Ion Beam Removal of Water and Dioctyl Phthalate from Cryogenic Mirrors

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This study details recent work on spectroscopic detection and ion beam removal of molecular contaminants on mirror surfaces. Results are presented for initial experiments that investigate the effects of irradiating contaminated, low-temperature mirror surfaces with ion beams. Effects of the ion beam on the clean cryogenic substrates are examined as well as the physical process occurring during ion bombardment of the contaminant films. Water and dioctyl phthalate are studied as principal contaminants on beryllium and copper mirror surfaces. Conditions necessary to remove these contaminants by ion beam bombardment were determined. Ion-beam-induced chemistry is observed for removal of water from a beryllium surface. These results demonstrate the importance of the chemical and physical nature of mirror surfaces with respect to contaminant removal by this method.

Introduction

OPTICAL missions in space are carefully designed to maximize signal intensity and spatial resolution between two or more closely spaced objects. In order to reduce background radiation and thereby monitor dim targets, many current and future systems require cryogenically cooled optics (< 100 K) upon which adsorption of contaminants is unavoidable. The performance lifetime of long wavelength infrared (LWIR) sensor systems in space is dependent on maintaining the optical integrity of the telescope and focal plane array. Contaminants can degrade optics in a number of ways, for example, by attenuating incoming radiations, which leads to an overall reduction in sensitivity and, by increasing the scatter from each optical surface, which leads to a degradation in spatial resolution. The latter condition particularly affects detection of low-intensity objects located close to more intense objects.

As the duration of the proposed missions increases, concern about degradation of the optics from prelaunch, launch and, particularly, orbital contamination, also increases. Prelaunch contamination can be reduced by increasing the level of cleanliness achieved and maintained during assembly and prelaunch operations. Protection of the optical surfaces during launch, however, may be necessary when vibrations can loosen particles and rocket emissions increase. After the launch phase, the deposition of molecular contamination increases as the optical train is cooled, and the electronic components become warm.

The exact nature of the postlaunch contaminant species depends on the local environment of the cryogenic surface. The main sources of contamination in space are from outgassing of vehicle and sensor electronic components (even if the rates of outgassing are relatively slow), emission from control rockets, and the space ambient environment.[1-4] Strong evidence exists showing that the outgassing can persist for more than seven years with concomitant contamination accretion.[5-7] The major contaminants have been identified in numerous experiments and can be divided into three classes depending on their source. Data from outgassing hardware show the predominance of species such as esters, aliphatic and aromatic hydrocarbons, silicones, and antioxidants.[1,2] These often arise from such materials as plasticizers, adhesives, and, in the case of some antioxidants, from wire insulation. A major step in reducing outgassing is the judicious choice of material for electronic and spacecraft components. In this area significant improvements have been made over the last 15 years.

Contaminant species from rocket propulsion systems depend on the specific type of rocket used, but the majority are small molecules such as water, carbon dioxide, and ammonia. Ambient species in space such as oxygen, oxygen radicals, and nitrogen also must be considered. With this information in mind it is necessary, therefore, to understand the effect of a wide variety of contaminants on the cryogenic optical surfaces. This is important not only for individual contaminants but also for a mixture of species. In addition, the effect of ultraviolet light and electron and proton radiation must be examined. These effects are important when the contaminants are organic molecules, as such species are often susceptible to polymerization or degradation when subjected to such forms of radiation.

Removal

As a result of the system degradation that occurs due to contamination buildup, it is anticipated that the cryogenic optical components will require cleaning in space periodically. These processes must be able to remove *all* contaminants from the mirror surfaces. To maintain sensitivity and spatial resolution of the sensor system, both particulate and molecular contaminants must be removed without increasing the temperature of the optics or damaging the optical surface.

The simplest removal techniques are thermal, laser, or electron beam induced desorption. However, each of these methods presents specific problems. The main difficulty is that they do not completely remove a wide variety of contaminants. This is because some species, instead of desorbing, decompose on the surface. Consequently, preferential cleaning can occur depending on the specific source and the extent of the decomposition reaction. It is also feasible that the contaminant may decompose and react with the mirror surface

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Presented as Paper 88-2729 at the AIAA Thermophysics, Plasmadynamics, and Lasers Conference, San Antonio, TX, June 27–29, 1988; received July 29, 1988; revision received Feb. 7, 1989.

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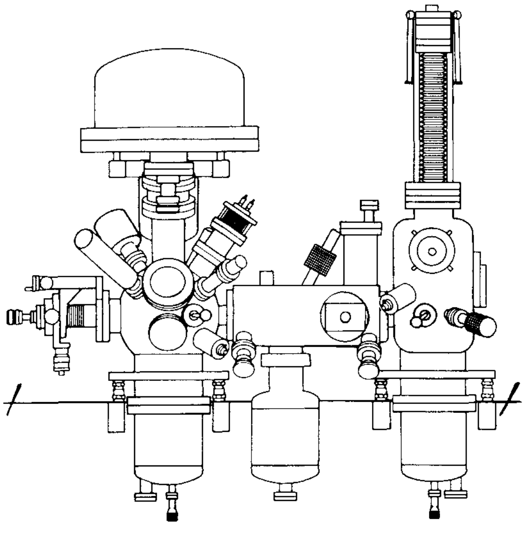
itself. For example, organic compounds may form surface carbides on heating.

Another method of contaminant removal involves directing a high-energy ion beam at the optical surface. This technique, commonly known as sputter cleaning or ion bombardment, removes surface atomic layers. Space-qualified ion guns have been designed and delivered,[8] and a previous study has shown that ion polishing of optical surfaces can be used to remove contaminants from high-energy laser mirrors at room temperature.[9] Such a contaminant removal method is not without problems, however. Removal of the mirror surface itself may occur under ion bombardment, which can produce a severely roughened reflector. This effect would create the types of problems it was trying to destroy, namely, increased scatter leading to reduced spatial resolution and sensitivity. In addition, removal of contaminants with this technique at temperatures under 100 K may present substantially different problems. The rare gases Xe, Kr, and Ar all condense at these temperatures and, thus, may contaminate the mirror themselves. Little research has been undertaken on ion beam irradiation of low-temperature surfaces, whether clean or covered by adsorbates.

It is also necessary to consider the ion source. A variety of ion "gun" designs are available that emit broad or focused beams created by ionization of rare gas atoms in a number of ways. Ion energies may range from 100 eV to hundreds of kiloelectron volts. Thus, parameters such as removal rate as a function of beam energy and current density must be studied to ascertain the most suitable ion source for removal of contaminants from space optics.



Analysis Chamber I	Preparation Chamber	Analysis Chamber II
XPS	Sputter Cleaning	LEED
AES	Evaporator	LEELS
SIMS	Crystal Clever	UPS
SEM		
ISS		
TDMS		

Fig. 1 Schematic diagram of the surface analysis system.

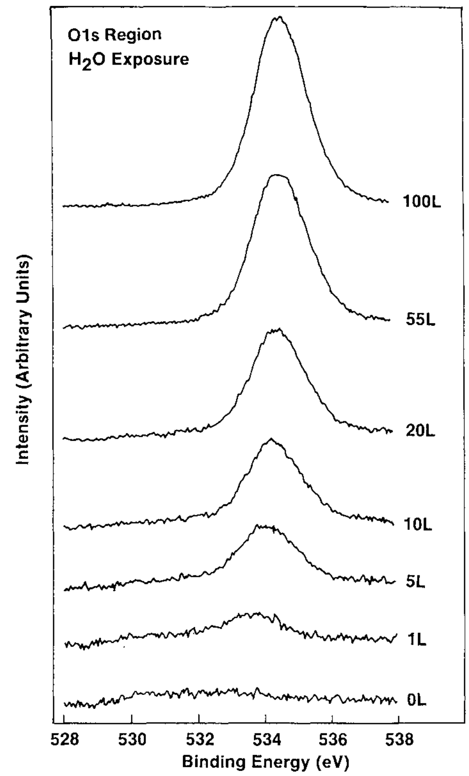


Fig. 2 O 1s region x-ray photoelectron spectra for increasing water exposures to a polished Cu surface.

Overview

The work reported here concentrates on the spectroscopic detection and ion beam removal of molecular contaminants on the surface of mirrors. Verification of contaminant removal is also accomplished spectroscopically using surface-sensitive techniques such as x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Results of initial experiments are presented that investigate the effects of irradiating contaminated, low-temperature mirror surfaces with an Ar ion beam as a function of various ion beam parameters. The effect of the ion beam on the clean cryogenic substrates is examined as well as the physical process responsible for contaminant removal during ion bombardment. Our goals are 1) to investigate the parameters and mechanisms involved in deposition of gases, mixtures of gases, and particulates on mirror surfaces at cryogenic temperatures; and 2) to determine the conditions necessary to remove these contaminants by ion beam bombardment without degrading the off-axis scattering properties of the mirror. The findings reported here demonstrate that both the physical and chemical properties of the mirror and contaminant are important in removal of contaminants by this method.

Experimental

All spectroscopic experiments were carried out in the multiprobe stainless steel and mu metal, ultrahigh vacuum system shown in Fig. 1. XPS is performed with a 150-deg spherical sector analyzer using either a dual anode (Al/Mg) or monochromatic Al x-ray source. SIMS is accomplished using a quadrupole mass spectrometer with a mass range of 1-800 amu. The ion gun used for SIMS and for sputter cleaning the mirrors is a differentially pumped, electron impact ionization source AG-61 (V.G. Scientific), operated by rastering the beam across the sample surface. Ion currents, measured at the sample, were typically in the range of 50-150 nA, whereas the ion beam energy varied from 1-5 keV.

Water was chosen as the first molecular contaminant, both alone and in conjunction with organics such as dioctyl phthalate (a high-molecular-weight ester that has been identified as one of the most common contaminants produced from outgassing of electronic components). Mirror substrates were exposed to water under ultrahigh vacuum (UHV) conditions by leaking purified water vapor into the chamber. Dioctyl phthalate (DOP) was deposited on mirror substrates by dissolving a small quantity in acetone and dropping the solution onto the mirror surface. The acetone evaporates under UHV conditions leaving only DOP on the surface. Substrates examined were highly polished Cu and hot isostatically pressed Be[10] mirrors. Cu was chosen simply as an available transition metal surface. A Be mirror was chosen because of its current use in the fabrication of radiation-hard, lightweight mirrors.

Initial contamination studies were conducted on clean, polished Cu surfaces. The XPS spectra of water at 160 K (Fig. 2) shows the gradual formation of multilayer water for exposures ranging from 1 L to 100 L (1 L = 1 langmuir = 10^{-6} Torr-s). Since we are interested in multilayer coverage, the 100 L exposure was chosen as an appropriate level of contamination. From Fig. 2 it is evident that multilayers of H_2O are formed on the surface from the increasing binding energy of the O 1s level as a function of H_2O exposure. The film, however, is not so thick as to prevent detection of sputtering by XPS. This exposure corresponds to an ice (condensed H_2O) thickness of approximately 50 Å. The ice was removed by bombarding with Ar ions under a variety of ion-beam current and voltage conditions. A typical experiment involved deposition of H_2O at 160 K followed by acquisition of XPS spectra prior to sputtering and as a function of sputter time. O 1s peaks were fitted and integrated to obtain the total amout of H_2O remaining on the surface. The total sputter rate was then calculated assuming 50 Å H_2O film. As an example, Fig. 3 shows the O 1s removal rate of H_2O on Cu as a function of current and ion beam energy. Similar experiments were also performed using organic adsorbants. Ion gun parameters necessary to effectively remove H_2O, organics, and mixtures were thus obtained.

Result and Discussion

Water Contamination

X-ray photoelectron spectra over the O 1s region as a function of H_2O exposure to a copper surface are shown in Fig. 2. At 0-L exposure, the spectrum shows two very low-intensity features at approximately 530 and 533 eV. These features most likely stem from emission of trace amounts of residual oxides at the Cu surface, i.e., CuO and Cu_2O. After 1-L H_2O exposure, the lower binding energy region of the spectrum remains unchanged, but a new feature at approximately 533.5 eV appears. Increased H_2O exposure shifts the 533.5 eV peak to higher binding energy that saturates at approximately 534.5 eV. From these data two points may be made. First, chemical reaction between H_2O and Cu at 160 K does not occur to any appreciable extent. If reaction did occur, we would expect an increase in intensity below 533.5 eV due to emission from copper oxides or copper hydroxide. Second, H_2O exposures greater than 20-L or so lead to multilayer H_2O coverage. This is evident from the increase in O 1s binding energy of the circa 534 eV peak as a function of exposure. The insulating H_2O multilayer charges slightly due to photoemission, which yields an O 1s peak at higher binding energy. As shown in Fig. 3, sputtering the layer of ice results in a decrease in the O 1s peak intensity with a concomitant increase in Cu $2p_{3/2}$ intensity. These data suggest that the H_2O layer is removed from Cu under ion beam irradiation.

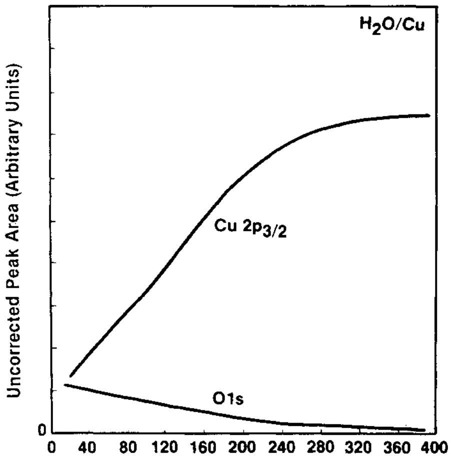


Fig. 3 Cu $2p_{3/2}$ and O 1s peak areas as a function of sputter time for a H_2O multilayer on a Cu surface. Peak areas have not been corrected for individual elemental sensitivities.

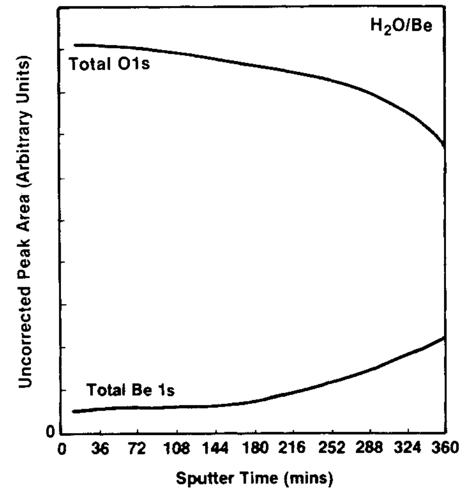


Fig. 4 Total O 1s and Be 1s peak areas as a function of sputter time for a H_2O multilayer on a beryllium surface. Peak areas have not been corrected for individual elemental sensitivities.

Results on Cu were compared with similar data obtained from ion beam bombardment of an H_2O multilayer on a Be mirror. In Fig. 4, data are presented for O 1s and Be 1s peak areas as a function of sputter time for a H_2O multilayer on Be surface at 100 K. In contrast to data shown in Fig. 3, ion beam bombardment of H_2O on Be does not lead to an increase in surface photoemission intensity or decrease in overlayer intensity until greater than 150-min sputter time. This suggests an apparently lower rate of H_2O removal from Be than Cu.

Some insight into the effect of ion bombardment of the Be surface can be gained from Fig. 5, which presents Be 1s spectra as a function of sputter time for a H_2O multilayer on a Be surface. Figures 5a and 5b show spectra for the clean and H_2O multilayer covered surfaces, respectively. Present in each spectrum is a single peak at 111.5-eV binding energy assigned to emission from Be metal. After 100 min of sputter time (Fig. 5c), a weak feature at 114.5 eV appears, but the 111.5 eV peak remains of constant intensity. Figs. 5d and 5e show increased intensities of both the 111.5 and 114.5 eV peaks after 200 and 300 min of sputtering time, respectively. As shown previously, the 114.5 eV peak is assigned to BeO presence on the surface.[11] The increase in intensity of this feature with sputtering indicates BeO is formed by bombardment of the H_2O multilayer covered surface. For this to occur, the interaction of the ion beam with the surface must involve processes other than direct removal of surface atoms. The reduced H_2O sputtering rate on Be vs Cu thus stems from an ion-beam-induced reaction where, instead of sputtering H_2O, the ion beam causes formation of a surface oxide.

Figure 6 shows a plot of O 1s, Be 1s (metal), and Be 1s (oxide) peak areas as a function of sputter time for an H_2O multilayer on Be surface. Correlating well with the spectra of Fig. 5, these data show formation of BeO with sputter time at a rate greater than that for the increase in Be (metal) peak area. Further inspection of Fig. 6 reveals a nonmonotonic increase in the area of the BeO peak and decrease in the area of the O 1s peak. In analysis of these data, we must keep in mind that the O 1s peak includes intensity from both H_2O and BeO. From the flat shape of the O 1s curve but increasing BeO peak area at sputter times less than 160 min, a significant portion of the ion beam energy goes toward reacting H_2O with the Be substrate, not H_2O removal. After 160 min of sputter time, the increased slopes of the BeO and Be metal peak area curve as well as the decrease in the O 1s peak area curve indicate

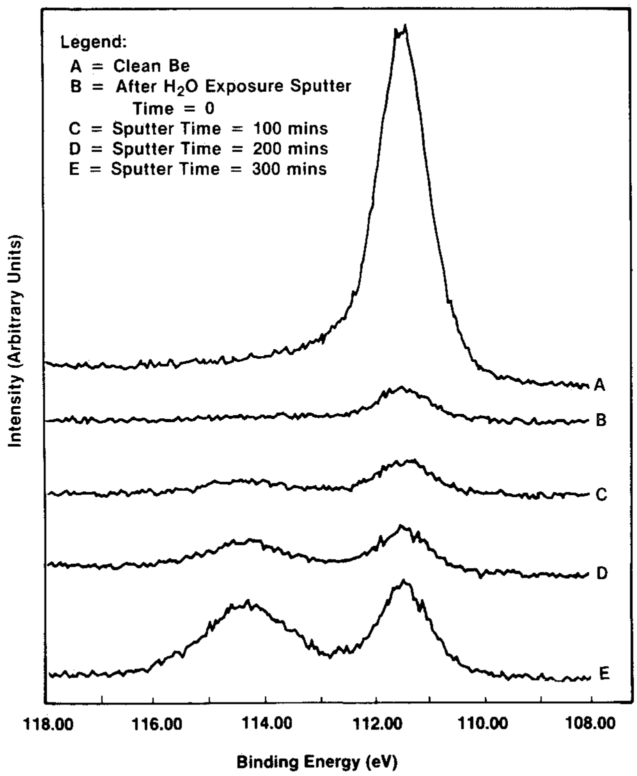


Fig. 5 XPS spectra over the Be 1s region for (a), clean (b) H_2O-covered, and (c–e) sputtered H_2O-covered Be surface. Note formation of the BeO peak at 114.5 eV as a function of sputter time.

sputter removal of the remaining H_2O overlayer. The 160-min etch time then corresponds to formation of a BeO layer thick enough to preclude H_2O reaction with the Be metal substrate. After this time, an increase in *both* BeO and Be peak areas is evident. We should note that the O 1s peaks for H_2O and BeO are not resolvable. Thus, further evidence for the preceding model is not available in the O 1s region of the photoelectron spectrum.

The mechanism of Be oxidation under ion bombardment has been presented previously[11] and is based on previous studies by Bar-Nun et al.[12] of Ne ion bombardment of ice at 140 K. Bar-Nun et al. report that the majority neutral species emitted from this surface by sputtering is not H_2O, but H_2 and O_2.[12] The mechanism associated with production of these species involves formation of H and O atoms along the track of the penetrant ion by breakage of O-H bonds in the ice overlayer. These ions then combine to form H_2 and O_2 molecules, which migrate through the ice lattice and are ejected from the surface. Formation of BeO in our experiments thus is believed to be due to the presence of O atoms at the Be surface formed by ion bombardment of the H_2O multilayer.

It is important to note that SIMS data support our XPS observations of ion bombardment of the H_2O-covered Cu and Be surfaces. SIMS spectra of a multilayer on Cu surface show protonated H_2O clusters but no copper oxide peaks. On the other hand, SIMS spectra of the H_2O-covered Be surface show the metal oxide, hydroxide, and the hydride ions, and nearly immeasurable intensity from H_2O clusters at low sputter times.

The sticking probability of H_2O on native BeO was found to be lower than that on a clean Be surface. A 100-L H_2O exposure produced a markedly lower H_2O O 1s peak area compared with a clean Be surface. Ion bombardment of the H_2O-covered BeO surface yielded no increase in BeO intensity with sputter removal of H_2O. It is reasonable to propose, similar to the situation after 160 min of sputter time of a H_2O-covered clean Be surface, that the native BeO layer is thick enough to inhibit O-atom reaction with the underlying Be surface.

Dioctyl Phthalate

Figure 7 shows data for ion beam removal of DOP from Be as a function of time. In this case, the Be surface is covered with the native oxide because the DOP was deposited in air. XPS spectra show no evidence for DOP chemical reaction with the Be surface. In sputtering the DOP-covered surface, the C ls peak are curve decreases with sputter time, indicating removal of DOP. An increase in Be 1s and O ls peak areas correlates well with this behavior. Since DOP is an ester, which contains oxygen, it is conceivable that the oxygen could react with the Be surface, possibly by a mechanism similar to that for the sputter-induced H_2O reaction. No evidence for such reaction was observed. As in the cae of ion bombardment of a H_2O-covered BeO surface, this may be due to the thickness of the oxide layer.

Mixture of Water and Dioctyl Phthalate

Mixtures of DOP and H_2O were deposited on native BeO by first adsorbing DOP in air, then adding H_2O under UHV conditions after the substrate had been cooled. It should be noted that exposing a toluene-covered Be surface to H_2O resulted in displacement of toluene, leaving only a multilayer of H_2O.

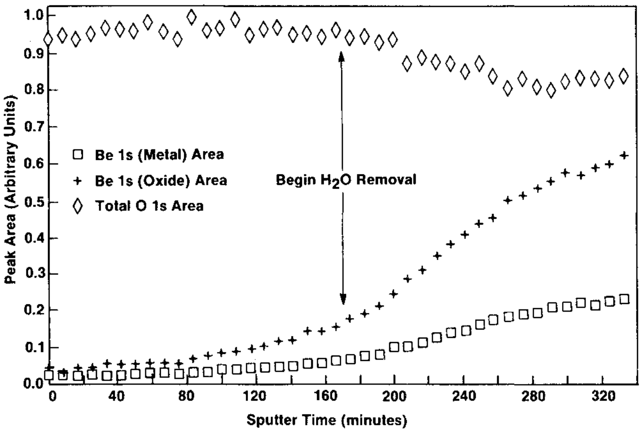


Fig. 6 Be (metal), Be (oxide), and O peak areas as a function of sputter time for a water multilayer on a Be surface. Note the break in shape of each curve after approximately 160 min of sputter time.

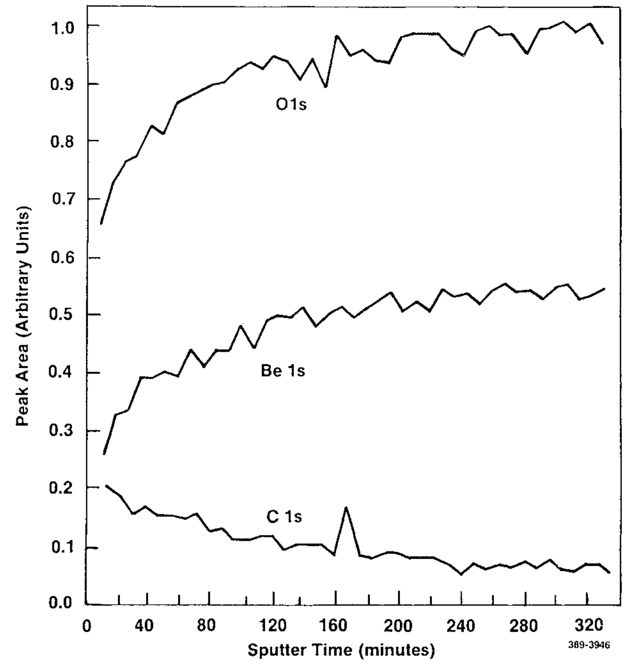


Fig. 7 C 1s and total Be 1s and O 1s peak areas as a function of sputter time for a thin film of DOP on a Be surface.

DOP and H_2O, on the other hand, can both adsorb sequentially on this surface. The sticking probability of H_2O on the DOP-treated surface, however, was considerably lower than on either the cleaned Be or the native BeO.

When the H_2O-DOP mixture is removed by ion beam bombardment, the C 1s area decreases whereas an increase in the Be and BeO intensities is observed. This behavior is similar to that observed for the DOP-only case. However, the initial increase in the Be and BeO peak areas is slower than that measured when removing only DOP from Be. Individual spectra over the Be 1s region show a slight increase in the Be oxide peak relative to Be metal during ion bombardment of this surface.

Conclusions

This study has examined the adsorption of some important contaminants on cryogenic mirror surfaces and established preliminary conditions for ion beam removal of these species. Our results indicate that contaminants are removed from mirrors at varying rates depending on the specific contaminant and mirror involved. Chemical interaction between the contaminant and surface are important even at the low temperatures used for these experiments and required for system operation. Water is removed at different apparent rates from different surfaces, under constant ion beam conditions.

Although the feasibility of using ion beams to clean small cryogenic mirror samples without creating excessive scatter damage has been established, much is still to be learned about these systems. Current and future experiments in our laboratory are aimed at furthering our understanding of ion beam/surface interactions at lower temperatures. In addition, we plan to compare different types of ion guns, monitoring the specific parameters necessary to remove surface contamination. Future plans also include increasing the number of contaminants to create complex mixtures. The overall goal of this study is to understand adsorption of complex mixtures of contaminants and their removal under appropriate ion beam conditions at temperatures below 100 K where the LWIR systems currently operate.

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Associate Editor