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C. L. Foerster, C. Lanni, and R. Lee
National Synchrotron Light Source
Brookhaven National Laboratory
Upton, NY 11973

G. Mitchell and W. Quade
Dow Chemical Advanced Cleaning Systems
Midland, MI 48674
Ann Arbor, MI 48109

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National Synchrotron Light Source
Brookhaven National Laboratory
Upton, NY 11973

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TESTS OF AN ENVIRONMENTAL AND PERSONNEL SAFE CLEANING PROCESS FOR BNL ACCELERATOR AND STORAGE RING COMPONENTS*

C. L. Foerster, C. Lanni, and R. Lee

Brookhaven National Laboratory

Upton, New York 11973

G. Mitchell and W. Quade

Dow Chemical Advanced Cleaning Systems

Midland, MI 48674

ABSTRACT

A large measure of the successful operation of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) for over a decade can be attributed to the cleaning of its UHV components during and after construction. A new UHV cleaning process, which had to be environmentally and personnel safe, was needed to replace the harsh, unfriendly process which was still in use. Dow Advanced Cleaning Systems was contracted to develop a replacement process without the use of harsh chemicals and which must clean vacuum surfaces as well as the existing process. Acceptance of the replacement process was primarily based on Photon Stimulated Desorption (PSD) measurements of beam tube samples run on NSLS beam line U10B. One meter long beam tube samples were fabricated from aluminum, 304 stainless steel and oxygen free copper. Initially, coupon samples were cleaned and passed preliminary testing for the proposed process.

*Work performed under the auspices of the U.S. Department of Energy, under contract DE-AC02-76CH00016 and W-31-109-ENG-38

Next, beam tube samples of each material were cleaned, and the PSD measured on beam line U10B using white light with a critical energy of 487ev. Prior to cleaning, the samples were contaminated with a mixture of cutting oils, lubricants, vacuum oils and vacuum grease. The contaminated samples were then baked. Samples of each material were also cleaned with the existing process after the same preparation. Beam tube samples were exposed to between 10^{22} and 10^{23} photons per meter for a PSD measurement. Desorption yields for H_2, CO, CO_2, CH_4 and H_2O are reported for both the existing cleaning and for the replacement cleaning process. Preliminary data, residual gas scans, and PSD results are given and discussed. The new process is also compared with new cleaning methods developed in other laboratories.

I. INTRODUCTION

Much has been written concerning chemical cleaning of construction materials for the ultra high vacuum (UHV) environment of accelerators and storage rings. There is also a large number of different chemical cleaning processes which were developed for the construction of the UHV beam chambers for these machines. The harsh chemicals used for the majority of the different cleaning processes are not safe for the environment nor the people working with them. The three main UHV construction materials[1] used so far have been aluminum, stainless steel (SS) and copper. Solvents, strong acids and base solutions have been used in most processes to clean the various components fabricated. A survey[2] of leading UHV organizations found practically every organization had a different procedure, selection of cleaning agents, rinsing agent and cleaning sequence.

Synchrotron Radiation Sources world-wide are evaluating[3,4] and changing their cleaning processes to more environmentally friendly cleaning agents. By 1990, due to environmental concerns, the majority of degreasing operations at BNL were changed to environmentally safe detergent solutions with and without ultra-sonic agitation. Trichloroethane and other similar environmentally unsafe degreasers were eliminated from the cleaning sequences. Photon stimulated desorption (PSD) testing of samples was performed, and the results used to approve any changes to NSLS cleaning procedures prior to their acceptance. PSD results measured from samples cleaned using the detergent solution for degreasing were as good as those cleaned using trichloroethane.

The UHV chemical cleaning facility[5] at BNL was originally set up by the NSLS during its construction and the NSLS has continued its operation as a service for the BNL community. In the near future, the facility is to be moved to a new centralized location at BNL, and is to be operated by the Central Shops division. Dow Chemical, Advanced Cleaning Systems Division (DACS) was retained by BNL to review the current facilities cleaning procedures and to find a less hazardous, environmentally friendly cleaning procedure for the new centralized facility.

II. DEVELOPMENT OF A PROPOSED PROCESS

The requirements for the NSLS ring UHV construction materials call for low outgassing rates and low PSD levels which are both necessary for good stored beam lifetime.[6,7] Since PSD testing is difficult and very time-consuming, x-ray photoelectron spectroscopy (XPS) was the method used to initially assess the efficiency of the proposed cleaning process. Twenty-four coupons ($3.0\times0.5\times0.12$ inches) of aluminum, 304SS, 316SS, and copper were fabricated and cleaned at BNL, then supplied to DACS to develop the new cleaning specification. Beam tubes, approximately one inch diameter by forty inches long, were prepared. Once the final process specification was determined by DACS using coupon testing, beam tubes of aluminum, stainless steel, and copper were contaminated and then cleaned following the new specification. PSD, outgassing, and residual gas analyzer (RGA) measurements were performed by NSLS for BNL acceptance of the final specification.

Contamination of coupons and beam tubes were performed using a mixture of vacuum pump oils (mechanical, TMP, and Diffusion), machine shop oils, cutting oils, and penetrating grease. The mixture was applied to the sample surfaces to be tested. Next the sample was spot heated to discolor the metal surface, then baked for 10 hours at 100°C. The coupons and beam tubes were then cleaned using either the BNL process or the new DACS process. The results[8] of the DACS coupon testing are summarized in this paper.

XPS was performed using a PH1 5400 XPS spectrometer and a Surface Science Instruments S-probe. The 5400 XPS spectras were obtained using a Mg kα X-ray source at 45° take off angle for electrons relative to the surface. The S-probe utilizes a monochromated Aℓ kα source at a 35α° take off angle. Base pressure for both are 10^{-10} torr. Measurements were made of BNL coupons using both acid and non-acid cleaning procedures. Three coupons of each type of metal were cleaned by the process developed by DACS and then analyzed. Aluminum coupons were analyzed using the S-probe and the rest were done using the PH1 5400 XPS instrument. One 304SS coupon was cleaned by BNL with acid and one was cleaned without the use of acid. The coupons were sputter depth profiled using he PH1 5400 XPS to determine the thickness of the oxide layer. The sputtering was performed using 3.0 keV Ar^+ ions at a rate of 20 Å per minute. Calibration was performed with a 1000Å thick oxide on a tantalum foil certified by the National Institute of Standards and Technology. The elemental surface compositions were determined from the survey spectra in the usual way, which assumes signals detected account for 100% of the elements present in the analyzed volume, thus, the concentration of element I,

$$Ci = (Ai/Si)\ \Sigma i\ (Ai/Si)^{*}\ 100\%$$

where: Ai = Area Under XPS Peak

Si = Instrument Sensitivity Factor for Element

Presence or Absence of Hydrogen is Ignored

III. RESULTS OF COUPON TESTING

A. 304L Stainless Steel Coupons (See Fig. 1)

XPS results for 304 stainless steel are shown in table 1. Three coupons were tested for each cleaning process and the result shown is the average. The XPS is sensitive to all elements except He and H with a detection threshold of around 0.5 atom % for this spectra. Only the elements detected are listed. Acid etching increased the ratio of FE and Cr and decreased the level of Ni on the surface. The acid etched coupons also had significantly larger amounts of F on the surface which was most likely absorbed from the etching solution. Carbon is the most abundant element on the surfaces. No F or CL was detected on the DACS coupons cleaned with their best process. Looking at the sum of Fe, Cr and Ni, the DACS cleaned was much larger than either BNL cleaned coupons.

XPS sputter depth profiles were performed to ascertain the effect of the acid etch on the oxide thickness for 304SS. Figure 1 compares the sputter depth profiles for a BNL stainless steel coupon cleaned without acid to a BNL stainless steel coupon cleaned with acid. Changes in level as a function of sputtering depth can be used to judge the oxide layer thickness as follows. The oxygen signal decreases with increased sputter depth and the metal signals increase concurrently until the oxide layer is completely removed. The point at which the oxygen signed goes to zero can be used to gauge the depth of the oxide layer. Thus, the oxide was determined to be 60Å thick for the acid cleaned coupon and to 40Å thick for the coupon cleaned without acid.

B. Copper Coupons

XPS results for copper are shown in Table 2. Three coupons were tested for each cleaning process and the result shown is the average. The carbon level was lower and the copper level was higher for BNL cleaning with acid than the BNL cleaning without acid. The level of Cu detected is substantially higher for the DACS cleaned coupons. Also the measured levels of CL were lower for the DACS process.

C. 6061 Aluminum Coupons

The XPS results for aluminum are shown in Table 3. Three coupons were tested for each cleaning process and the results shown is the average for each process. Acid cleaning removed the elements P and Mg, lowers the carbon and fluorine level, and increases the level of aluminum and oxygen on the surface as detected by XPS. No P or F was detected on the DACS samples, but a large amount of Mg and Cu was found. The surface O and C of the DACS and the BNL acid cleaned samples were approximately the same.

D. 316L Stainless Steel Coupons

The results for 316 stainless steel were measured and are shown in Table IV. Three coupons were tested for each process and the result is the average for the process. The F level was highest for the BNL acid cleaned coupons and were most likely deposited from the acid etch. Similar to the 304 stainless steel, the total metals for BNL with or without acid were almost the same. The DACS cleaned samples were higher.

IV. FINAL TEST RESULTS FOR DACS PROPOSED PROCESS

The acceptance of the DACS UHV cleaning process was based on PSD results, periodic RGA scans, and visual inspection. Some light discoloration not removed by the new process was accepted for both coupons and for beam tubes.

The RGA results are summarized in table 5. The RGA, gauges, conductance, pumping and procedures were the same for all runs. Raw data is given for comparison and evaluation. Outgassing for DACS cleaned aluminum (Run #3) and for DACS cleaned copper (Run #4) was excessive, so PSD data plots were not made.

The experimental setup is the same as previously described[9] for PSD measurements for the SSCL20 TeV proton collider. In summary, the measurements of the beam tubes were made on NSLS beamline U10B at BNL. Beam tube samples were not baked after beamline installation prior to exposure measurements. Tubes were run at a 12 mrad photon incident angle exposing 1 m of length along one side of the sample. White light having 487eV critical energy is collimated at one end of the sample. The collimation yields 2.02×10^{14} photons/mA/s and has a vertical cut of energy less than 14eV (FWHM). Pressure rises ($\Delta P/I$) during exposures are obtained from calibrated NIG and RGA readings and the respective yields are calculated[9].

Acceptance of the DACS proposed cleaning process for Stainless Steel were based on the PSD results for 304L stainless steel. PSD tests were not run on 316L stainless steel.

A. 304L Stainless Steel Beam Tube. (See Fig 2 & 3)

One 304LSS tube cleaned by DACS was first run (Run #1) then compared to the PSD result from a 304LSS tube (Run #2) NSLS cleaned with acid. Initially the NSLS tube levels are slightly higher but both are almost the same after 10^{22} photons of exposure. The NSLS result was almost the same as a previously measured[10], preconditioned, unbaked 3m 304SS beam tube. The CO level was higher in this measurement. The PSD from the DACS cleaned sample was lower than the BNL cleaned PSD for all principal gases.

B. Aluminum Beam Tube (See Fig. 4 & 5)

The outgassing from the aluminum beam tube was found to be excessive after being cleaned by DACS with their final process (Run #3), (See Table IV). PSD for the aluminum beam tube recleaned by DACS (Run #5) was found to be higher than the PSD for an aluminum beam tube cleaned with the BNL process (Run #6). The PSD plotted data for Run #3 and Run #5 is not shown. The DACS process was modified by adding a second alkaline cleaner to the process, the tube recontaminated and recleaned with the modified process, PSD was then remeasured (Run #7). PSD from the tube with the modified cleaning was a little better than the PSD from the BNL process (Run #6), for all principal gases.

C. Copper Beam Tube (see Fig. 6)

PSD from a copper beam tube cleaned with the DACS process was compared to the results from a beam tube cleaned at BNL using the acid process. The first measurement (Run #4) results were excessive outgassing and the RGA scans also indicated excessive hydrocarbons (See Table V).

The Beam Tube was recleaned and remeasured. The next copper PSD measurement (Run #8) was accepted even though the principal gas levels were higher than desired. An alkaline cleaner (ALMECO 18) was added to the DACS cleaning steps to improve the process.

V. COMMENTS

The final DACS cleaning process meets the UHV requirements for the NSLS.

Although PSD measured high for copper cleaned using the DACS cleaning process, outgasing and RGA measurements indicate it will be acceptable. Copper is not a principal construction material for UHV chambers at BNL.

The Advanced Photon Source at Argonne National Laboratory uses ALMECO 18 as their main cleaning[4,11] agent for their aluminum UHV beam chambers. The addition of ALMECO 18 to the DACS process will ensure improved cleaning.

A new centralized facility is under construction at BNL and will use the finalized DACS cleaning procedure. The DACS process will be used to clean aluminum, stainless steel, and copper for UHV applications.

DACS Process Summary:

The cleaning process developed to clean parts for the Brookhaven National Labs (NSLS Vacuum Chamber) is a multi-step, batch type operation consisting of eight distinct steps in separate tanks. The parts to be cleaned are stainless steel, aluminum and copper. The equipment used in the cleaning process include the washing tanks with ultrasonics, rinsing tanks, an air knife dryer, an automated material handling hoist and an exhaust venting system to remove odor, water and alcohol vapor from the top surface areas of the tanks.

Process Steps:

#1 RIDOLINE™ 18) solution at 170 F (77C)

#2 Deionized (DI) water immersion rinse at 140 F (60C)

#3 BUFF OFF™ 16000 solution at 170 f (77C)

#4 DI water immersion rinse at 140 F (6C)

#5 CITRANOX™ solution at 170 F (77C0)

#6 DI water immersion rinse at 140 F (60C)

#7 Non-denatured ethanol 190 rinse at 77 F (25C)

#8 Air Knife Dry at 77 F (25C) at 15 PSIG (1.0 bar)

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FIGURE LEGENDS

Fig. 1. XPS depth profiles for BNL cleaned 304 stainless steel coupon without acid and BNL cleaned 304 stainless steel coupon with acid.

Fig. 2 Molecular desorption yields for DACS cleaned 304 stainless steel beam tube (Run #1).

Fig. 3. Molecular desorption yields for NSLS (BNL) cleaned 304 stainless steel beam tube (Run #2).

Fig. 4. Molecular desorption yields for NSLS (BNL) cleaned aluminum beam tube (Run #6).

Fig. 5. Molecular desorption yields for DACS cleaned aluminum beam tube (Run #7).

Fig. 6. Molecular desorption yields for DACS cleaned copper beam tube (Run #8).

Table I. XPS Analysis of 304SS Sample Coupons (Elemental Surface Composition in Atom %)

Cleaning	Fe	Cr	Ni	O	C	F	Si	SUM*
BNL-No Acid	2.3	1.9	0.3	28	66	ND**	1.1	4.5
BNL-W/Acid	1.9	4.6	N.D.	26	62	4.6	0.5	6.5
DACS	6.4	9.1	1.1	42	39	ND	2.0	17

*SUM = Fe + Cr + Ni
**ND = Not Detected

Table II. XPS Analysis of Copper Coupons (Elemental Surface Composition in Atom %)

Clean D	Cu	O	C	CL
BNL-No Acid	9.3	21	69	0.7
BNL-W/Acid	17	24	56	3.0
DACS	44	30	26	0.3

Table III. XPS Analysis of Aluminum Coupons (Elemental Surface Composition in Atom %)

Cleaning	AL	O	C	F	Mg	P	Na	Cu	SUM*
BNL-No Acid	13	31	36	4.6	12	3.0	0.2	ND**	25
BNL-W/Acid	30	45	22	2.4	ND	ND	ND	ND	30
DACS	21	45	21	ND	12	ND	ND	0.5	33

*SUM = AL + Mg
**ND = Not Detected

Table IV. XPS Analysis of 316L Stainless Steel Coupons (Elemental Surface Composition in Atom %)

Cleaning	FE	Cr	Ni	Mo	O	C	F	P	Si	CL	SUM*
BNL-No Acid	5.2	7.8	0.4	0.5	49	33	1.3	2.6	0.5	0.3	14
BNL-W/Acid	5.4	8.2	0.6	1.0	45	34	5.1	1.2	ND**	ND	15
DACS	5.0	10	1.4	0.7	55	29	1.0		ND	ND	17

*SUM = Fe + Cr + Ni + Mo
**ND = Not Detected

Table V. RGA Results During PSD for Various UHV Cleaning Procedures, After Exposure to 10^{22} Photons/Meter. (Except Background, Run #3 and Run #4). Data is Raw and is uncorrected for Sensitivity and other Factors.

Run #	Beam Current ma	Total Pressure $\times 10^{-8}$	Major Peaks (m/e) Torr									
			2 $\times 10^{-10}$	14 $\times 10^{-12}$	18 $\times 10^{-11}$	28 $\times 10^{-10}$	32 $\times 10^{-13}$	39+41 $\times 10^{-12}$	40 $\times 10^{-12}$	44 $\times 10^{-11}$	55 $\times 10^{-13}$	69 $\times 10^{12}$
1	663	1.8	3.1	5.5	1.8	1.3	5.0	1.5	1.1	7.9	0.1	1.6
2	605	5.1	5.3	8.8	1.1	2.1	7.3	1.2	2.7	1.1	1.5	0.6
3	0	3.1	5.0	0.9	4.9	1.3	43	31	1.6	1.6	110	58
4	0	43	-	-	-	-	-	-	-	-	-	-
5	727	7.5	37	38	19	6.5	16	45	7.9	34	41	38
6	720	6.1	16	22	27	7.0	52	12	4.5	37	9.1	8.5
7	721	1.9	5.1	8.7	5.2	2.5	6.6	1.0	1.1	7.0	0.9	2.8
8	699	5.4	29	27	31	2.8	21	1.8	5.9	12	18	4.0

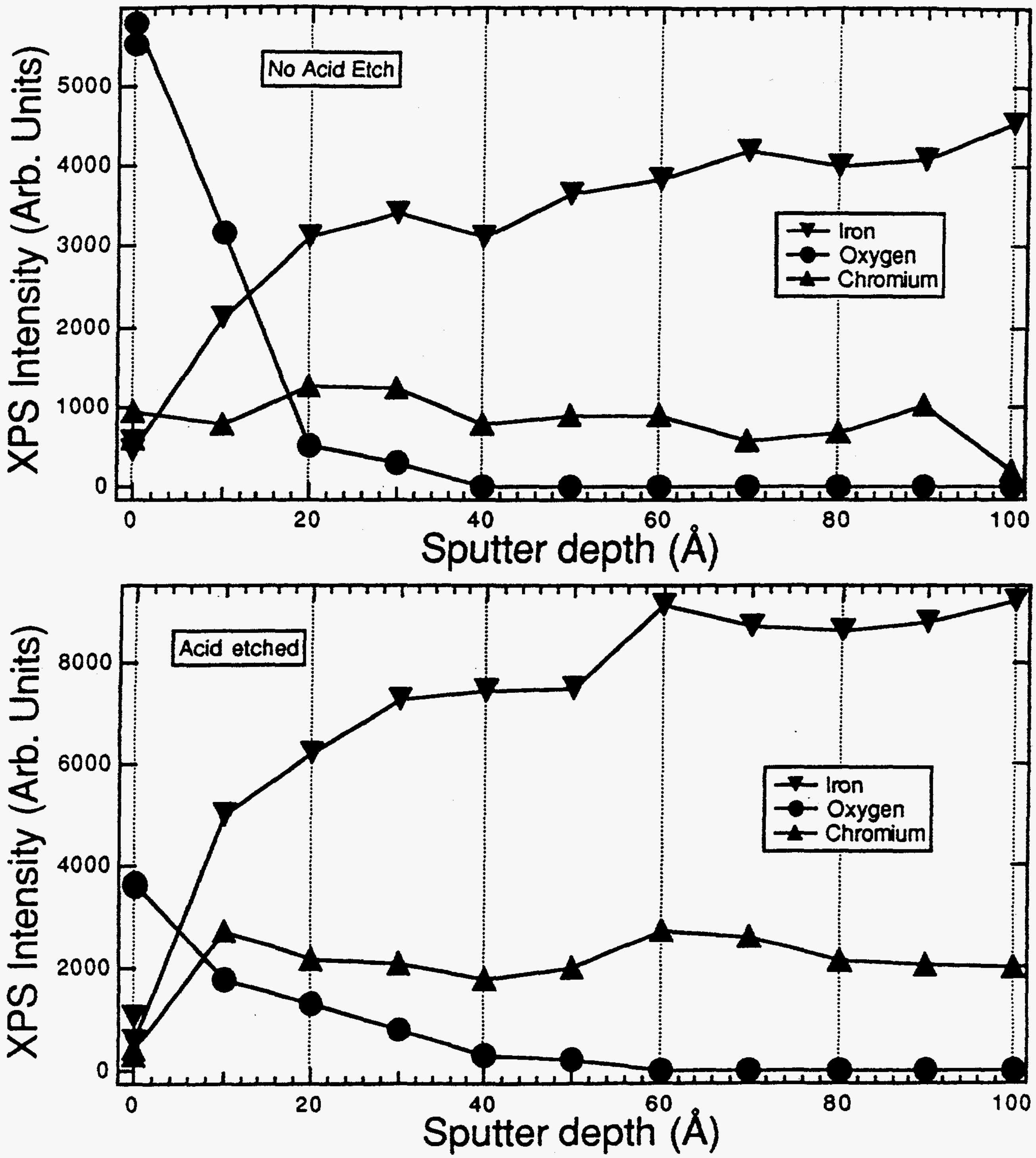
No Acid Etch
XPS Intensity (Arb. Units)
0
1000
2000
3000
4000
5000
Iron
Oxygen
Chromium
0
20
40
60
80
100
Sputter depth (Å)
Acid etched
XPS Intensity (Arb. Units)
0
2000
4000
6000
8000
Iron
Oxygen
Chromium
0
20
40
60
80
100
Sputter depth (Å)

FIG. 1

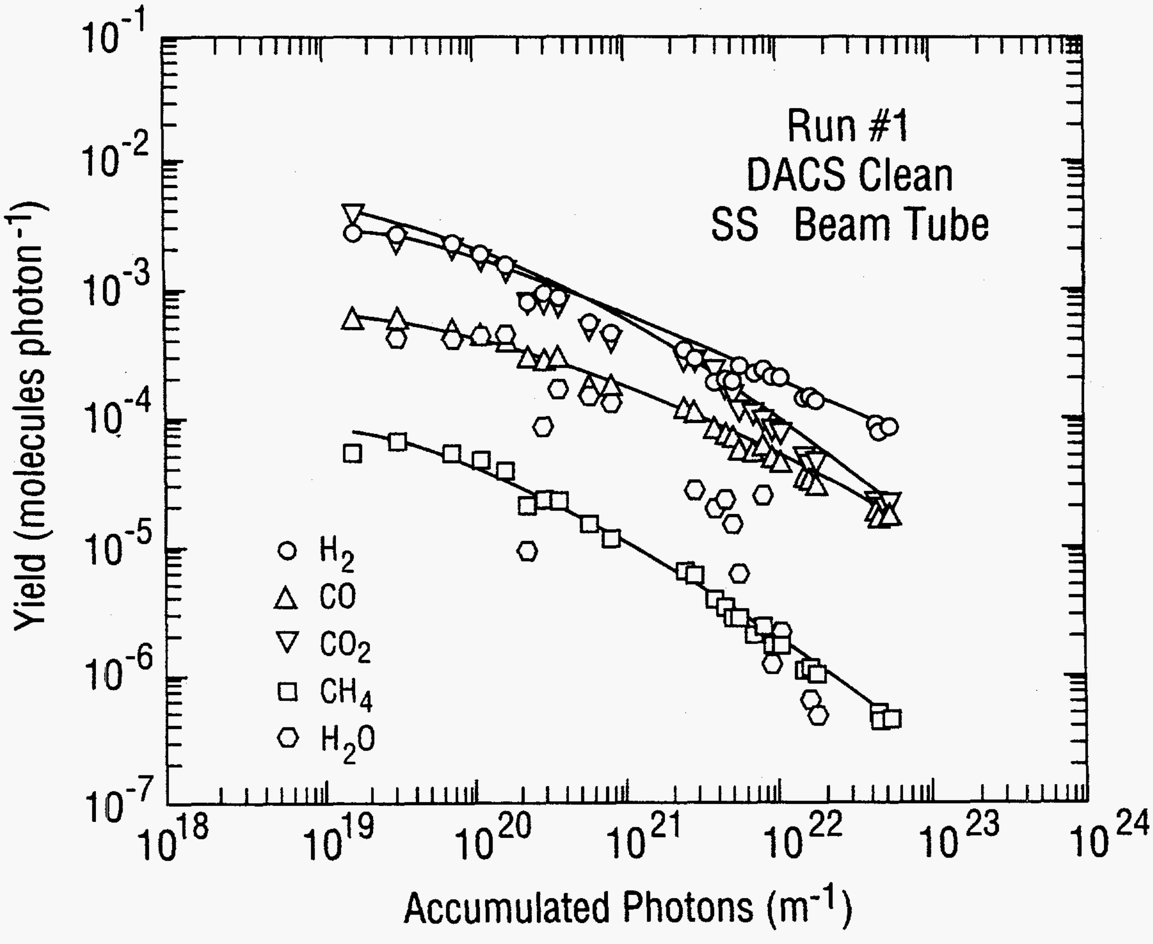
Run #1
DACS Clean
SS Beam Tube
Yield (molecules photon^{-1})
Accumulated Photons (m^{-1})
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{18}
10^{19}
10^{20}
10^{21}
10^{22}
10^{23}
10^{24}
○ H_2
△ CO
▽ CO_2
□ CH_4
⬡ H_2O

Fig 2

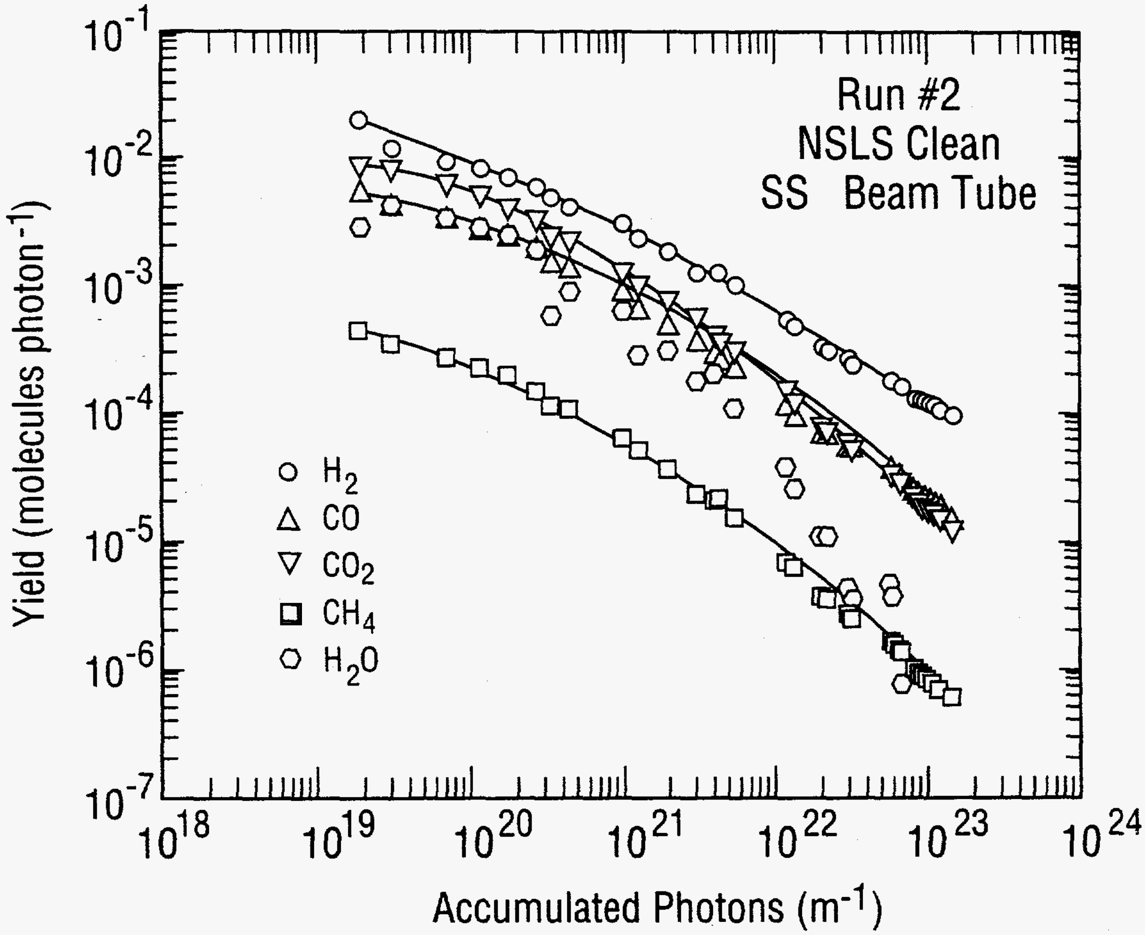

FIG 3

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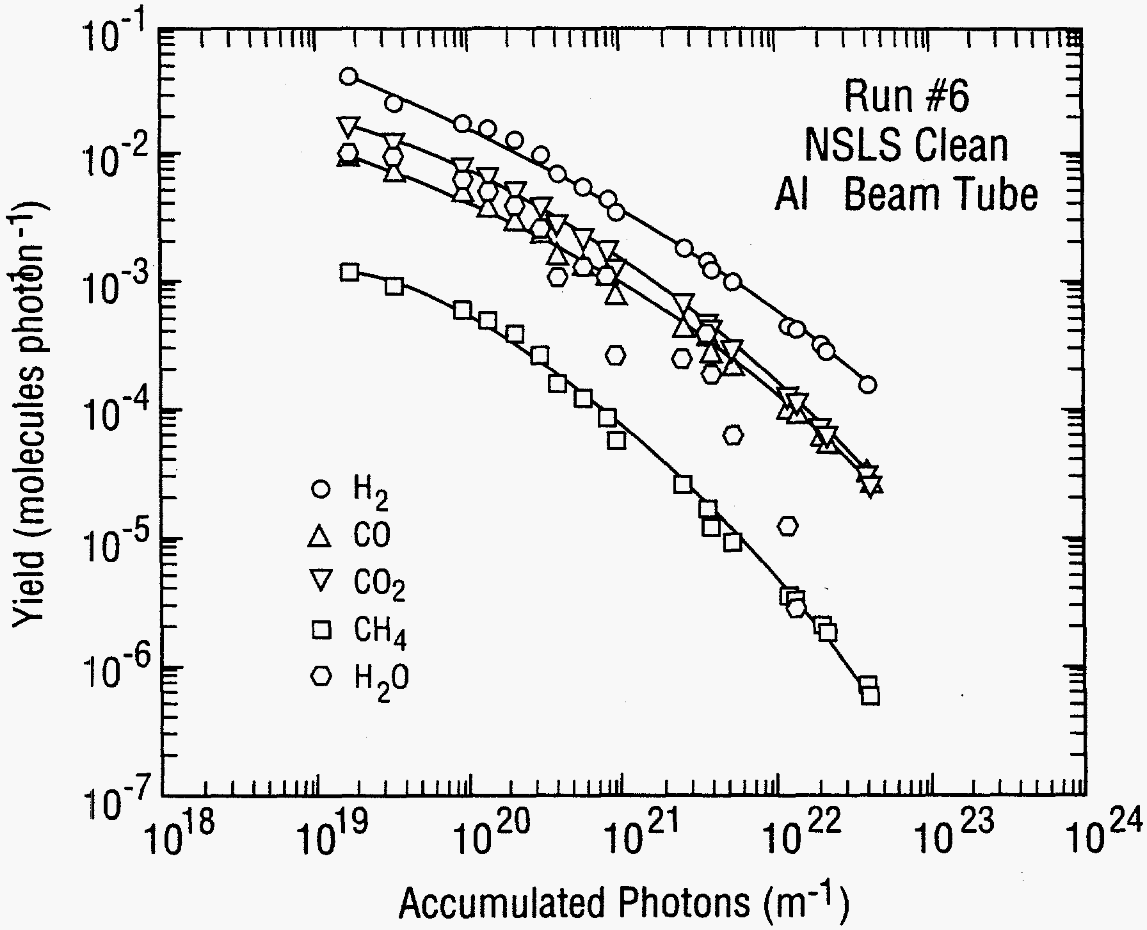

FIG. 4

Foerester 3. 8/96 judy

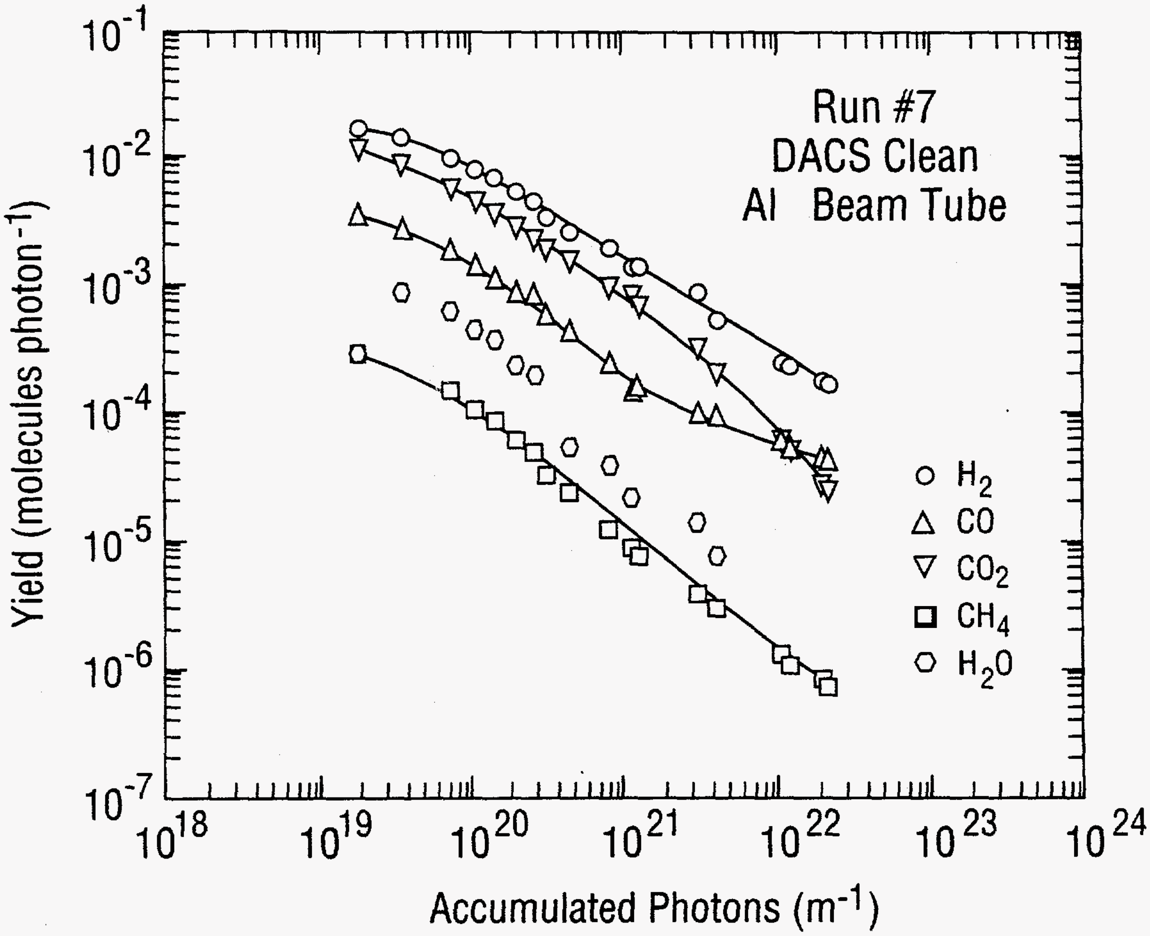

Fig 5

Foerester 2 8/96 judy

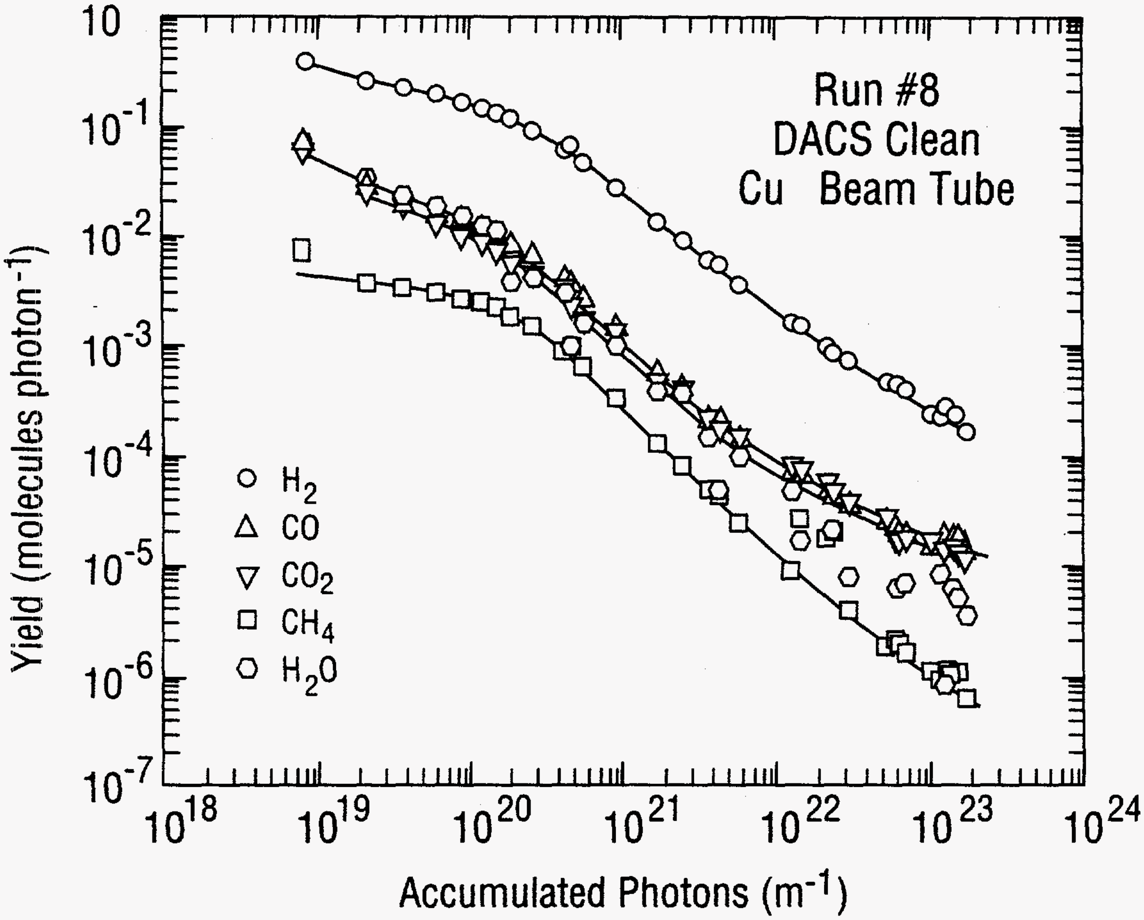

FIG 6

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