

CONF-8503134--1

MASTER

CONF-8503134--1

DE85 010276

**ADSORPTION/DESORPTION PROPERTIES OF VACUUM MATERIALS  
FOR THE 6 GeV SYNCHROTRON\***

Alan R. Krauss  
Chemistry/Materials Science & Technology Divisions  
Argonne National Laboratory  
Argonne, IL 60439

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**DISCLAIMER**

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

To be presented at:

Machine Workshop on the 6 GeV  
Synchrotron Radiation Source  
Gaithersburg, MD

March 28-30, 1985

\*Work performed under the auspices of the Office of Basic Energy Sciences,  
Division of Materials Sciences, U.S. Department of Energy.

M18

## INTRODUCTION

Considerable attention must be paid to the vacuum and adsorption/desorption properties of all materials installed inside the vacuum envelope if the design goals of the 6 GeV synchrotron are to be met. Unfortunately, the data is very sparse in several key areas. Additionally, some procedures normally associated with good vacuum practice, such as air baking, may prove to be totally unsuitable on the basis of desorption properties. We present here a brief discussion of the adsorption, outgassing, electron-stimulated desorption (ESD), and photon-stimulated desorption (PSD) properties of vacuum materials as they relate to the design of a 6 GeV synchrotron.

The principal vacuum consideration concerns the attainable composition and pressure of the residual gas in the beam chamber during operation. One obvious way of minimizing the background pressure is to provide as high a pumping speed as geometrically possible. However, additional considerations apply to synchrotron design. Gas phase collisions between the beam and residual gas result in scattered electrons and bremsstrahlung, both of which result in gas desorption from the beam chamber walls, which are very close to the beam path. The desorbed gas is largely neutral and contributes to an overall rise in the residual gas pressure. The relatively small ion fraction of the desorbed gas may, however, prove to be a much more serious problem since ions will be trapped by the space charge of the beam.

The synchrotron radiation itself will hit the photon absorber (Fig. 1), which must be actively cooled to handle the power load. Thermal desorption and photon-stimulated desorption produces a gas load for the distributed pumping system. Additional gas is also produced by thermal desorption from the walls of the pumping chamber and by scattered electrons and photons from the photon absorber. Since current designs specify pumping only within the

pumping chamber, the pressure in the beam chamber will always be higher than in the beam chamber.

The outgassing properties depend not only on the materials and the pre-treatment, but also on the cleaning process used as part of the operating procedure. Techniques such as air baking, vacuum baking, hydrogen, oxygen or argon discharge cleaning affect both the gas composition and the total outgassing rate.

#### ADSORPTION

The two materials most commonly used for vacuum chamber design, stainless steel and aluminum, have low sticking coefficients because the surface is actually an oxide rather than a metal. Stainless steel adsorbs most of the common gases found in vacuum systems until a passivating chromium oxide layer is formed. Aluminum adsorbs fewer gases than stainless, but adsorbs oxygen and CO very strongly. Oxygen adsorption produces an oxide layer, even at room temperature, and CO is the principal intrinsic adsorbed (and therefore the principal desorbed) species. Hydrogen, which has a rather low solubility in aluminum is present principally in the form of water trapped during the formation of the oxide layer.

In order to minimize outgassing and stimulated desorption, it is necessary to produce surfaces which either do not desorb the adsorbed gases, or which do not adsorb gas (Fig. 2) in the first place. This latter approach, which is especially important for the photon absorber, can be pursued by using materials such as Ag or Au, perhaps in the form of a coating. The coating must however be both reasonable in cost and durable enough to withstand repeated cleaning cycles such as glow discharge cleaning. Various techniques such as surface modification by ion beam implantation and the production of

self-sustaining coatings by Gibbsian segregation in dilute alloys need to be investigated as means of producing low sticking coefficient surfaces.

## OUTGASSING

The vacuum outgassing properties of stainless steel, copper, and aluminum as measured at two different laboratories are shown in Fig. 3. The gas composition and total outgassing rate vary considerably, depending on the baking procedure. In particular, air baking or oxygen discharge cleaning significantly reduces the outgassing rate for both stainless steel and aluminum as the result of the formation of an oxide surface. The two sources cited, however, differ considerably on the composition of the desorbing gas. Halama and Herrin<sup>1</sup> find a relatively large outgassing rate for aluminum, consisting almost entirely of hydrogen. Dobrozemsky and Moraw, on the other hand, find a lower outgassing rate consisting primarily of CO. The difference presumably stems from different fabrication and surface preparation techniques. It has been found, for example, in the magnetic fusion program that hydrogen glow discharge cleaning substantially reduces the hydrocarbon, CO and O concentration on the vessel walls, while producing a large hydrogen inventory in the near-surface region. Since beam lifetime in a synchrotron depends strongly on the amount of desorbed CO, it is important to know the variation in gas composition resulting from differing fabrication and cleaning procedures.

## STIMULATED DESORPTION

### Electron Stimulated Desorption

Electron stimulated desorption is believed to arise as the result of electronic excitation of the adsorbed gas species, although several different mechanisms have been offered to explain the details of the process. In

general, however, it is observed that desorbed species are primarily neutral, although for experimental reasons it is more often the positive ion yield that is studied. It is sometimes found that the desorption rate of a gas from a given surface varies as much as 3-4 orders of magnitude, depending on the thermal history of the adsorbate (Fig. 4). Because of the ion trapping mechanism, desorbed ions are of serious concern for synchrotron operation. Until relatively recently, there was almost no information on the emission of negative ions. More recently<sup>3-6</sup> electron stimulated desorption of negative ions has been observed on tungsten and molybdenum (Fig. 5). Measured desorption cross sections range from 3% to 100% of the positive ion values. So far there has been no work on the stimulated desorption of negative ions from materials relevant to synchrotron design. To the extent that positive ions are desorbed in greater quantity than negative ions, the effect of ion trapping can be reduced by using a positron, rather than an electron beam. However, the efficacy of positron beams as a means of reducing ion trapping may be limited if the negative ion desorption cross section is comparable with that of the positive ions.

#### Photon-Stimulated Desorption

The PSD cross section depends strongly on the photon energy, exhibiting a threshold effect (Fig. 6) at energies corresponding to adsorbate excitation energies for desorption from metals, and to band gap excitation for desorption from insulators and semiconductors.<sup>7</sup> The desorbed gas has been reported to be predominantly CO, CO<sub>2</sub>, and O<sub>2</sub>.<sup>8</sup> There is essentially no information on negatively charged gas species desorbed by PSD. On oxide surfaces such as that of aluminum or passivated stainless steel, the PSD cross section is almost as large as that of ESD, i.e., about  $10^{-17}\text{cm}^2$ . For unoxidized metal surfaces such as that of Ni or W, the desorption cross section is up to 6 orders of

magnitude smaller, corresponding to a quantum efficiency of  $10^{-8}$ - $10^{-9}$  molecules per photon. PSD exhibits the same threshold behavior as ESD and the energy dependence of the PSD yield is similar to that of the photo-electron yield. The number of photo electrons is too small to account for PSD as the result of ESD by photoelectrons. Both processes are, however, believed to be associated with the same excitation process.<sup>9,10</sup> It should therefore be possible to simulate much of the PSD behavior by electron bombardment studies, although in-synchrotron and laser experiments are needed for a complete picture of PSD.

#### SUMMARY

##### 1. Adsorption Properties

The materials most commonly used for vacuum chamber construction, stainless steel and aluminum, strongly adsorb most common gases, a condition not favorable for synchrotron operation. Specifically, aluminum and stainless steel are very strong oxygen adsorbers and form oxides at room temperature. Materials such as Ag, Au, and Cu should be considered as vacuum-side materials, possibly as thin films or self-sustaining coatings. The coatings should be sufficiently durable to withstand repeated discharge cleaning.

##### 2. Outgassing Properties

The composition of outgassing products for an aluminum vacuum vessel as a function of surface treatment (e.g., vacuum bake, air bake, hydrogen, oxygen or argon discharge cleaning) is not well established. Existing data are contradictory.

##### 3. Electron Stimulated Desorption

The desorption cross section from an oxide surface, such as that of aluminum or stainless steel, is several orders of magnitude larger than that of a metal surface. For a given system, the desorption cross section may vary

by several orders of magnitude depending on thermal history. Very little data exist on the desorption of negative ions, but the existing data indicate that the desorption cross section for negative ions may be at most 30x smaller than for positive ions. This fact may limit the utility of using a positron beam as a means of reducing trapped ion effects.

#### 4. Photon-Stimulated Desorption

PSD cross sections for metal surfaces are extremely small, rising by 4-5 orders of magnitude for the oxides. PSD exhibits strong threshold effects at energies corresponding to adsorbate transitions or, for oxides and semiconductors, to band gap radiation. PSD cross sections are somewhat smaller than the corresponding ESD cross sections, although the two processes exhibit qualitatively similar behavior and are probably the result of the same mechanism. The photoelectron yield appears to be too low to account for PSD as being the consequence of ESD by photoelectrons.

### RESEARCH NEEDED

#### 1. Materials

Surface preparation

Coatings

Surface modification

Self-sustaining films

Ion implantation

Ion damage modification (e.g., diamond-like carbon)

#### 2. Desorption Properties

Negative ion yields for both ESD and PSD

Effect of bake or discharge procedures on gas composition.

### 3. Means

Electron impact desorption at appropriate fluxes & energies.

Photon-stimulated desorption at energies between ~ 10 and 1000 eV.

Surface analysis by "static" techniques (SIMS, SARISA, TOFISS).

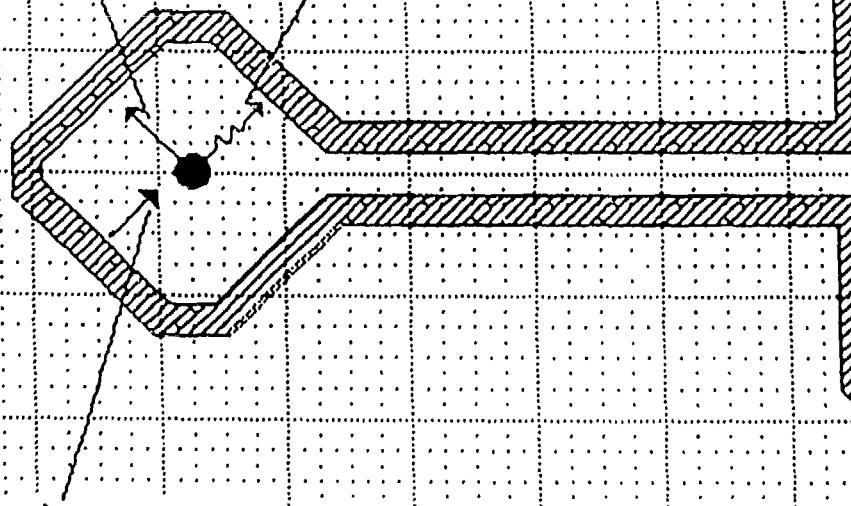
Simultaneous desorption analysis of all species from sample surface according to species and charge state (SIMS, SNMS).

### REFERENCES

1. H. J. Halama and J. C. Herrern, Proc. 22nd National Vacuum Symposium, Philadelphia, PA, 10/28-10/31, 1975.
2. R. Dobrozemsky and G. Moraw, Electron Fisc. Appli. 17 (1974) 235.
3. M. L. Yu, Phys. Rev. B19 (1979) 5995.
4. M. L. Yu, J. Vac. Sci. Technol. 16 (1979) 518.
5. J. L. Hock, J. H. Craig, Jr. and D. Lichtman, Surf. Sci. 85 (1979) 101.
6. J. L. Hock and D. Lichtman, Surf. Sci. 77 (1978) L184.
7. P. Feulner, R. Treichler, and D. Menzel, Phys. Rev. B24 (1981) 7427.
8. D. Lichtman, Proceedings of the First International Workshop on Desorption Induced by Electron Transitions, Williamsburg, VA, May 12-14, 1982.
9. D. Woodruff et al., Phys. Rev. B21 (1980) 5642
10. M. L. Knotek, V. O. Jones, and V. Rehn, Phys. Rev. Lett. 43 (1979) 300.

scattered  
electron

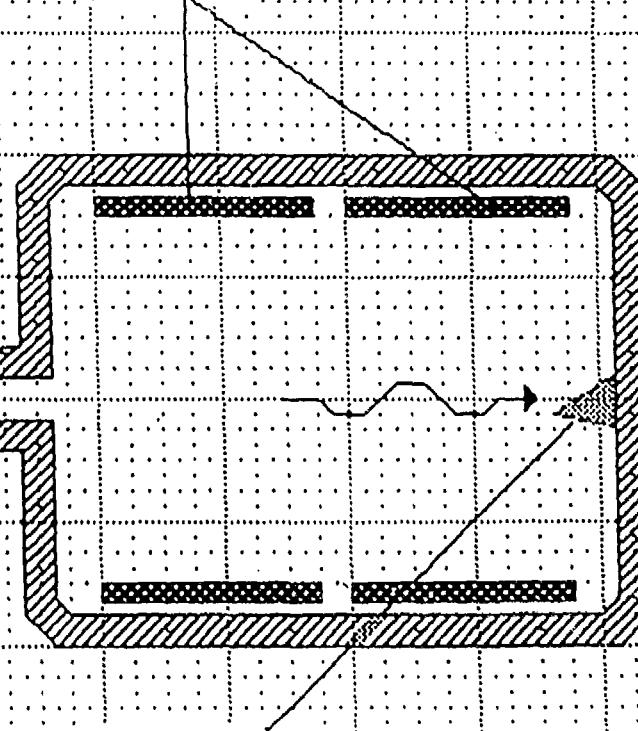
bremstrahlung



trapped  
ion

getter  
panel

photon  
absorber



# VACUUM MATERIALS

## ADSORPTION/DESORPTION PROPERTIES

### 1. PUMPING CHAMBER

Photon-stimulated desorption from photon absorber.

Outgassing of chamber walls.

Back-streaming into beam chamber.

### 2. BEAM CHAMBER

Vacuum properties:

Outgassing rate.

Gas Composition.

Desorption properties:

Photo-desorption, photon-stimulated & electron-stimulated desorption cross sections.

Material

Treatment

Photon Energy

Desorbing species

Chemical identity

Charge state

Classification of metals based on adsorption properties  
 at 300 K. (A=adsorption, A<sup>\*</sup>=activated adsorption,  
 NA=no adsorption)

Group	Metals	Gases				
		O <sub>2</sub>	CO	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>
A	Ti,Zr,Hf,Y,Nb, Ta,Cr,Mn,W,Re	A	A	A	A	A
B	Fe	A	A	A	A	A <sup>*</sup>
C	Ni,Co	A	A	A	A	NA
D	Rh,Pd,Pt,Ir	A	A	A	NA	NA
E	Al,Mn,Cu	A	A	NA	NA	NA
F	Au	NA	A	NA	NA	NA
G	Mg,Zn,Cd,In,Sn, Pb,As,Sb,Bi	A	NA	NA	NA	NA
H	Ag	A <sup>*</sup>	NA	NA	NA	NA
I	Se,Te	NA	NA	NA	NA	NA

## Outgassing Rates ( $10^{-14}$ torr-liter/sec)

Ref.	Temp	Q <sub>t</sub>	% H CO CO <sub>2</sub>		
			H	CO	CO <sub>2</sub>
SS (vac bake)	a	100	100	82	13
Cu (vac bake)	a	100	110	4	76
Al (vac bake)	a	100	4	17	52
SS (air bake)	a	100	10		
Cu (air bake)	a	100	30		
Al (air bake)	a	100	2.8		
Al (vac bake)	b	100	80		
Al (High temp O <sub>2</sub> <sup>+</sup> discharge)	b	100	40		
Al (vac bake)	b	150	10	97	1.5
Al (High temp O <sub>2</sub> <sup>+</sup> discharge)	b	150	7	98	1

(a) Dobrozemsky and Moraw

(b) Halama and Herrin

# DESORPTION PROPERTIES

## Electron-Stimulated Desorption (ESD)

$$10^{-17} \leq \sigma^{-0} \leq 10^{-21} \text{ cm}^2$$

$$10^{-4} \sigma^{-0} \leq \sigma^{-+} \leq 10^{-3} \sigma^{-0}$$

$$10^{-2} \sigma^{-+} \leq \sigma^{- -} \leq \sigma^{-+}$$

## Photon-Stimulated Desorption (PSD)

Mostly CO, CO<sub>2</sub>, O

High cross section on oxide surfaces, low on metal surfaces: 2500 Å/ CO<sub>2</sub> adsorbate

$$\sigma \sim 10^{-17} \text{ cm}^2 (\text{Al}_2\text{O}_3 \text{ & oxidized SS})$$

$$e \sim 10^{-3} - 10^{-4} \text{ molecules/photon}$$

$$\sigma \leq 10^{-23} \text{ cm}^2 (\text{Ni, W})$$

$$e \sim 10^{-8} - 10^{-9} \text{ molecules/photon}$$

Behavior is similar to ESD and both processes appear to be related to core-hole excitation. The de-excitation probability for metals is ~1, resulting in a very small cross section for metals.

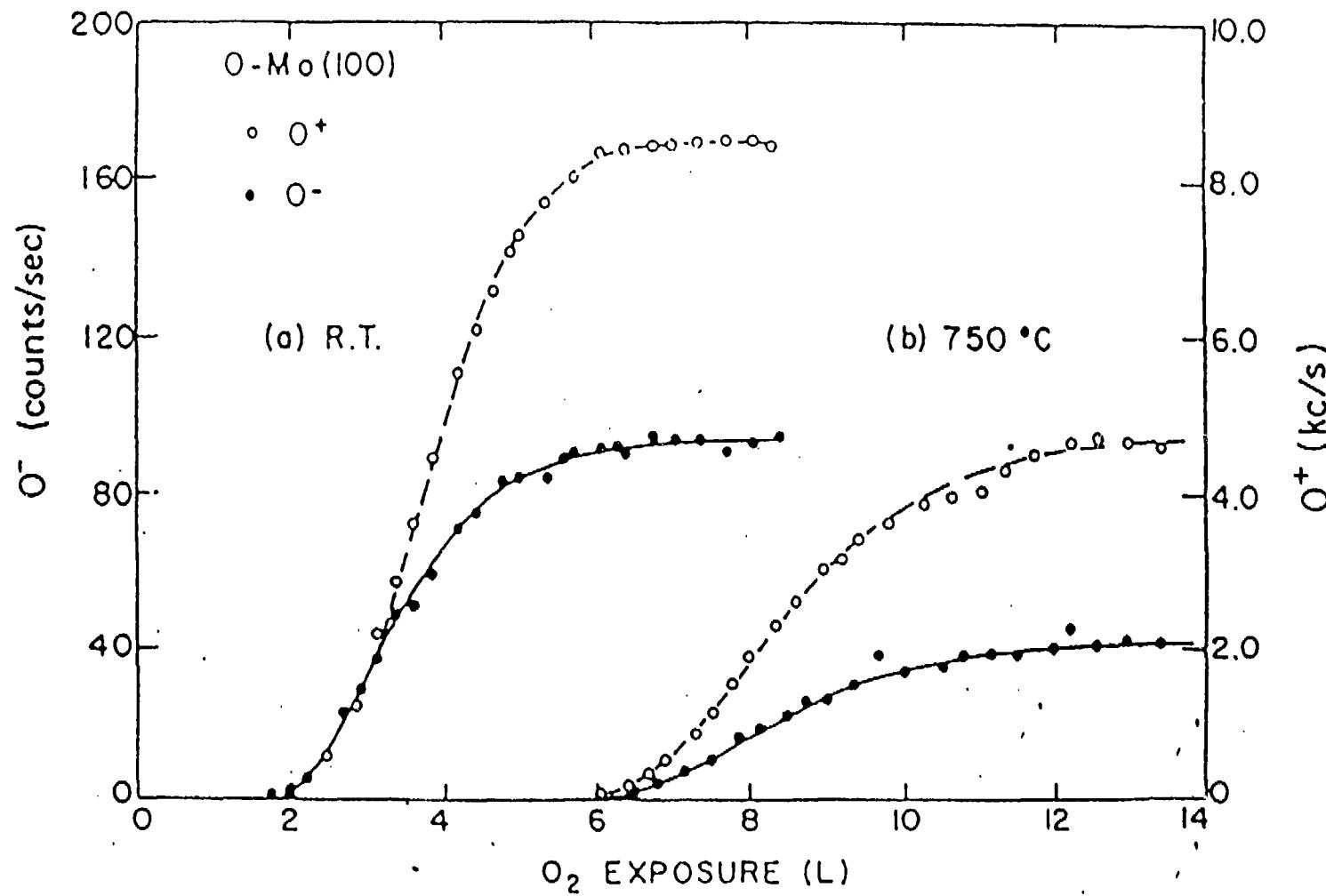


Fig. 1.  $O^-$  and  $O^+$  ESD from Mo(100) as a function of  $O_2$  exposure at (a) 300K and (b) 1000K [7]

TABLE IV. Summary of electron impact desorption results (for 80-100-eV electrons).

System	Conditions	Cross section for desorption (cm <sup>2</sup> )	Approached state
O <sub>2</sub> /W	fully covered, 20°K	4.5×10 <sup>-19</sup>	$\phi = 5.72$
O <sub>2</sub> /W	$\phi < 5.7$ , 20°-600°K	<2×10 <sup>-11</sup>	...
H <sub>2</sub> /W	fully covered, 20°K (Regime 1) (Regime 2)	3.5×10 <sup>-20</sup> 5×10 <sup>-21</sup>	$\phi = 4.99$ clean surface ( $\phi = 4.50$ )
H <sub>2</sub> /W	heated to 385° after dosing (20°-150°)	7.3×10 <sup>-21</sup>	clean surface ( $\phi = 4.50$ )
Ba/W	$\theta = 0.8-2$	<2×10 <sup>-22</sup>	...
CO/W	virgin CO	2-5×10 <sup>-19</sup>	$\phi = 5.14$
CO/W	$\beta$ -CO	5-8×10 <sup>-21</sup>	clean surface (?) <sup>a</sup>
CO/W	$\alpha$ -CO	3×10 <sup>-18</sup>	depends on coverage
CO/W	conversion $\nu \rightarrow \beta$	$\geq 10^{-19}$	depends on coverage

System	O/W(110) [8]	v-CO/W(110) [8]		
Species	O <sup>+</sup>	O <sub>2</sub>	CO <sup>+</sup>	CO
$\sigma$ [cm <sup>2</sup> ]	$5 \times 10^{-22}$	$\sim 10^{-17}$	$\sim 10^{-21}$	$5 \times 10^{-17}$

Table 1

Total ESD cross section for oxygen on tungsten as measured by the O<sup>+</sup> and O<sup>-</sup> ion signal decay; the estimated uncertainty in the measured cross section is  $\pm 10\%$

Electron beam energy (eV)	$Q$ from O <sup>+</sup> signal decay ( $\times 10^{-18}$ cm <sup>2</sup> )	$Q$ from O <sup>-</sup> signal decay ( $\times 10^{-18}$ cm <sup>2</sup> )
1000	1.8	2.0
900	1.6	1.7
800	1.6	2.1
700	2.4	2.0
600	2.3	2.0
500	2.3	1.7
400	1.7	1.8

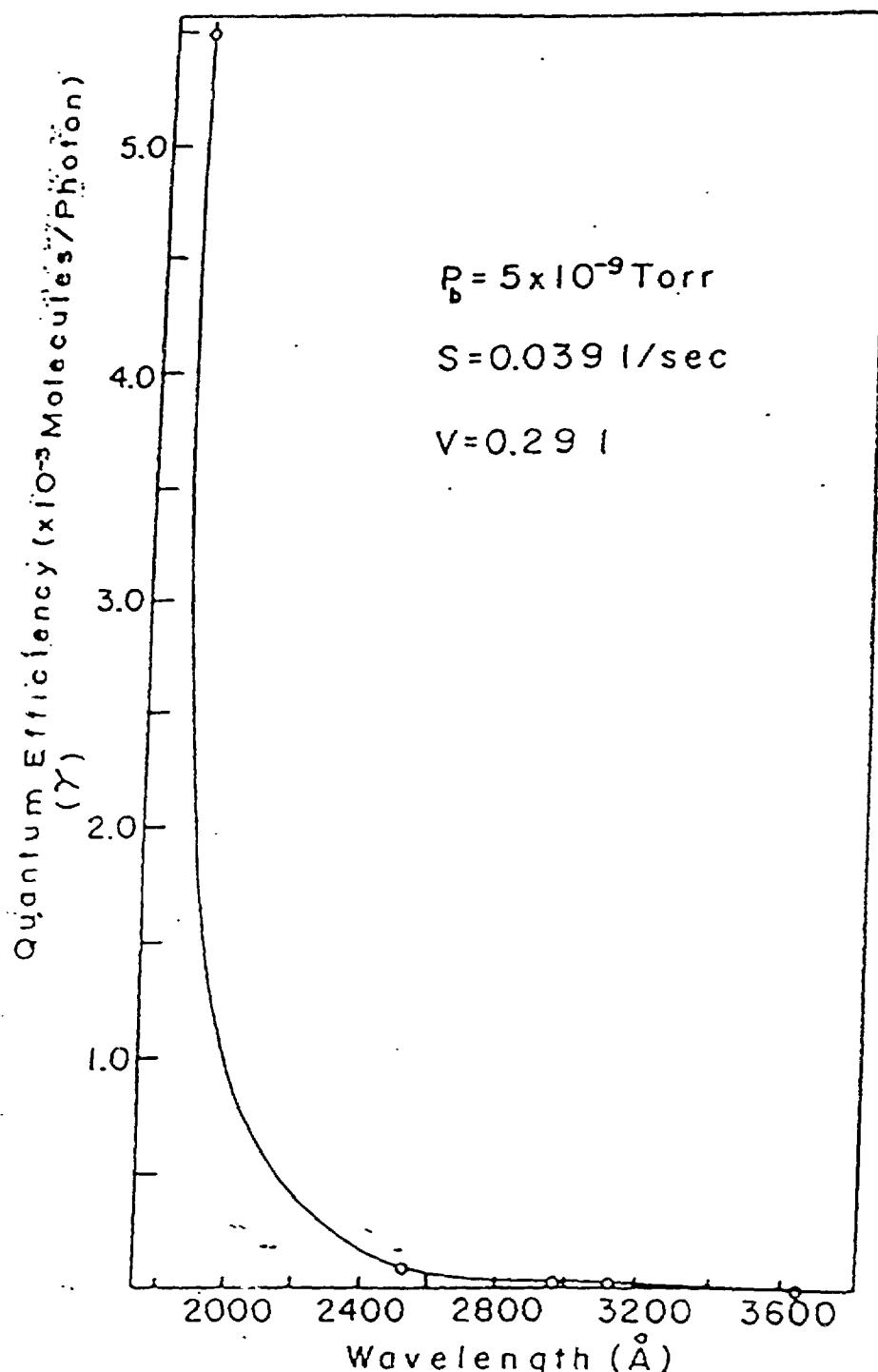


FIGURE 11. Photodesorption efficiency as a function of wavelength from a 304 stainless steel surface. Note order of magnitude of the ordinate as compared to previous curves. (Adapted from Fabel, G. W., Cox, S. M., and Lichtenman, D., *Surf. Sci.*, 40, 571, 1973. With permission.)

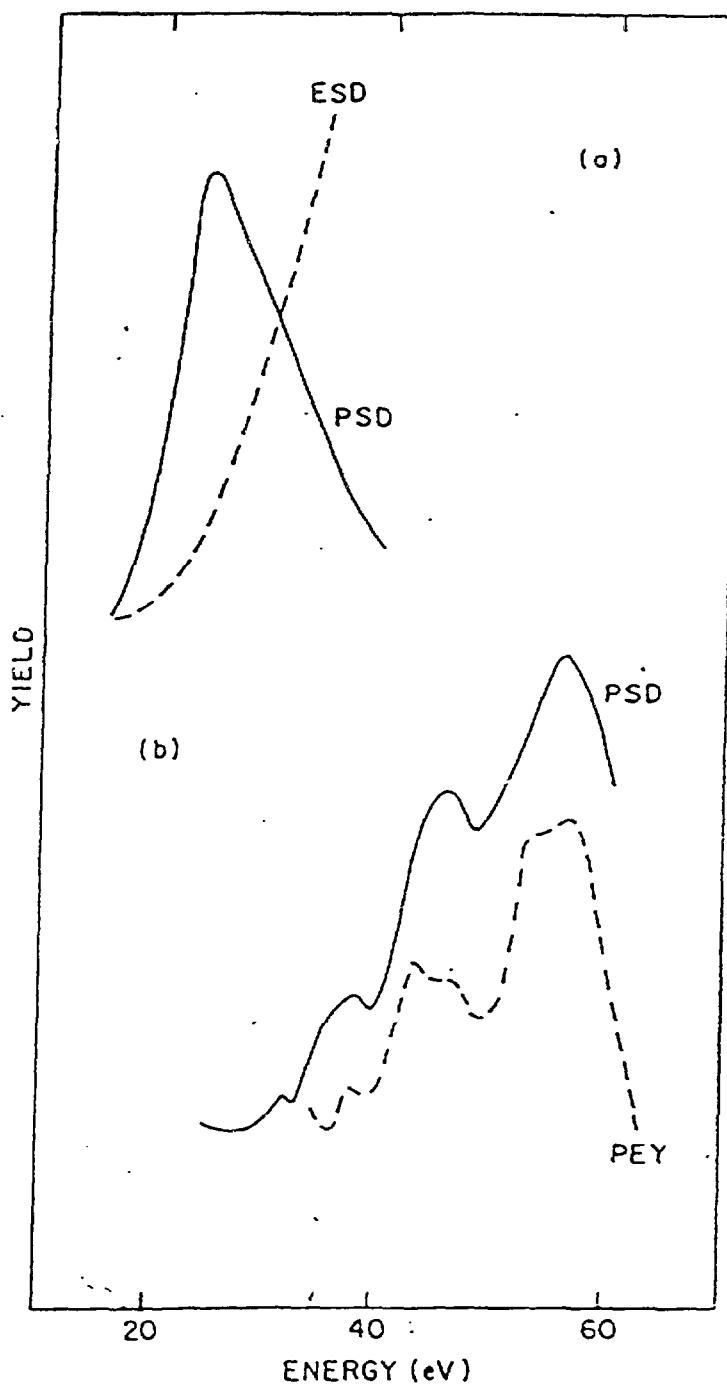
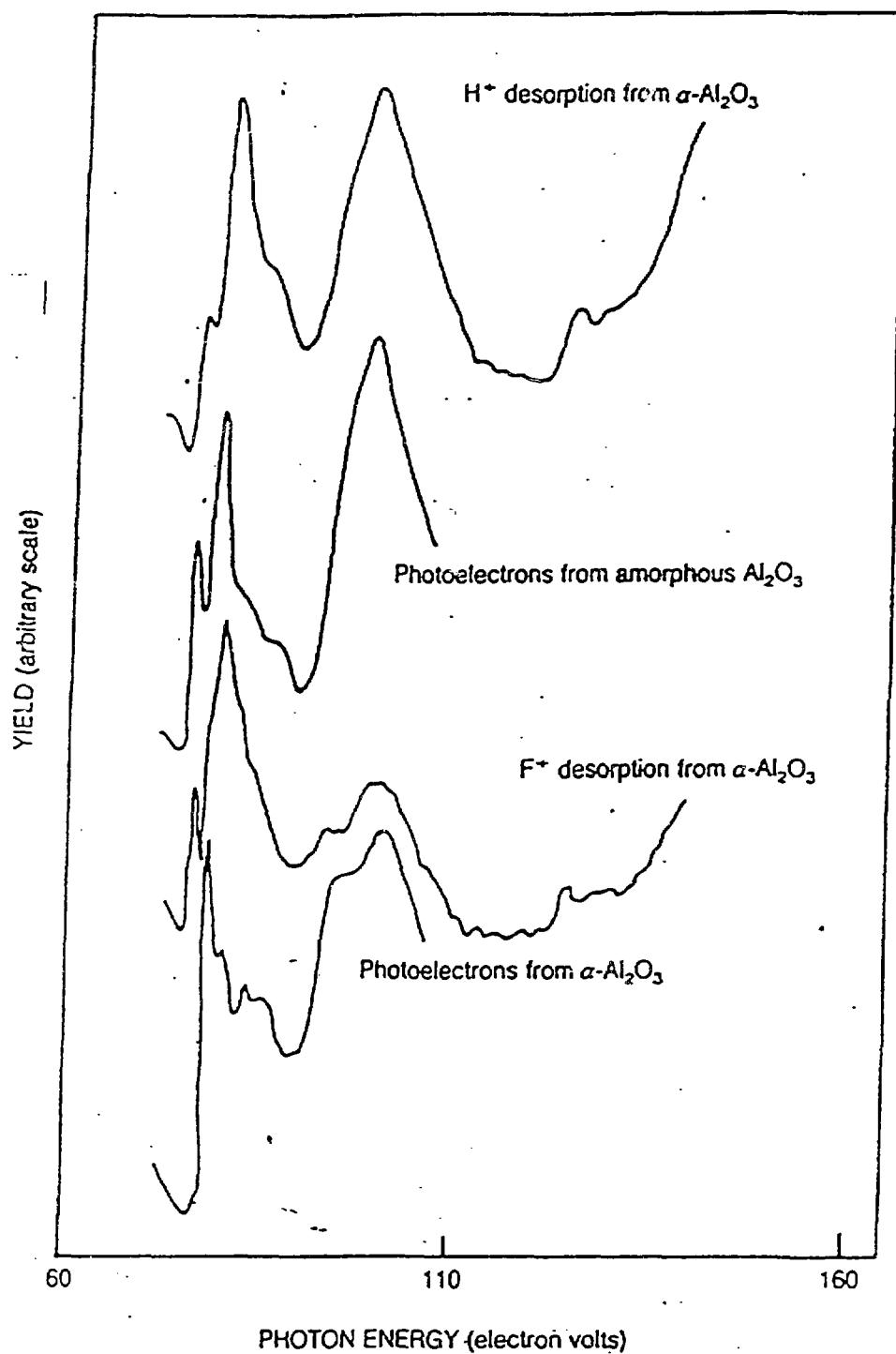


FIG. 3. (a) ESD and PSD yields for Cl<sup>+</sup> desorption from W(100) taken at an ion kinetic energy of  $\sim 2$  eV; (b) PSD yield for O<sup>+</sup> desorption at a kinetic energy of  $\sim 8$  eV from W(100) and total photoelectron yield (PEY) from an evaporated W film (Ref. 14). PSD and ESD curves are only roughly normalized to the incident flux; scaling for the PEY curve is arbitrary.



Photon stimulated desorption spectra and corresponding photoelectron spectra. Plot shows the desorption yield of  $H^+$  and  $F^+$  from  $\alpha\text{-Al}_2\text{O}_3$  and the photoelectric yield from amorphous  $\text{Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$  in the vicinity of the L edge of aluminum. The site of the H bond has the signature of a tetrahedral geometry like that of amorphous  $\text{Al}_2\text{O}_3$ , while the site of the F bond more resembles the octahedral geometry of bulk  $\alpha\text{-Al}_2\text{O}_3$ .

## STIMULATED DESORPTION

System	Efficiency	$\sigma$ ( $\text{cm}^2$ )	Source	Ref.
$\text{CO}_2/\text{Ni, W}$	$< 10^{-8}$	$< 10^{-23}$	photon 2500 Å	Lichtman
$\text{CO}_2/\text{SS}$ (oxidized)	$8 \times 10^{-5}$	$-10^{-19}$	photon	Lichtman
$\text{O}_2/\text{Al}_2\text{O}_3$	$2 \times 10^{-3}$	$10^{-18}$	photon	Lichtman
$\text{CO/W}$	$10^{-6}-10^{-3}$	$10^{-21}-10^{-18}$	electron	Menzel &
$\text{H}_2/\text{W}$	$7 \times 10^{-6}$	$7.3 \times 10^{-21}$	electron	Gomer
$\text{H}_2/\text{W}$	$4 \times 10^{-7}-6 \times 10^{-4}$ (atoms) $7 \times 10^{-9}-1 \times 10^{-5}$ (ions)		electron	Redhead
$\text{CO & H}_2/$ $\text{W(100)}$	$10^{-1}$	$1 \times 10^{-16}$	electron	Menzel
$\text{O}^+/\text{W(100)}$	$10^{-7}-10^{-8}$	$10^{-22}-10^{-23}$	photon	Woodruff
$\text{O}^+/\text{W(oxide)}$	$3 \times 10^{-8}$ $1 \times 10^{-6}$	$3 \times 10^{-23}$ $1 \times 10^{-21}$	photon electron	Madey Madey

$$\sigma^- \text{ (oxide)} = (10-10^4) \times \sigma^- \text{ (metal)}$$

$$\sigma^- \text{ (electron)} = (1-100) \times \sigma^- \text{ (photon)}$$

$$\sigma^- \text{ (neutral)} = (10^2-10^4) \times \sigma^- \text{ (+)}$$

$$\sigma^- \text{ (+)} = (1-30) \times \sigma^- \text{ (-)}$$

## SUMMARY

### 1. Adsorption Properties

The materials most commonly used for vacuum chamber construction, stainless steel and aluminum, strongly adsorb most common gases, a condition not favorable for synchrotron operation. Specifically, aluminum and stainless steel are very strong oxygen adsorbers and form oxides at room temperature.

Materials such as Ag, Al, and Cu should be considered as vacuum-side materials, possibly as thin films or self-sustaining coatings. The coatings should be sufficiently durable to withstand repeated discharge cleaning.

### 2. Outgassing Properties

The composition of outgassing products for an aluminum synchrotron vacuum vessel as a function of surface treatment (e.g. vacuum bake, air bake, hydrogen, oxygen or argon discharge cleaning) is not well established. Existing data are contradictory.

### **3. Electron Stimulated Desorption**

**The desorption cross section from an oxide surface, such as that of aluminum or stainless steel, is several orders of magnitude larger than that of a metal surface.**

**For a given system, the desorption cross section may vary by several orders of magnitude depending on thermal history.**

**Very little data exist on the desorption of negative ions, but the existing data indicate that the desorption cross section for negative ions may be at most, 30 x smaller than for positive ions. This fact may limit the utility of using a positron beam as a means of reducing trapped ion effects.**

### **4. Photon-Stimulated Desorption**

**PSD cross sections for metal surfaces are extremely small, rising by 4-5 orders of magnitude for the oxides.**

**PSD exhibits strong threshold effects at energies corresponding to adsorbate transitions or, for oxides and semiconductors, to band gap radiation.**

**PSD cross sections are somewhat smaller than the corresponding ESD cross sections, although the two processes exhibit qualitatively similar behavior and are probably the result of the same mechanism. The photoelectron yield appears to be too low to account for PSD as being the consequence of ESD by photoelectrons.**

# RESEARCH NEEDED

## 1. Materials

- Surface preparation
- Coatings
- Surface modification
  - Self-sustaining films
  - Ion implantation
  - Ion damage modification  
(e.g. diamond-like carbon)

## 2. Desorption Properties

- Negative ion yields for both ESD and PSD
- Effect of bake or discharge procedures on gas composition.

## 3. Means

- Electron impact desorption at appropriate fluxes & energies.

- Photon - stimulated desorption at energies between ~10 and 1000 eV.

- Surface analysis by "static" techniques (SIMS, SARISA, TOFISS)

- Simultaneous desorption analysis of all species from sample surface according to species and charge state. (SIMS, SNMS)