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SURFACE INTERACTIONS RELEVANT TO SPACE STATION CONTAMINATION PROBLEMS

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Abstract. The physical and chemical processes at solid surfaces which can contribute to Space Station contamination problems are reviewed. Suggested areas for experimental studies to provide data to improve contamination modeling efforts are presented.

Introduction

A number of consequences have been recognized as serious and problematic in terms of contamination and materials degradation from placing platforms and vehicles in various earth orbits. (Roux and McKay, 1984; Leger et al., 1986; Bareiss, 1987).

Identified Sources of Contamination:

- outgassing, leaks, dumping, and thruster engine firing
- interaction of "source" surfaces with above
- the ambient space environment ($h\nu$, e^-, ±ions, neutrals)
- interaction of "source" surfaces with environment
- possible electrostatic discharges
- mechanical failure (microcracking, fracture, spallation)

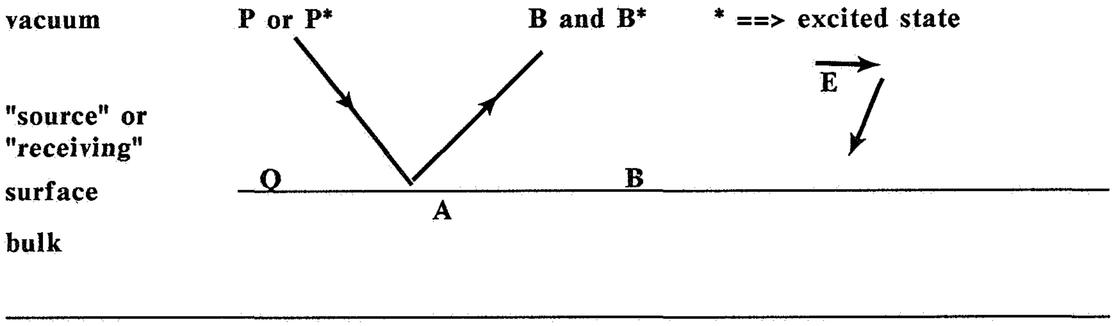
Consequences:

- "space-phase" particles and particulates (=>absorption, glow, etc.)
- condensation/deposition on "receiving" surfaces
- modification/degradation of surfaces-materials (roughness, optical, electrical, mechanical properties)
- charging

Figure 1 shows schematically the surface interactions in a general sense that contribute to the emission or uptake of matter at a substrate. Surface Science has traditionally focused on: (1) describing, quantifying, and explaining phenomena, and (2) surface analysis (quantitative and qualitative analysis). Although the latter can contribute to our understanding of the contamination-surface effects, the former is more important. Also, it should be emphasized that both surface and near surface phenomena need to be considered and coupled. For relatively simple processes, we might expect:

Emission OR Condensation/Absorption Probability =

f (Flux$_P$, Energy$_P$, Concentration$_A$, Temperature, Surface Roughness, Mechanical Stress, Relevant Cross Sections, Activation Energies, Rate Constants). (1)



A represents	Bound Species Absorbed Species Adsorbed Species	(near or on surface)
P represents	Incident "particles"	($h\nu$, e^-, ±ions, neutrals, phonons-heat)
B represents	Ejected OR Absorbed/Condensed Product(s)	(same as **P**)
Q represents	Surface Charge; $\vec{E}$ is the associated electric field.	

Fig. 1. Schematic of possible interactions with a surface that can lead to the release of particles.

Thus, quantitative predictions may require a detailed understanding of the physics and chemistry of the process as well as the appropriate parameters and constants. In many cases, synergisms (e.g., Effect of $(P_1 + P_2) >>$ Effect of P_1 + Effect of P_2), internal electronic/rotational/vibrational energy, angles of incidence, and interfaces (e.g., coating/substrate interface) may also have to be considered. As an example, it is entirely possible that simultaneous electron bombardment and O atom exposure would result in significant increases in the oxidation of a polymer.

For modeling purposes, empirical equations might suffice to predict relatively complicated effects. An example might be the outgassing rate of volatile compounds from a thermally cycling polymer matrix or the production of decomposition products from fast atom bombardment of a polymer. Of utmost importance is to be able to predict the rates of emission/uptake, the direction and velocity of the emission, the sticking probability of a emitted species at another surface, and the possible changes in properties caused by the presence of this new species.

Important Surface Phenomena are listed in Table 1.

Table 1. Important Surface Phenomena which can play a role in Contamination Processes.

Equilibrium Processes:

Permeation and diffusion (may be rate limiting in many processes) (Jost, 1952)

Adsorption (physisorption, chemisorption), absorption, desorption, sublimation (thermally regulated) (Redhead et al., 1968)

Catalytic Reactions (Somorjai, 1981)

Non-equilibrium Processes:

"Hot" atom, ion, and radical/surface reactions including activated adsorption/desorption (Ceyer et al., 1987)

Electron and photon induced desorption (Knotek, 1984)

Electron, ion, and photon induced/enhanced chemistry (Chuang, 1981)

Photoelectron and secondary electron emission (Cardona and Ley, 1978)

Chemically and radiation induced luminescence/electron emission from surfaces (Chen and Kirsh, 1981)

Sputtering (Stuart, 1983)

Emission of excited and/or reactive species (Hagland and Tolk, 1986)

Radiation induced polymerization and cross-linking of organic molecules (Wright, 1978)

Incident particle/stressed substrate interactions (Dickinson, 1987)

Electrostatic breakdown (Kendall et al., 1986)

The phenomena listed under Equilibrium Processes are well known; diffusion and the ad(b)sorption/desorption phenomena certainly are critical in the outgassing and build-up of contamination layers on exposed surfaces. The catalytic behavior of metals and metal oxide surfaces should not be ignored if large areas of such materials come under consideration, particularly in possible reactions involving oxygen, hydrogen, nitrogen, and water.

Under Non-Equilibrium Processes, we have listed a set of irreversible phenomena, usually involving incident particles with non-thermal internal/translational energies. Space limitations do not allow a detailed description of all of these effects to be given here; references have been cited for obtaining additional information.

Examples and Discussion

A simple example of a non-equilibrium process is the emission of electrons from a polymer surface exposed to UV radiation. For illustration we consider the polymer Kapton-H and radiation consisting of pulses of 248 nm Excimer laser light (20 ns pulse width). Figure 2 shows the time-of-flight of the electrons over a distance of 5 cm, digitized at 5 ns/channel. (Tonyali et al., 1988). The data were taken for unstressed and stressed material, showing that the elongated Kapton actually yields considerably more photoelectrons. The sources of these charged particles are weakly bound electrons in electron traps located above the valence band of the polymer. In this case, mechanical stress in the presence of intense 248 nm radiation

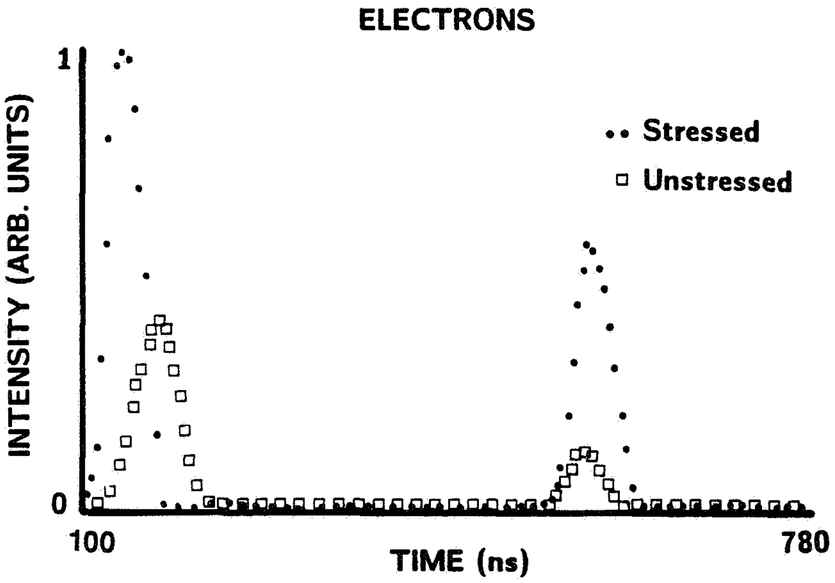


Fig. 2. Electron emission TOF spectrum of stressed and unstressed Kapton-H samples. The specimens were elongated to 70% strain and then subjected to 0.7 J cm^{-2} pulsed laser radiation @ 248 nm.

significantly alters the population of these states. For a given density of trapped electrons in a single state, n_e, the yield of photoelectrons is first order in the photon flux. If $h\nu$ is larger than the binding energy of this state, the yield is weakly dependent on hv, particularly over the range of the solar spectrum. Thus, if we assume that n_e is constant, the photoelectron yield, Y, is simply:

$$Y = (\text{fluence})\ (\text{"cross-section"})\ n_e \tag{2}$$

Einstein's equation predicts the energy of the photoelectrons:

$$E = h\nu - E_b. \tag{3}$$

The UV photon flux incident on an orbiting structure should be fairly accurately known and cross-sections could be measured. Correct modeling of the yields of emission of such charge would require relatively accurate n_e.

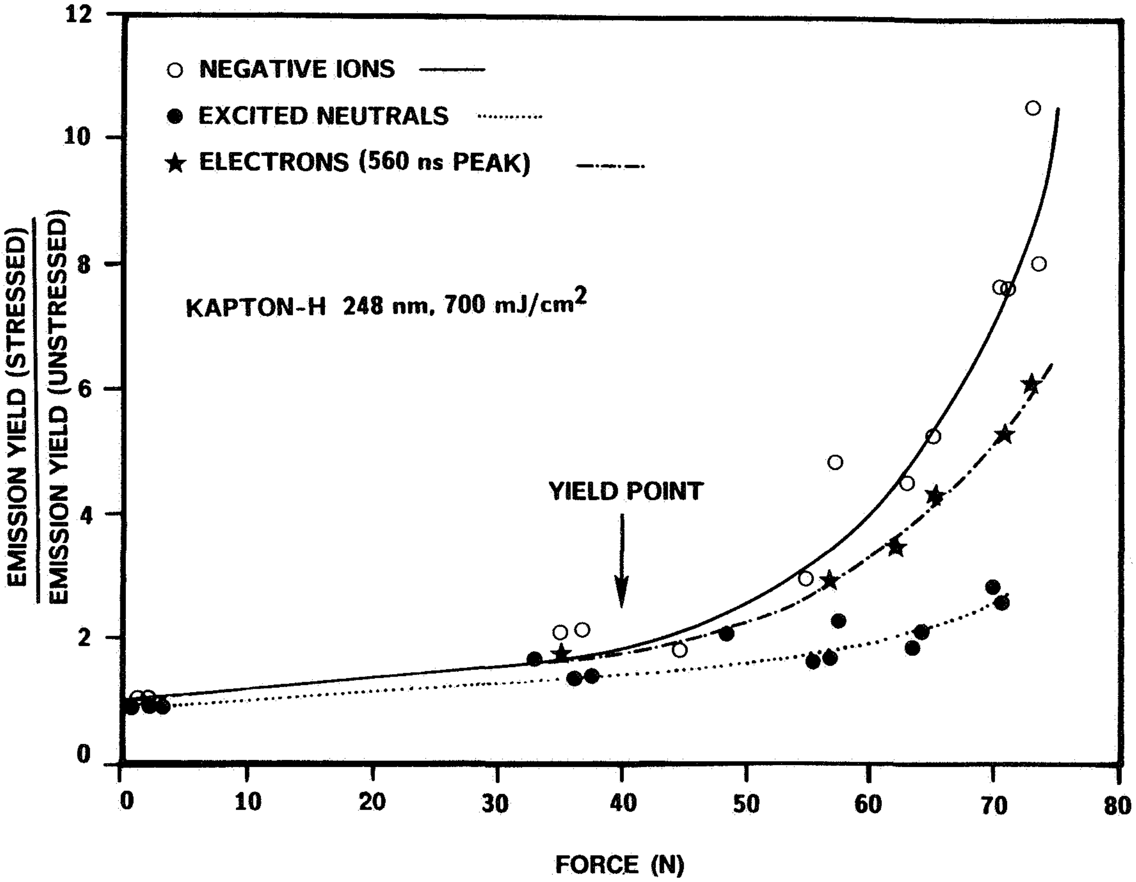


Fig. 3. The effect of an applied force on the negative ion, electron, and excited neutral emission yield. The laser fluence to the sample was 0.7% J cm^{-2} @ 248 nm.

We have also shown (Tonyali et al., 1988) that mechanical deformation influences the yield of other products of UV laser bombardment at 248 nm of Kapton-H. Figure 3 shows the dependence of the negative ions, excited neutrals, and one of the electron peaks (at 560 ns), all showing increases with applied force, particularly at forces beyond the onset of plastic deformation of the Kapton. The emitted negative ions are principally in the region of mass 28.

Another example of an electron emission process involving traps is thermally stimulated electron emission (TSEE). If a wide bandgap material (e.g., ceramic, glass, polymer) is irradiated with electrons, x-rays, ions, etc. of sufficient energy to create defects such as color centers and free radicals, trapped charge can be stimulated thermally to react with these defects. Energy that is released during this reaction can result in luminescence (radiative decay) or electron emission (via an Auger process). An example of the latter is shown in Figure 4a,

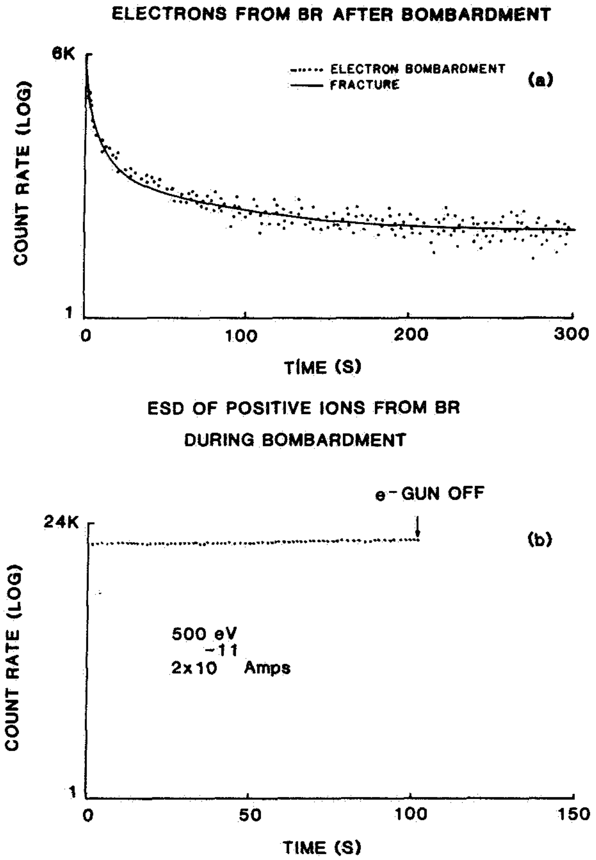


Fig. 4. (a) Emission of electrons from a thin film of polybutadiene (BR) following bombardment of the film with 500 eV electrons(...). The solid line is a typical fracto-emission (electrons) curve following fracture of BR, normalized at a single point. (b) Electron stimulated desorption of positive ions during bombardment of the BR with 500 eV electrons at 2 x 10^{-11} A.

where an elastomer surface (polybutadiene) has been irradiated with 500 eV electrons (2 x 10^{-11} Amps) for a few seconds only (Dickinson and Jensen, 1985). The TSEE which follows this bombardment is shown; it decays away according to a well described set of equations (Halperin and Braner, 1960) involving moving trapped electrons to recombination sites near and on the surface of the polymer. If we now thermally stimulate the material with a linear temperature sweep, we obtain a "glow-curve" in the emitted electrons which give the activation energy for mobilizing the electrons, in this case 0.6 eV. If we observe the surface with a detector sensitive to positive ions, we see that during bombardment, we see electron stimulated desorption of positive ions (Figure 4b) which disappears immediately when the electron current is turned off. Although we did not measure the mass of these ions at the time, from other work we have done on similar polymers, a likely candidate is H^+. The ion yields for this particular experiment were 2 x 10^{-4} ions/electron.

Catalytic reactions involving oxygen may be important on inorganic substrates, e.g., metal oxides. As an example of a surface science experiment involving a clean metal surface, we examine the oxidation of CO on the surfaces of small, supported Rh particles. The method used involves chemisorbing a saturated layer of oxygen on the Rh, then quickly introducing a step function of CO partial pressure above the sample. A quadrupole mass spectrometer monitors the resulting desorbed CO_2, shown in Figure 5 for four different metal particle sizes. This type of data can assist in working out the reaction mechanisms. In this case, all of the data can be computer-fit very well by a simple

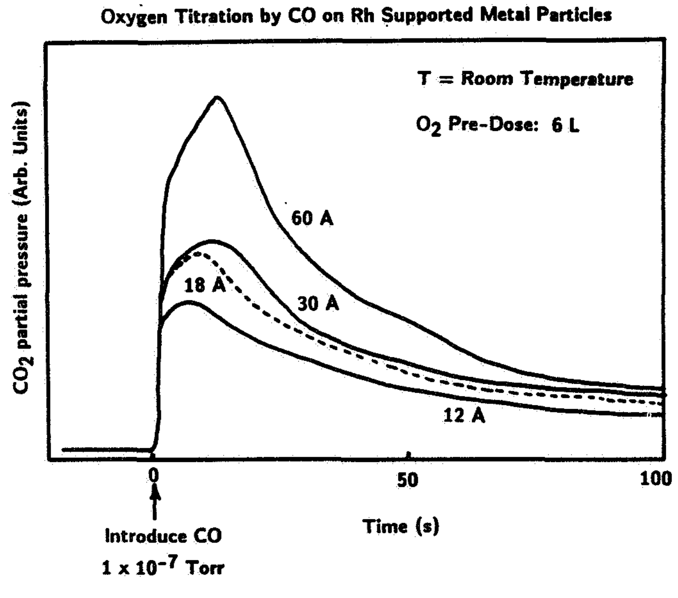


Fig. 5. CO_2 partial pressure produced by the titration of O(ads) by CO(gas) from the surface of small Rh metal particles supported on an oxide substrate. The different curves represent different average particle sizes.

Langmuir-Hinshelwood mechanism (CO_{ad} reacting with O_{ad}) and yields absolute reaction rates.

A surface process that is analogous to chemiluminescence was studied in much the same way for the system involving the chemisorption of molecular fluorine on tungsten. One finds that when the clean surface is exposed to a beam of F_2, electrons are emitted during the uptake of the fluorine. In Figure 6, we show the resultant electron emission vs. time at three different substrate temperatures (Loudiana et al., 1985). The lines represent a model we developed for fitting these emission vs. time curves. The mechanism involves a dynamic electronic transition resulting in an excited surface intermediate that can again decay via the emission of a photon or an electron. The temperature dependence (increased yield with increasing temperature) is a consequence of raising the electron energies above the Fermi level in the metal, making them easier to eject into the vacuum. The number of electrons emitted/adsorbed atom

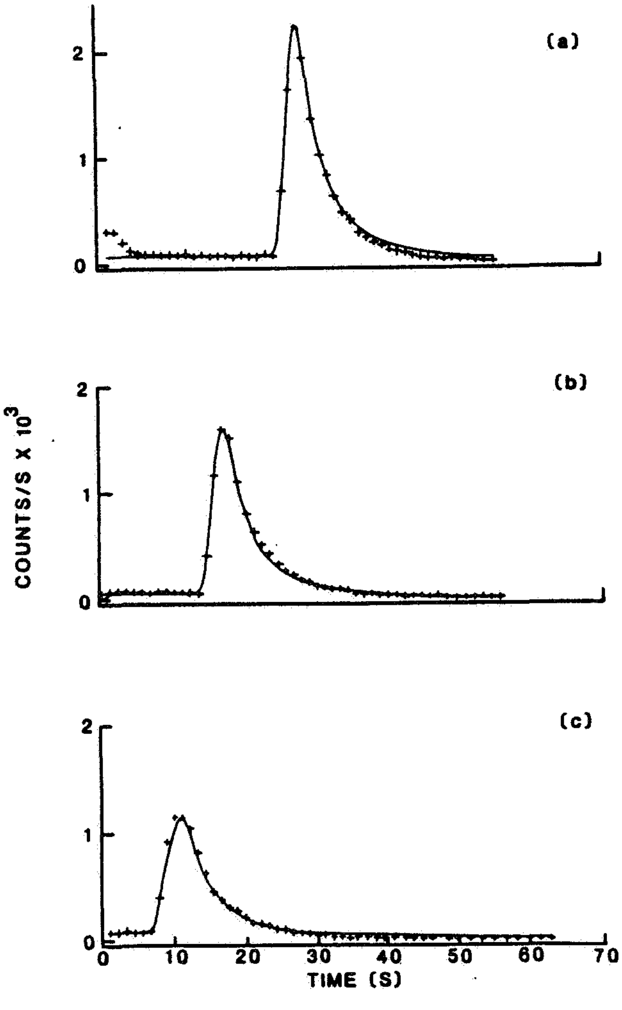


Fig. 6. Chemisorptive electron emission created by exposing a clean W metal surface to nearly a step function of F_2(gas). The three curves are for different W surface temperatures; the largest yield of electrons occurs for the highest temperature.

ranges from 10^{-6} to 10^{-10} for reactive molecules such as O_2 and F_2. Chemisorptive luminescence, a parallel process, have much higher yields because they are one electron processes vs. two for chemisorptive electron emission.

XeF_2 is a relatively unstable noble gas compound such that when it hits a surface, it easily dissociates, yielding atomic fluorine, a species not all that different from atomic O. Exposure of a material such as SiO_2 to a beam of XeF_2 shows chemisorption of fluorine, as detected by a mass microbalance and Auger Electron Spectroscopy. No evidence for removal of substrate atoms has been observed for gas exposure alone. However, if we bombard the surface simultaneously with electrons, ions, or energetic photons, we see quite high yields of surface etching. (This happens to be a reaction of considerable interest to the semiconductor processing industry.) In Figure 7, we show mass spectrometer measurements (Dickinson et al., 1988) of two mass peaks, mass 16 (atomic O and O_2) and mass 104 (SiF_4) which are the principal product gases released during electron induced etching of SiO_2. The etch rates at high reactive gas coverages can be as high as unity (e.g., SiO_2 units lost/incident particle). We have also shown that in a number of inorganic thin films, chemisorbed F atoms are dramatically driven into the film (absorbed) due to electron bombardment. The rate for this process was a maximum for 50 eV electrons.

Using simultaneous microbalance measurements and pulsed electron sources, one can get quite accurate yields, energy dependences, and product kinetic energy information for this type of etching reaction. Similar results for O atom plus radiation exposures of materials should be possible in conjunction with the NASA-sponsored laboratory studies. In addition to radiation, O atom exposure of mechanically stressed polymers should also be tested.

An example of an adsorption process that normally has zero sticking coefficient is the activated adsorption of CH_4. When thermal methane molecules at reduced pressures are incident on clean metal surfaces such as single crystal (111) Ni, no evidence of chemisorption is observed. When the translational velocity of the CH_4 is increased to a few tenths of an eV, Ceyer et al. (1987) have shown that the molecules begin to dissociatively chemisorb (forming adsorbed CH_3 and H); the sticking probability increases exponentially with the normal component of kinetic energy. The mechanism for this process is believed to involve collisionally induced distortion of the molecule which greatly enhances quantum mechanical tunneling of the hydrogen atom into a surface bonding state. It should be noted that some molecules decrease their sticking probability with increased kinetic energy due to reduced time in the interaction region. Also, recently Cardillo (private communication) has shown direct evidence that fast atom collisions with surfaces can generate electronic excitations in the substrate, indicating energy transfer channels not normally considered.

We briefly mention the work by Kendall et al. (1986) utilizing TOF mass spectroscopy. They have analyzed the neutral atoms and molecules emitted during electrical breakdown of thin

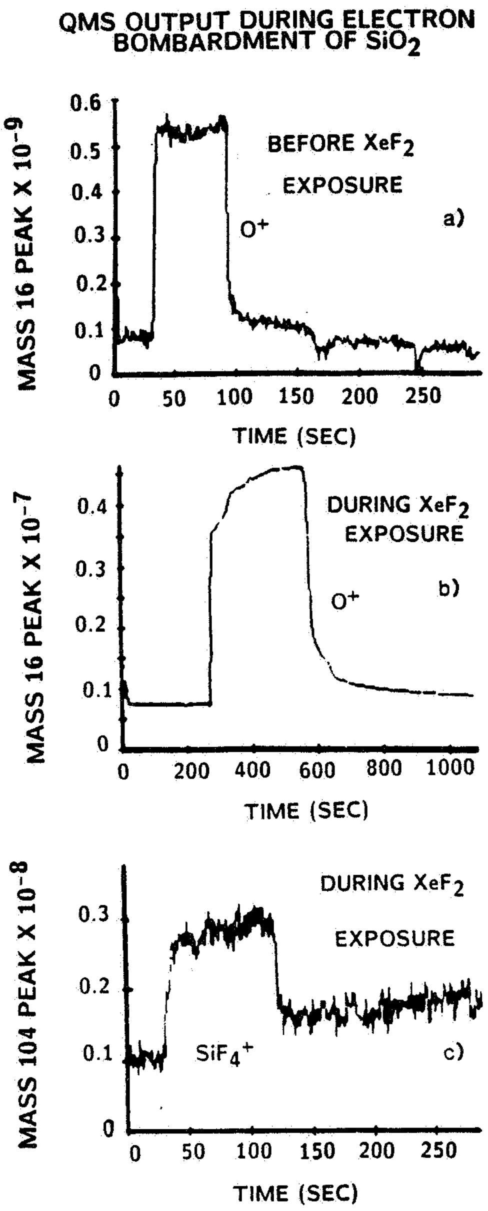


Fig. 7. Output of a quadrupole mass spectrometer during the exposure of SiO_2 thin films to electron bombardment. (a) Curve shows the mass 16 response due the electron stimulated desorption from SiO_2. (b)-(c) Curves show the mass 16 and mass 104 responses, respectively, for the simultaneous exposure of the SiO_2 to the same electron bombardment and XeF_2.

sheets of Kapton and Teflon. The spectra provide the product species, quantity emitted, and the time evolution of the emission relative to the breakdown event.

We also mention a recent study by Dursch and Hendricks (1987) on the consequences of exposure to an oxygen plasma of a anodized Al foil protected graphite/epoxy tube. In particular, they examined the consequences of a pin hole in the foil, showing considerable etching beneath the hole. This should be examined in terms of the contamination problem.

Finally, of relevance to the production of excited species that contribute to the glow phonomena, we mention a series of experiments by Lebsack (1977) which showed that the escape probability of a number of metastable species (including N_2*) increased with normal velocity and surface condition. The more "passive" a surface (e.g., highly oxidized, hydrocarbon covered, etc.), the less quenching of long-lived excited states would occur. The implications concerning the production, survival, and resulting angular distributions of metastable species are evident.

Conclusion

We conclude by presenting a list of surface science problems that should be investigated to provide improved information to address Space Station contamination problems. It is assumed that the surfaces of interest have been identified, i.e., the range of materials, coatings, and substrates are reasonably well defined, and are available for study.

Relevant Surface Science Problems

- Measurements of necessary sticking probabilities, reaction and process rates, product species.
- Measurements of dependence on process rates on incident particle internal and kinetic energies, incident angle.
- Measurements of product internal and kinetic energies, angular distributions. (This includes, for example, metastable molecules such as N2* which may play a key role in glow phenomena.)
- Determining "State of the Surface" for the various materials of interest as a function of time (months, years). Chemical, physical characteristics of the surfaces of interest (both "source" surfaces/"receiving" surfaces).
- Determining potential Synergisms: e.g.,
  - -- O atoms/Electrons
  - -- O atoms/electric fields
  - -- UV or O atoms/mechanical stress
  - -- UV/chemisorbed organics
- Determining mechanisms of the important processes will facilitate making design changes, materials choices in the long run.
- Studies related to protective coatings (including adhesion), repair/resurfacing of "sources", and removal of contaminants from critical surfaces.

- Studies on the interaction of penetrated foil/G-E Composite structures with O atom environment. (Fluxes of released products, composition, angular distributions, etc. of gases released from pinholes).

- Experimental tests of models for solar release of particulates.

- Determination of a complete description of the environment experienced by these surfaces.

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