputtering as monitored by the LEIS signal from the Mo substrate. The ordinate is evaluated, according to Eq. (2), and the slope of the straight line corresponds to the carbon desorption cross section σ_D .

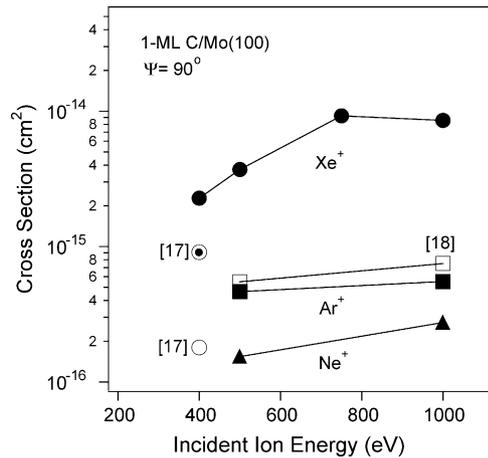


Fig. 5. Ion-induced desorption cross sections for C adatoms on $\text{Mo}(1\ 0\ 0)$ at room temperature by Xe^+ (●), Ar^+ (■) and Ne^+ (▲) ions at various energies. Also included for comparison are values for bulk carbon sputtered by Xe^+ (○) [17], bulk molybdenum sputtered by Xe^+ (⊙) [17], and adsorbed carbon on molybdenum sputtered by Ar^+ (□) [18].

the data. The slope of the line in this semilog plot can be used in Eq. (2) to calculate the cross section for removing C from the $\text{Mo}(1\ 0\ 0)$ surface, and in this case $\sigma_D = 1.68 \times 10^{-16} \text{ cm}^2$. Random errors in the sputtering measurements cause an uncertainty of about 10% in the slope of the line and in values reported for the sputtering cross sections.

Similar plots were obtained for variations in the incident ion energies, polar angles, and substrate temperatures for C desorption from $\text{Mo}(1\ 0\ 0)$ surface induced by Xe^+ , Ar^+ , and Ne^+ incident ions. These results are presented in Figs. 5–7.

In discussing the trends observed in this data, it is helpful to first review the mechanisms for ion-induced desorption that have been proposed by Winters and Sigmund [15]. An illustration of three mechanisms to describe how incoming Xe^+ , Ar^+ , or Ne^+ ions cause desorption of adsorbed C adatoms on a $\text{Mo}(1\ 0\ 0)$ substrate is shown in Fig. 8:

- Direct collision between an incident ion and the adsorbed atom, which is either knocked off directly, or after some penetration, is then reflected from the substrate.
- Collision between an adsorbed atom and a primary ion after this ion penetrates into the substrate but is reflected by the substrate such

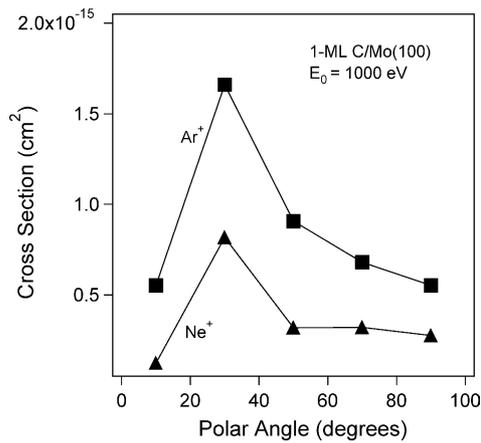


Fig. 6. Influence of the ion incident angle Ψ , measured from the surface plane, on the Ar^+ and Ne^+ ion-induced desorption cross sections for C adatoms on Mo(1 0 0).

that it eventually hits the adsorbed atom and knocks it out.

- (c) Outward collision cascade of substrate atoms caused by the impinging ion which causes the adsorbed atom to be knocked out by a substrate atom on its way out.

Fig. 5 shows that the desorption cross section of C increases with increasing incident ion energy and mass. This was expected based on previous results [14,16]. With increasing incident ion energy and/or mass, ions penetrate more deeply into the substrate,

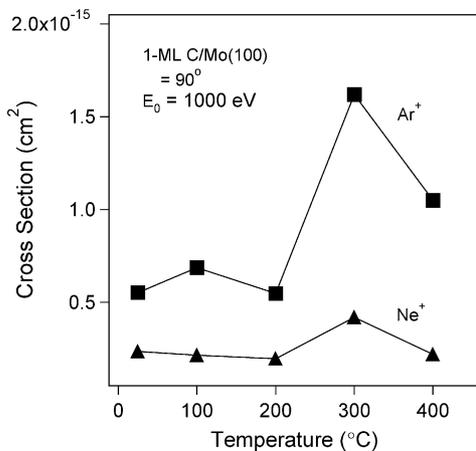


Fig. 7. Influence of the Mo substrate temperatures on the Ar^+ and Ne^+ ion-induced desorption cross sections for C adatoms on Mo(1 0 0).

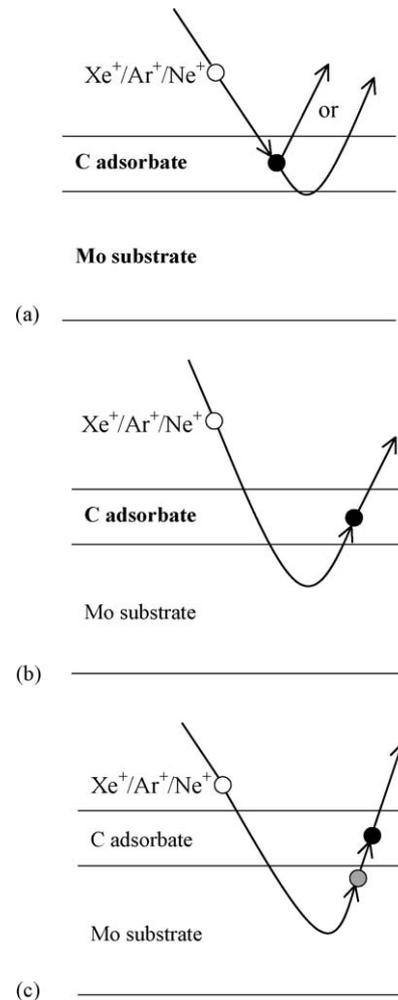


Fig. 8. Three mechanisms for ion-induced desorption, or sputtering, of C adatoms at the Mo substrate surface.

and so the contributions to the sputtering process from mechanisms (a) and (b) decrease and that from mechanism (c) increases [14,16]. Thus, collision cascades of substrate atoms initiated by energy losses of the incident ion increase with increasing incident ion energy and/or mass.

Desorption cross sections of C vary significantly with the incident angle Ψ , and there is a maximum near $\Psi = 30^{\circ}$ as shown in Fig. 6. At large polar angles, the sputtering efficiency would be expected to be increased as the incident angle Ψ decreases from 90° by a factor of $1/\sin \Psi$ based on a simple argument [11] in which the penetration of ions into the substrate

decreases. This causes the whole scattering cascade to become more concentrated in the surface region. However, at very small polar angles near grazing incidence, the sputtering efficiency of C will decrease with decreasing incident angle because impinging ions are efficiently scattered by the surface [11]. At small incident angles, ion penetration and collision cascades are less likely. Also, in our particular case, C adatoms adsorb in four-fold hollow sites on the Mo(1 0 0) surface and are nearly coplanar with four Mo atoms at the surface [7,8]. Thus, a shadowing effect of Mo on C will be very significant at low incident angles and this will stop ions from impinging on C. All of these effects cause the sputtering yield to be reduced within the small-angle range, and therefore, a maximum desorption cross section is achieved at an intermediate angle ($\psi = 30^\circ$). Similar results for $\text{He}^+ \rightarrow \text{O}_2/\text{Si}(1\ 1\ 1)$ [14] and $\text{Ne}^+ \rightarrow \text{S}/\text{Ni}(1\ 1\ 1)$ [16] were observed by Taglauer et al.

As shown in Fig. 7, the substrate temperature also affects the desorption cross sections for C on Mo(1 0 0). Between 25 and 200 °C, the desorption cross section remains roughly constant. There is a maximum near 300 °C, and the desorption cross section decreases above 400 °C. One would expect that phonon-assisted processes such as sputtering should increase with increasing temperature. It is possible that segregation of C to the surface of the Mo crystal occurs at high temperatures, and that this would interfere with the measurement of the sputtering yield at 400 °C by reducing the apparent yield.

As a final comment, we refer to Fig. 5 which compares directly our results for sputtering the carbon monolayer on Mo(1 0 0) using Xe^+ , Ar^+ , and Ne^+ ions with results for sputtering bulk C and Mo using Xe^+ ions [17] and one previous study of sputtering interfacial carbon on Mo using Ar^+ ions [18]. The desorption cross section of bulk C induced by 400-eV Xe^+ ions is much lower than that of bulk Mo. This raises a serious concern in measuring ion engine erosion rates in ground tests because contaminate carbon deposited on Mo grid surfaces will protect the Mo grids and therefore reduce the sputtering rate of the Mo grids and lead to an optimistic projection of ion engine lifetimes. Over most of the Mo grid surface, there is no macroscopic carbon build-up visible, but monolayer levels of C are still a source of concern [1]. We find that the measured desorption

cross sections of a carbon monolayer from a Mo(1 0 0) surface by Xe^+ ions with incident energies between 400 and 1000 eV are about $2\text{--}8 \times 10^{-15} \text{ cm}^2$ for a polar angle ψ set to 90° in order to simulate the sputtering geometry in ion engine ground tests. These are about one order of magnitude higher than cross sections for bulk C. Moreover, they are about two orders of magnitude higher than estimates for the cross section for C needed to reduce the Mo grid erosion rate [1]. Therefore, the effect of monolayer amounts of deposited C to protect Mo against sputtering is negligible, and the measured ion engine erosion rates in long-duration, ground-testing can be used with confidence to predict ion-engine lifetimes in space.

4. Conclusions

LEIS has been used to measure ion-induced desorption cross sections of chemisorbed carbon on a Mo(1 0 0) surface for a $p(1 \times 1)$ carbon monolayer using Ne^+ , Ar^+ , and Xe^+ ions. Desorption cross sections of C adatoms on Mo(1 0 0) by 400-eV Xe^+ ions at normal incidence on the surface are about $2 \times 10^{-15} \text{ cm}^2$, about one order of magnitude higher than that of bulk C. Desorption cross sections increase with increasing mass and energy of the impinging ions, and this can be explained by the increasing contribution to carbon sputtering from collision cascades with the outward flux of substrate atoms. Geometric effects on the incident ion flux and a shadowing effect within the small polar angle range are proposed to lead to the observed maximum in the desorption cross sections at an ion incident angle of about 30° from the surface plane. Desorption cross sections also increase with substrate temperature up to at least 300 °C.

In particular, desorption cross sections of a C monolayer on a Mo substrate are about two orders of magnitude higher than the cross section for C that has been estimated to reduce Mo accelerator grid wear rate during Xe^+ ion sputtering during ground tests of ion engine lifetime. Thus, protection from monolayer amounts of deposited C to reduce the Mo sputtering rate is negligible, and the ion engine erosion rates measured in long-duration, ground-tests can be used to reliably predict ion engine lifetimes in space.

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