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UNDER EXPOSURE TO ELECTRONS, LASER RADIATION  
AND ATOMIC HYDROGEN

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February 1986

UTIAS Report No. 303  
CN ISSN 0082-5255

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## ACKNOWLEDGEMENTS

This research was supported by the Canadian Fusion Fuels Technology Project, the Natural Sciences and Engineering Research Council of Canada and the Ontario Ministry of Energy. Contributions by other members of the UTIAS Fusion Research Group, through enlightening discussions are also acknowledged. Special thanks go to Charles Perez for his contribution during the commissioning of the facilities. We also thank Dr. B. L. Doyle of Sandia National Laboratories, NM, for performing NRA measurements for us.

## SUMMARY

In an attempt to lower radiation losses due to metal plasma impurities in the JET fusion device, the use of low-Z wall coatings has been proposed (Si, TiC, SiC, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> on Inconel 600). This report presents experimental results obtained by exposing these samples to electron, laser radiation and atomic hydrogen impact. The studies performed include measurements of (i) gases evolved due to low energy (300 eV) electron bombardment, (ii) inherent gas content in the near-surface region, and (iii) retained deuterium subsequent to exposure to sub-eV D<sup>0</sup>. Also described is the Laser Release Analysis technique which has been developed to enable us to perform the last two sets of measurements.

Electron impact desorption rates for hydrogen and methane due to electron bombardment span the range 10<sup>-1</sup> to 10<sup>-3</sup> H<sub>2</sub>/e<sup>-</sup> and 10<sup>-2</sup> to <10<sup>-4</sup> CH<sub>4</sub>/e<sup>-</sup>. Following normal system bakeout at 500 K for 24h, the major species released by laser heating were found to be H<sub>2</sub> and CO, with levels up to ~7×10<sup>16</sup> H/cm<sup>2</sup> and ~4×10<sup>16</sup> CO/cm<sup>2</sup>. A similar concentration of argon was found for the TiC coating produced by sputter ion plating. Further heating of the samples to 800-900K for 1h resulted in a reduction of hydrogen and CO release levels by about an order of magnitude. Subsequent to the 800-900 K heating procedure, the samples were exposed to sub-eV D<sup>0</sup> atoms to fluences of ~2×10<sup>19</sup> D<sup>0</sup>/cm<sup>2</sup>, and deuterium retention levels were measured to be of the order of 10<sup>14</sup> - 10<sup>16</sup> D/cm<sup>2</sup> for the various coatings. Implications of these results for JET's first-wall tritium inventory are discussed.

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## 1.0 INTRODUCTION

The JET vacuum vessel is constructed of Inconel 600, a nickel-based alloy. When JET is operated with bare, uncoated Inconel walls and graphite limiters, the radiation level is high,  $P_{\text{rad}}/P_{\text{ohmic}} = 90\text{-}100\%$ , partly as a result of strong nickel radiation. The ultimate source of metals in the plasma is evidently the walls, although the metals are observed spectroscopically to enter the plasma primarily from the graphite limiters. A two-step process appears to be involved in which the metals first contaminate the limiter, followed by plasma contamination from the limiters.

A fundamental change in the energy balance has been achieved in JET by coating the walls and limiters with fresh carbon, deposited by glow discharge in a mixture of 1-10%  $\text{CH}_4$  in  $\text{H}_2$  or  $\text{D}_2$ . In September 1984, and again in January/February 1985, JET discharges with such carbonized walls were characterized by  $P_{\text{rad}}/P_{\text{ohmic}}$  down to  $\sim 40\%$ .

An alternative approach to protecting the plasma from metal contamination would involve coating the Inconel with other low-Z coatings, most probably by pre-coating, but possibly by coating in situ. Samples have been prepared of Si, TiC, SiC,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  deposited on Inconel and various properties of these coatings have already been reported.<sup>1,2</sup>

These coatings contain various gases from their time of manufacture which can be released by thermal processes at the wall or by the impact of plasma species. The release of these gases due to photon impact<sup>3</sup> (thermal release) and by electron impact<sup>4</sup> is reported here.

The retention of hydrogen deposited in the wall coatings as a result of plasma exposure influences a number of important processes including particle re-cycle and fueling. When JET is operated with tritium, then tritium retention in the coatings will contribute to the radioactive inventory of the facility.

The retention of energetic hydrogen ions, 50-1000 eV, in these coatings has been reported by Erents.<sup>2</sup> The flux of hydrogen to the walls of a fusion reactor, however, will be dominated by very low energy particles, partly due to the large flux of  $\sim 2$  eV Frank Condon atoms arising from the electron impact dissociation of molecules entering the edge plasma from the walls. This flux can be inferred from spectroscopic measurements of

hydrogen- $\alpha$  radiation near the walls in JET. The flux of low energy atoms at the wall increases with the line average density in the main plasma, and with the plasma elongation, spanning the range  $10^{14}$ - $10^{16}$  H<sup>0</sup>/cm<sup>2</sup>·s.

Results are also reported here for the retention of deuterium in these coatings after exposure to sub-eV D<sup>0</sup>, which is used to simulate Frank-Condon atoms.

The primary objective of this study was to obtain a comparative first order assessment of the gas content of these coatings, and not to produce an exhaustive study which would include detailed surface characterization. This approach is justified since the coatings produced are highly non-uniform "engineering materials", as would be the case if such coatings were to be used in tokamaks. In the case of the sub-eV D<sup>0</sup> retention measurements, the aim was to investigate the possible existence of anomalous effects for the trapping of low energy hydrogen (~1 eV) vis-a-vis energetic ions (~100's eV), as had been earlier observed for the case of carbon.<sup>5</sup> Since our sub-eV D<sup>0</sup> retention results are to be compared with the energetic ion data of Erents,<sup>2</sup> we followed similar sample preparation, viz, no special sample treatment (i.e., mechanical or chemical) was employed prior to experimentation.

## 2.0 JET SAMPLES

### 2.1 Preparation of Samples

The samples studied here were provided by JET, and were prepared for the JET project by the United Kingdom Atomic Energy Authority, Harwell.<sup>1</sup> Most of the samples tested by us were coatings deposited on Inconel 600 by plasma spraying (PS), with thicknesses of about 0.1 to 0.3 mm. Two coatings produced by different techniques were also studied. A TiC on Inconel sample was produced by sputter ion plating (SIP), yielding a coating thickness of ~15 $\mu$ m. A SiC sample with a Mo interlayer was produced by plasma activated vapor deposition (PAVD); a SiC coating of 5 or 10  $\mu$ m was deposited on a Mo interlayer of about 6  $\mu$ m thickness. All samples were of 10 mm diameter and 6 mm thickness.

The processes used for coating deposition are summarized as follows:

- (a) Plasma spraying. A Metco 3M (superseded by a 7M) system was used with nitrogen as the main plasma gas, and powders specially formulated for plasma

spraying. Hydrogen was added in small quantity to the plasma in order to increase the power level and to minimize oxidation of the hot spraying particles and substrate surfaces. All substrates were grit blasted with -16+50 mesh alumina at a pressure of about 2 mTorr immediately before coating. Process times were selected to give nominal coating thicknesses of 0.1, 0.2, and 0.3 mm at spray distances of 50, 70, and 95 mm. Argon jets were blown over substrates to further minimize oxidation.

(b) Sputter ion plating. The coating material was sputtered from large area targets in a glow discharge, and deposited on substrates which were surrounded by the target plates. Relatively high argon pressures (10-100m Torr) were used for the glow discharge to ensure good throwing power. The deposition chamber was preheated to above 300°C and the samples were cleaned by ion bombardment to achieve excellent adhesion. The samples were biased with low voltage during deposition, which contributed to the formation of dense coatings.

(c) Plasma activated vapor deposition. The samples were placed in a silica reaction tube surrounded by a rf induction coil, which was used to heat the samples by induction. The reactive gases used to prepare SiC samples analyzed in this work were SiH<sub>4</sub> and NH<sub>3</sub>, which reacted on the hot substrates to form Si<sub>3</sub>N<sub>4</sub>, SiH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>, finally leading to the formation of SiC coatings. Deposition temperatures were in the range of 500-850°C, since previous experience indicated that coatings with low expansion are best deposited at temperatures which are close to those at which they will be used in subsequent service.

Further details concerning the sample preparation as well as some coating characteristics are given in Reference 1.

Comparison studies were carried out employing samples provided by the General Atomic Company in the U.S. These consisted of POCO graphite disks covered with TiC and C-SiC coatings. The TiC coating, formed by chemical vapor deposition (CVD), was about 15-25 μm thick, on a sample of 25 mm diameter and 6 mm thickness. The C-SiC sample used for our test was 25 mm in diameter, 1.5 mm thick, with a coating thickness of ~125 μm. The C-SiC coatings were formed as an isotropic carbon matrix with a uniform dispersion of SiC of ~200Å diameter particles. The coatings were deposited on POCO graphite substrates by chemical vapor deposition in a bed of ceramic particles fluoridized by the gaseous reactive mixture.<sup>6</sup>



## 2.2 X-Ray Diffraction and Auger Analyses of Samples Including Comparison with Coatings on POCO graphite

Some characteristics of the JET samples were determined by Harwell; these included thermal measurements, hydrogen ion trapping evaluation, and fracture behaviour and microstructural examination.<sup>1</sup> However, there appears to be no indication of whether stoichiometric analyses have been performed. Therefore, we performed such studies, for some samples, using the X-ray diffraction technique, which yielded the results summarized in Table 1.

As can be seen in the table, the TiC coating on Inconel (JET-PS-TiC No. 2), produced by plasma spraying, contained a mixture of TiC and C phases, for both the unbaked and baked samples. The Ni and Mo lines observed were probably due to some segregation effect. The most interesting change observed in an electron-irradiation JET sample (JET-PS-TiC No. 1) was the appearance of Ti diffraction lines, in addition to those of TiC and C, when analyzing the bombarded area. This suggests that some electron-induced decomposition of TiC might have occurred, although it is not clear at present what mechanism could be responsible for such a phenomenon. The interpretation of this effect appears to be complicated by the fact that chemical vapor deposited TiC coatings on POCO graphite (GA-21) showed no change, after electron bombardment, in the X-ray diffraction pattern. A comparison between TiC coatings from JET and GA suggests that the coating process may have some influence on the probable existence of an electron-induced decomposition effect.

Nonstoichiometric ratios of Ti and C, obtained by Auger analysis, of the e<sup>-</sup>-irradiated TiC on Inconel sample (JET-PS-TiC No. 1) confirmed the existence of segregated Ti and C in addition to TiC. Similar Auger analysis of the TiC on POCO graphite (GA-21) sample yielded a 1:1 stoichiometric ratio of Ti and C, in agreement with the X-ray diffraction analysis.

The SiC coatings from JET (JET-PAVD-SiC No. 1) have shown strong lines of Mo and Ni besides those of Si and C, whether the samples were baked or not. No SiC lines were identified, neither on the virgin samples nor on the baked ones, suggesting that these coatings may not have a SiC phase at all. The presence of strong Mo and Ni lines is consistent with previously reported analyses showing strong spalling and segregation of atoms from the substrate to the surface.<sup>1</sup> In contrast, the GA sample (C-SiC on POCO graphite)

showed the existence of a distinctive SiC phase mixed with phases of C, for both the unbaked and baked samples. The X-ray analysis results suggest that the coating process has a definite influence on the film characteristics.

### 3.0 ELECTRON IMPACT DESORPTION FROM UNEXPOSED SAMPLES

In order to establish the condition of the samples in their natural state, i.e., before hydrogen loading, they were subjected to various baking conditions, then bombarded by low energy electrons.

The experiments were performed in a UHV chamber evacuated by a turbomolecular pump. Base pressures in the system were  $\sim 10^{-10}$  Torr ( $\sim 10^{-8}$  Pa), consisting mainly of  $H_2$ . The samples, mounted on a heatable stainless steel stage, were exposed to a beam of electrons ( $\sim 5$  mm diameter) originating from a UHV compatible electron gun. A beam current of 300  $\mu$ A at 300 V was used. RBS analysis of some of the samples confirmed that negligible W deposition resulted from the tungsten filament in the gun.

A quadrupole mass spectrometer was used during the electron exposure to monitor the release of gas species as a function of time. The species that were most affected by the electrons were  $H_2$  and  $CH_4$  (mass 15 was used to monitor methane). The evolution of  $H_2$  and  $CH_4$  yields as a function of time, for the JET samples, are shown in Fig. 1. Although other gases were observed in the vacuum chamber upon the introduction of the samples, the levels of these gases remained unaltered, for most samples, during the  $e^-$  exposure tests. For some of the samples the CO and  $H_2O$  signals were also affected by the electrons. For example, the virgin sample of plasma sprayed TiC and samples of  $MgAl_2O_4$  and Si baked for 24 h at 450 K, exhibited an initial release of CO (mass 28) which decayed with time, approaching the base levels (i.e., with no electrons) in about 10-15 min. A similar behaviour was also noted for the  $H_2O$  (mass 18) signal, when bombarding the Si coating.

In the case of a  $TiO_2$  coated sample, an almost instantaneous decrease in the partial pressure of mass 28 (CO and/or  $N_2$ ),  $H_2O$  and mass 20 was observed when starting the electron bombardment, followed by a gradual increase to the initial partial pressure level. The initial decrease can perhaps be attributed to an electron-induced pumping effect on the sample due to some composition change in the coating; however, further studies, including surface analysis, will be necessary to understand this effect.

We note the following major features for the JET samples. The virgin sample of plasma sprayed TiC [case (a), Fig. 1] during initial exposure to electrons ( $2 \times 10^{15}$  e<sup>-</sup>/s) produced yields of  $\sim 10^{-1}$  H<sub>2</sub>/e<sup>-</sup> and  $\sim 10^{-2}$  CH<sub>4</sub>/e<sup>-</sup>. After about 5 min exposure the levels fell by close to one order of magnitude. Another sample of TiC [case (b), Fig. 1] which has been previously heated to about 1000 K for 5 min and exposed to electron impact (1000 eV electrons) and then exposed to atmosphere for 16 months, during the current tests yielded  $\sim 10^{-4}$  CH<sub>4</sub>/e<sup>-</sup> after  $\sim 10$  min exposure. This methane yield is about the same as that obtained for earlier tests with the same sample.<sup>7</sup> A third sample of TiC [case (c), Fig. 1] yielded  $\sim 10^{-3}$  CH<sub>4</sub>/e<sup>-</sup> after a normal bakeout (24 h at 450 K) and a few minutes of electron exposure. The yield was reduced to  $\sim 10^{-4}$  CH<sub>4</sub>/e<sup>-</sup> after heating the sample for 30 min at 750 K. It should be noted that for the electron fluxes used here the resolution of the detection system for methane was  $\sim 10^{-4}$  CH<sub>4</sub>/e<sup>-</sup>. The above results indicate that sample preparation via heating at 750-1000 K for about 30 min will yield  $\sim 10^{-4}$  CH<sub>4</sub>/e<sup>-</sup>. Furthermore, exposure to atmosphere will not require new high temperature baking of samples in addition to normal system bakeout.

In general, all of the JET samples produced, after 30 min heating at 750 K, methane yields of  $\sim 10^{-4}$  CH<sub>4</sub>/e<sup>-</sup> or less while the corresponding H<sub>2</sub> yields were in the range  $10^{-3}$  to  $3 \times 10^{-3}$  H<sub>2</sub>/e<sup>-</sup>.

The initial preparation of the TiC (GA-18) and C-SiC General Atomic samples consisted of a 30 min bakeout at 1200 K in a separate vacuum chamber. This procedure was followed because some previous experiments with a TiC coated sample (GA-21) resulted in relatively high levels of CH<sub>4</sub> yields ( $\sim 10^{-3}$  CH<sub>4</sub>/e<sup>-</sup>) even after 12 min of sample heating at 900-1000 K, in addition to 12 h system bakeout at  $\sim 500$  K.<sup>7</sup> The current tests were performed after 12 months of exposure to air following the 1200 K bakeout. Before the e<sup>-</sup> impact tests the samples were again heated for 24 h at 450 K. The measured yields for TiC were  $\sim 10^{-3}$  H<sub>2</sub>/e<sup>-</sup> and  $< 10^{-4}$  CH<sub>4</sub>/e<sup>-</sup>. Similar sample preparation for the C-SiC coated POCO graphite also yielded  $< 10^{-4}$  CH<sub>4</sub>/e<sup>-</sup>.

#### 4.0 DEVELOPMENT OF LASER RELEASE ANALYSIS TECHNIQUE

It is possible to measure the near-surface gas content of samples, including hydrogen retained after plasma or simulated-plasma exposure, using

a high power laser to thermally desorb or ablatively release the gases, which are then measured mass spectrometrically.<sup>8-13</sup> Whether the release is by thermal desorption, and thus non-destructive, or by ablation, depends on the power density in the focal spot and the thermal and reflective properties of the coatings.

While such a Laser Release Analysis, LRA, technique is clearly not capable of the refinement and precision of techniques such as Nuclear Reaction Analysis, NRA, etc., LRA has the following advantages: (a) It is relatively inexpensive, (b) all gases can be readily measured, (c) acceptable accuracy for the technological coating materials studied here (sample-to-sample variation is likely to be substantial and it is only meaningful to identify approximate values of gas content). While sample destruction during LRA (for the cases where the release is ablative) would normally be considered to be a limitation for the technique, it was not a major concern for the present studies.

In order to establish the characteristics and limitations of LRA, hydrogen retention experiments were performed using pure graphite (single crystal and pyrolytic), with comparisons being made between LRA and NRA, the latter being carried out by Dr. B. L. Doyle, at Sandia National Laboratories, Albuquerque.<sup>14</sup>

#### 4.1 Experimental Apparatus and Technique

All LRA experiments were performed in a UHV system, pumped by a turbomolecular pump, see Fig. 2. Base pressures of  $\sim 10^{-10}$  Torr, mainly  $H_2$  and  $D_2$ , were normally achieved after baking 48 h at 500 K. The graphite samples were held in place by three tungsten pins, mounted in a stainless steel support. The single crystal sample was a 9 mm disk of 2 mm thickness; the pyrolytic graphite was of a quasi-circular shape of the same size with a thickness of 0.2 mm. A tungsten filament mounted behind the sample allowed the samples to be heated to  $\sim 1800$  K for several minutes by electron bombardment before overheating of the stainless steel support occurred. The target chamber was connected to the vacuum pump through a UHV valve, which allowed the chamber to be isolated during the desorption experiments. Total and partial pressure measurements were made with an ionization gauge and a quadrupole mass spectrometer, which were calibrated against an MKS spinning-rotor absolute pressure gauge.

Atomic deuterium (with sub-eV energy) was produced by contact dissociation of deuterium gas on a tungsten filament (13 mm long and 1 mm wide) heated to ~1800 K. During the D<sup>0</sup> exposure of the carbon samples, the target chamber was backfilled with deuterium to a pressure of ~4×10<sup>-4</sup> Torr (D<sub>2</sub>). Under these conditions, impurity levels (e.g., D<sub>2</sub>O, CO) were measured to be ≤ 10<sup>-8</sup> Torr. The D<sup>0</sup> atom production rate was measured by isolating the target chamber and measuring the initial rate of D<sub>2</sub> pressure decrease when the tungsten loading filament was turned on, see Hickmott.<sup>15</sup> Taking geometry into consideration, the D<sub>0</sub> flux density on the sample was estimated to be ~4×10<sup>14</sup> D<sup>0</sup>/cm<sup>2</sup>·s, for filament temperatures of ~1800 K. At higher filament temperatures, higher fluxes were measured. However, D<sup>0</sup> retention results obtained at W temperatures > 2000 K were affected by W deposition on the graphite sample surfaces; see discussion below. The temperature of the carbon samples during loading (with the W filament at 1800 K) was measured with an optical pyrometer to be ~600 K. This temperature resulted from radiation loading of the sample by the hot W filament. Somewhat higher sample temperatures were measured for higher filament temperatures (e.g., sample 800 K @ W 2400 K).

During the deuterium desorption process, the laser beam entered the target chamber through a glass viewport and was focused onto a 4 mm spot on the sample. A Phase-R DL2100A pulsed dye laser, with a Rhodamine 590 dye solution was used for all experiments. The laser light was centered at ~590 nm, with a bandwidth of < 10 nm. Since the primary purpose of the laser was to deposit energy on a well defined area on the sample, no attempt was made to narrow or tune the laser frequency. The laser energy was measured to be 120-190 mJ, using a Scientech 38-0101 volume absorbing disk calorimeter, yielding an energy density of 0.9 - 1.4 J/cm<sup>2</sup> striking the sample surface during the 1 μs laser pulse. This resulted in sample surface temperatures of > 3000 K, measured by thermionic emission of electrons from the heated spot.<sup>16,17</sup>

The partial pressure rise resulting from the LRA pulse was detected by a Spectramass 100D quadrupole mass spectrometer, using a Faraday plate collector. The laser shot was immediately followed by a step rise in the D<sub>2</sub> partial pressure. With the chamber volume and the laser spot size known, retention values were readily calculable. The equilibrium pressure in the test chamber, while isolated (prior to desorption), was ~6×10<sup>-8</sup> Torr D<sub>2</sub>,

which was comparable to the laser-induced pressure rise from the crystal samples. Thus the step rise in the  $D_2$  pressure was followed by a plateau, or a gentle drop, caused by wall pumping. For the pyrolytic graphite samples, the pressure rise was much larger ( $\sim 3 \times 10^{-6}$  Torr) and as expected more pronounced wall pumping was observed. By backfilling the chamber to  $\sim 5 \times 10^{-6}$  Torr  $D_2$ , the wall pumping could be eliminated in the latter case without affecting the magnitude of the measured LRA pressure rise. For both the single crystal and pyrolytic graphite samples the magnitude of the initial pressure rise was used to determine the retained D. Therefore, it was important to minimize wall pumping which might have a "clipping" effect on the initial pressure rise step. Part of this wall pumping was likely caused by the atomic deuterium produced on the quadrupole and ionization gauge filaments, and subsequently absorbed by the walls.

For several samples,  $D^0$  retention was also measured by the  $D(^3\text{He},p)^4\text{He}$  nuclear reaction analysis in order to test the validity and potential applicability of the LRA technique. NRA was performed with a 0.7 MeV  $^3\text{He}$  beam directed at the sample, and protons from the  $D(^3\text{He},p)^4\text{He}$  exothermic reaction were monitored. Corrections were made for  $^{13}\text{C}$  (about 1%  $^{13}\text{C}$  is present in natural carbon) which through the  $^{13}\text{C}(^3\text{He},p)^{15}\text{N}$  reaction produces a background yield of protons. Thus the resolution of this NRA method was limited to  $\sim 10^{13}$   $D^0/\text{cm}^2$ .

Since hydrogen retention is a strong function of the surface recombination coefficient which in turn depends on the surface state, it was important to identify the presence of impurities on the sample surface. This was especially important in the current experiments where the  $D^0$ -producing W filament was in close proximity to the sample. In some experiments, W was purposely deposited on the sample surface in order to study its effect on  $D^0$  retention; see discussion below. Surface impurities were measured using RBS.

#### 4.2 LRA Results for Graphite

The primary retention results of this study are presented in Fig. 3; data which have been determined by NRA are also shown. Three retention curves have been drawn, representing different atom loading situations. By operating the  $D^0$  producing tungsten filament at temperatures  $>2000$  K, retention levels were found to be considerably greater than those obtained

for 1800 K. It is postulated that the higher retention values at W temperature  $>2000$  K are caused by the deposition of evaporated tungsten on the surface. With the W filament at 1800 K, the tungsten deposition is negligible ( $<0.01$  monolayers measured by RBS) and the retention under these circumstances consequently represents a base line retention level for  $D^0$  on single crystal graphite. For the three single crystal samples studied, good agreement was found between the LRA and NRA techniques; see Table 2. It should be noted that Sample #2, after several LRA shots and subsequent  $D^0$  loading, yielded similar NRA results both on the laser spot and off the laser spot, implying that the retention characteristics of the single crystal are not affected by the laser. This is also consistent with observations of negligible damage appearing on SEM photographs of the sample surface; see Fig. 4.

Experiments were also performed with pyrolytic graphite. Comparison of LRA and NRA results (Sample #3 in Table 2) indicates that complete removal of the deuterium was not achieved with a single laser shot. However, the sum of the desorbed levels by LRA and NRA from the laser spot are equal to the retention level measured by NRA on the sample off the laser spot. Also included on Fig. 3 is an NRA measurement for pyrolytic graphite obtained in a different vacuum system for another sample (of different size and shape);<sup>18</sup> excellent agreement is found for the two cases.

Two possible explanations for partial desorption by LRA are as follows: (1)  $1 \mu s$  may not be long enough for complete desorption at low surface coverages (say  $<10^{13} D^0/cm^2$ ); (2) because of the cracks and crevices of the pyrolytic graphite, the  $D^0$  may be able to penetrate "deep" into the sample, from where it may not be easily removed during the  $1 \mu s$  laser pulse. In either case, the summation of desorption signals from successive laser shots might be used to find the total retention levels. A further alternative would be to employ a laser with a longer pulse length to allow sufficient time for surface diffusion from inner crevices and surface recombinations at low surface coverages.

The retention of deuterium in the single crystal samples ( $\sim 3 \times 10^{13} D^0/cm^2$ ) was found to be  $\sim 50$  times smaller than the retention in pyrolytic graphite, the latter being based on the NRA measurement. This result can be explained, at least partially, on surface roughness effects associated with pyrolytic graphite. Previous  $D^0$  retention results with papyex indicated

that most of the atoms are retained in the first few monolayers on surfaces including internal surfaces of a rough structured material.<sup>18</sup> Since no surface roughness is associated with the single crystal sample, we might conclude that the surface roughness of our pyrolytic graphite sample is about 50.

As mentioned earlier, the effect of W contamination on the surface of a single crystal graphite sample was also investigated. When the loading filament was operated at high temperature (~2400 K), more than 10 monolayers of tungsten and/or tungsten oxide were deposited on the carbon surface (measured by RBS). This surface coverage had the effect of increasing the amount of retained deuterium by a factor of about 10 and also reducing the tendency towards saturation for fluences  $\sim 10^{19}$  D<sup>0</sup>/cm<sup>2</sup>. At intermediate filament temperatures, ~2100 K, much less tungsten was deposited, <1 monolayer; however, there was still a noticeable increase in retention. The increased retention in the tungsten covered samples might be attributed to a combination of factors including changes in surface recombination coefficient, solubility, sticking coefficient, etc. Taking these factors individually, however, does not explain the observed results, e.g.,  $K_r^W/K_r^C \sim 10^{10}$  (Ref. 19) and  $S^W/S^C \sim 10^{-6}$  (Ref. 20), both of which would lead to lower retention values. Another possible explanation follows Pick et al<sup>21</sup> by assuming that on clean graphite, hydrogen preferentially occupies sites on the surface, as opposed to sites in the lattice, e.g., due to a deep chemisorption well. The addition of tungsten with a lower desorption energy may allow distribution of hydrogen into the bulk. If the surface layer consists of tungsten oxide, instead of the pure metal, a mechanism is difficult to predict.

#### 4.3 Applicability of the LRA Technique

The retention of sub-eV D<sup>0</sup> in single crystal graphite has been measured to be  $\sim 3 \times 10^{13}$  D<sup>0</sup>/cm<sup>2</sup>. This value is about 50 times smaller than the retention in pyrolytic graphite ( $\sim 2 \times 10^{15}$  D<sup>0</sup>/cm<sup>2</sup>). Based on previous results indicating that deuterium is trapped in the near surface regions of carbon,<sup>18</sup> we conclude that the surface roughness factor of the pyrolytic graphite sample studied is about 50.



The LRA technique has been highly successful on single crystal graphite samples for which good agreement was found with the NRA method. We thus anticipate that LRA could be extended to other materials with "smooth" surfaces for which atom penetration is not too deep, and the surface area is not "too large" to prevent efficient recombination. For very rough surfaces, like pyrolytic graphite, the 50% removal of deuterium certainly gives a good preliminary indication of retention levels. In addition, further laser shots could be taken to remove the retained deuterium more completely. For the experiments with the JET samples, typically 3-5 shots were taken (see Section 5).

For graphite samples it appears that the laser power density employed resulted in thermal, rather than ablative, release of the near-surface gas content. This was almost certainly the case for the single crystal sample. With regard to the measurement of hydrogen/deuterium retained by the sample after exposure to low energy  $H^0/D^0$  — the accuracy of LRA is better than a factor of two for graphite samples, even for highly roughened surfaces. We therefore conclude that, with regard to the measurement of retained low energy  $H^0/D^0$ , LRA should be adequate for providing first order estimates for the JET coatings.

## 5.0 APPLICATION OF LASER RELEASE ANALYSIS TO JET SAMPLES

### 5.1 Experimental Procedure

The gas release experiments for the JET coatings were performed in a very similar manner to the retention experiments with carbon samples. The same vacuum system was used, and the only change in the apparatus was the addition of a thermocouple placed between the sample and one of the supporting tungsten pins.

The partial pressure rise resulting from the laser pulse was again detected by a Spectramass 100D quadrupole mass spectrometer. The entire spectrum from  $M/e = 1$  to 50 was scanned in a 9s period following the laser shot. The hydrogenic species, masses 2 to 4, were always monitored within one second of the laser pulse. This prevented significant loss of signal due to atomic hydrogen (produced on the ionizer filaments) being pumped by the walls. The drop-off in the molecular hydrogen pressure was characterized by a time constant of  $\sim 5s$  in the isolated target chamber. The other

two gases of major interest, CO and Ar, rose to levels which remained reasonably stable, so that a delay of 10-20s in their measurement would have no effect on the measured value. The equilibrium pressure in the target chamber, while isolated (prior to desorption), was  $\sim 6 \times 10^{-8}$  Torr, mostly hydrogen. For most experiments, this was much lower than the pressure due to released gases ( $10^{-6}$  -  $10^{-5}$  Torr); however, in some cases, the pressure rise was of the same order of magnitude, and corrections for background signals were necessary.

Atomic deuterium for the sub-eV  $D^0$  retention experiments was again produced by contact dissociation of  $D_2$  on a tungsten filament (20 mm long and 1.5 mm wide) heated to  $\sim 1850K$ . All loading was done at this W temperature to avoid W contamination of the surfaces (see Section 4 for discussion of D trapping in graphite). The resulting  $D^0$  flux density on the sample was estimated to be  $\sim 1 \times 10^{15}$   $D^0/cm^2s$ . There was some heating of the samples during the  $D^0$  loading process due to radiation from the filament; in general, the sample temperature was  $\sim 500K$ .

The measurements of retained atomic deuterium were performed in a very similar manner to the gas release experiments. This time, however, only masses 2, 3 and 4 were scanned by the mass spectrometer (with a 1s period), and the scans were made continuously. This allowed easy differentiation between released and background  $D_2$  signals.

## 5.2 Inherent Gas-Release Experiments

Three sets of experiments were performed on each of seven different samples. The first two sets consisted of gas release measurements discussed in this section, and the third set involved the D retention study, see below. For the first series of experiments, the samples, after being baked in a uhv system at 500K for 24h, were allowed to cool to room temperature for one or more days, until pressures of  $\sim 10^{-9}$  Torr were reached. Between 5 and 7 laser pulses were taken at the same spot for each sample with the target chamber being isolated before each shot. Following the partial pressure measurements, the chamber was opened to the vacuum pumps to remove the released gases, and to reduce the background level in preparation for the next laser shot. Figure 5 illustrates a typical mass spectrum trace. The respective partial pressure rises for the different masses following

each shot were added to produce a total partial pressure rise from which the trapped gas values were calculated, see Table 3.

Following the first series of experiments, the samples were exposed to atmosphere for periods ranging from one day to several months. When they were again placed in the target chamber, they were positioned so that the laser would be striking a new area on the sample. Thus the second series of experiments should be independent of the first. The vacuum system was now baked for 40-48h at 500K, after which the samples were further heated to 800-900K by electron bombardment from the rear. Again, after cooling, the laser was fired at the samples following the procedure previously used. A maximum of three shots were taken at the samples in this series of experiments, to avoid modifying the coatings as much as possible. These results are also given in Table 3.

### 5.3 Retention of Sub-eV D<sup>0</sup> Atoms

The third series of experiments was performed following the second series, without removing the samples from the system. The coatings were loaded with sub-eV atomic deuterium with a total fluence of  $\sim 2 \times 10^{19}$  D<sup>0</sup>/cm<sup>2</sup>. After allowing one or more days for the deuterium pressure in the target chamber to decrease, the laser was fired at exactly the same spot used in the second series of experiments in order to ensure that D trapping is measured on a spot which is devoid of inherent H in the near-surface region. Four laser shots were taken at each sample, and the amount of deuterium removed is presented in Table 4.

The selection of the total D<sup>0</sup>-loading fluence of  $2 \times 10^{19}$  D<sup>0</sup>/cm<sup>2</sup> was based partially on the data of Erents<sup>2</sup> and our own fluence dependence measurements for Si and TiC. Erents<sup>2</sup> observed saturation for all coatings, except TiC (sputter ion plated), at fluences of  $\sim 10^{18}$  D<sup>+</sup>/cm<sup>2</sup>, for ion energies >50 eV and 300K sample temperature. TiC was found to trap D<sup>+</sup> continuously for temperatures  $\leq 800$ K.<sup>2</sup> Based on D-fluence dependence measurements performed for the present study, with sub-eV D<sup>0</sup> impacting on sputter ion plated TiC and plasma sprayed Si, Si was found to saturate at  $\sim 10^{17}$ - $10^{18}$  D<sup>0</sup>/cm<sup>2</sup> and some evidence of a trend to saturation with TiC was noted for fluences of  $\sim 10^{19}$  D<sup>0</sup>/cm<sup>2</sup>, see Fig. 6. The differences between the tabulated and plotted retention values are attributed to the use of different samples.

## 5.4 Discussion

For the first two series of experiments, the major gases released in all but two of the samples were  $H_2$  (also HD and  $D_2$ ) and CO. For the TiC-SiP and SiC samples, Ar was also released in large quantities. There were no difficulties in identifying the hydrogenic species, masses 2, 3 and 4, or argon, mass 40 (and also mass 20); however, mass 28 could be attributed to either  $N_2$  or CO. For the signal to originate from  $N_2$ , the ratio of the mass 14 to mass 28 peak heights would have to be  $\sim 0.07$  (quadrupole ionizer characteristic). This was never the case, with the ratio normally being  $< 0.01$ . Therefore it is assumed that the majority of the mass 28 signal was due to CO.

Usually there were noticeable partial pressure rises for masses 12 through 20 (in the two special cases mentioned above, mass 20 was due to Ar). These pressure rises usually fell into the range of 1-10% of the hydrogen partial pressure rise, and there is the possibility that these gas components could have been produced in the quadrupole ionizer region.<sup>22</sup> Because the ionizer region was enclosed, and therefore had a low pumping speed, atomic hydrogen produced on the ionizer filament could have reacted with adsorbed species on the walls,<sup>23</sup> producing spurious results.<sup>22</sup> For this reason, the surface concentration of these gases, corresponding to the observed partial pressure rises, are not included here.

As is revealed in Table 4, protium is also released from the surfaces which have been 'cleaned' by the laser, and then loaded with deuterium atoms. There are several possible sources for this hydrogen: it may have migrated from regions on the surface which have not been 'cleaned' by the laser, or it could have been released due to laser ablation of the surface layers. For the  $Al_2O_3$  sample, the amount of protium could be attributed to inherent hydrogen which was not removed in the second series of experiments.

One of the major difficulties with the LRA technique is the assessment of its success. It was clearly evident from performing the experiments that a single laser shot was not sufficient to release all of the trapped gas from the samples. Since the thermal response of the coatings to the laser pulse was unknown, as were the desorption properties, the only indication of how successful the desorption processes were, was the drop-off in gas released with successive laser shots. For the best-behaved coatings, the

gas released per shot was reduced to <10% of the first shot value after a few shots. This was almost always the case for the release of CO; however, the hydrogenic species were more difficult to remove from some of the samples. The numbers given in brackets in Table 3, and the last column of Table 4 are ratios of the partial pressure rise from the last laser shot taken to the partial pressure rise from the first shot. These numbers give a good indication of how completely the gases have been removed from the area exposed to the laser.

Two of the samples in which difficulty was encountered in the removal of hydrogen, TiO<sub>2</sub> and SiC, were also two of the samples most altered by laser heating. On the TiO<sub>2</sub> sample, there was some discoloration, as well as a visible reduction in coating thickness. In the case of TiO<sub>2</sub>, the 800-900K sample heating might have resulted in a change in sample properties vis-a-vis hydrogen release, as evidenced in the last to first laser shot ratios in Table 3. On the SiC sample, cracking of the coating due to laser impact was evident. For these samples, it is possible that hydrogen trapped deep in the bulk of the coating was being released as surface layers were being removed or modified.

Laser modification of some of the coatings before the third series of experiments (i.e., D<sup>0</sup> trapping) could not be avoided. In Figure 7, SEM photographs show how some of the coatings were affected by laser irradiation. Figures 7a to 7c clearly show the modification of the SiC-PAVD sample due to exposure to the laser. From Figure 7c, the edge of the laser irradiated area is estimated to have a width of ~100µm, while the spot size is 4 mm in diameter. The next two photographs (7d and 7e) show the Si-PS sample, unexposed and exposed to the laser. There is very little evidence of surface modification, although after many laser shots, some marking of the coating was visible. Figure 7f shows part of the laser spot on the TiC-PS sample. While the surface structure does not appear to be greatly modified, there is evidence of some ablation. A similar result is shown for TiO<sub>2</sub>-PS in Figure 7g.

In order to obtain an independent check on the applicability of LRA for near-surface gas release, two of the coatings (but different samples) were also analyzed using Nuclear Reaction Analysis (NRA) for deuterium uptake by the D (<sup>3</sup>He,p)<sup>4</sup>He reaction. NRA was performed for us by Dr. B. L. Doyle of Sandia National Laboratories, Albuquerque, NM, for SiC and TiC, subsequent

to sub-eV D<sup>0</sup> exposures at 600K to fluences of  $\sim 4 \times 10^{19}$  D<sup>0</sup>/cm<sup>2</sup>. In TiC, a surface concentration of  $7.7 \times 10^{15}$  D/cm<sup>2</sup> was measured; the 1/e depth ( $\lambda$ ) was about 0.8  $\mu$ m. For SiC the corresponding values are  $2.6 \times 10^{15}$  D/cm<sup>2</sup> and 0.3  $\mu$ m. Our current LRA results obtained under similar sample conditions and D<sup>0</sup> fluences, agree within a factor of three with the above NRA measurements. While such comparisons are limited to two coatings, the noted agreement was adequate to justify application of the LRA method to meet our initial objective, which was to obtain a first order estimate of sub-eV D<sup>0</sup> retention in order to establish the possible existence of anomalous H-trapping characteristics.

## 6.0 CONCLUSIONS

It is apparent from the laser studies that large amounts of hydrogen and CO could be released from most of the coatings, even after degassing at high temperature. The two coatings containing Ar require special attention due to the high Z-number ( $Z = 18$ ) of argon. If these two coatings are to be of further interest for fusion applications, the possibility of using He instead of Ar during the coating discharge process should be investigated. The concentration of gases such as H<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> released by the LRA process were too small to allow quantitative conclusions to be drawn.

Typically, the amounts of both CO and H removed from the samples by the laser was reduced by an order of magnitude, following the heating to 800-900K for 1h. Similar reductions in H<sub>2</sub> and CH<sub>4</sub> yields were observed when the samples were baked for  $\sim 30$  min at  $\sim 750$ K for the electron desorption studies. One of the strongest deviations from this result is the sputter ion plated sample of TiC, indicating a large trapping energy for the molecules concerned. Such trapping might be explained by the existence of pure Ti along with TiC. A similar explanation was offered by Erents for the large uptake of D<sup>+</sup> ions in the same type of coating.<sup>2</sup>

For the first five coatings in Tables 3 and 4 (Si, TiC-PS, TiC-SIP, SiC and TiO<sub>2</sub>), the amount of deuterium retained after exposure to sub-eV D<sup>0</sup> fluences of  $\sim 2 \times 10^{19}$ /cm<sup>2</sup> was found to be about the same as or larger than the amount retained in pyrolytic graphite ( $\sim 2 \times 10^{15}$  D<sup>0</sup>/cm<sup>2</sup>).<sup>14,18</sup> In general, the retention levels were about an order of magnitude less than the inherent hydrogen content in the samples, measured after normal baking (500K for 24h). This might indicate that sub-eV atoms are trapped in a region very close to the surface, while the inherent hydrogen originates from deeper in

the bulk of the coating, possibly as a result of the manufacturing process. Inconsistencies in the results for some of the coatings may be due to alteration of the coating by the laser.

The values of retained  $D^0$  may be compared with the results reported by Erents<sup>2</sup> for energetic  $D^+$  bombardment, 50-1000 eV. At 500K loading temperature, and 1000 eV  $D^+$ , the retained levels, as measured by Erents, for the various coatings are in the range  $0.4 \times 10^{17}$  -  $1.3 \times 10^{17}$  D/cm<sup>2</sup>. At 300K loading temperature, the retained level increases by a factor of 3-6 as  $D^+$  energy is raised from 50 to 1000 eV. Assuming a similar energy dependence at 500K, we estimate that for 500K loading temperature (as employed for our sub-eV  $D^0$  studies), the retained levels would be of order  $10^{16}$  D/cm<sup>2</sup> for 50 eV  $D^+$  ions. While our retention levels for sub-eV atoms appear to be below this level, the uncertainties in the two sets of results (present data for sub-eV  $D^0$  and Erents' results for ions) make it difficult to determine the actual energy dependence for hydrogen trapping in the sub-eV to 50 eV range.

One of the principal aims of the study was to establish whether or not an anomalously high retention of sub-eV  $H^0$  exists for these coatings, as had been reported for graphite.<sup>5</sup> Although the LRA technique is not quantitatively precise when applied to these coatings, it has provided an adequate first order estimate of  $D^0$  retention, and indicates that there is not a high retention level. Indeed, the retained levels are below those for low energy ion impact (~100's eV), as would be expected from simple extrapolation based on particle energy. With regard to the implications for tritium inventory of a DT fusion device, the energetic ions are thus likely to be the controlling factor rather than the ~eV neutral atoms in most cases. Certainly this will be the situation for the majority of the first wall actually facing the plasma since the flux of Frank Condon atoms is comparable to the flux of energetic charge exchange particles. For other situations, such as the divertor region where high re-cycling can result in low ion temperatures and copious molecular dissociation, the tritium loading of structures may be dominated by low energy particles. There does not appear, however, to have been any proposal to employ coatings such as those tested here for divertors.

The measured high levels of inherent hydrogen in the samples confirm that these materials can, like graphite, retain enormous quantities of

hydrogen isotopes if their entire bulk is loaded. Whether or not surface deposited hydrogen (atomic or ionic) results in bulk loading depends on the bulk diffusion coefficients of the coatings and the temperatures at which they are exposed. The diffusion properties of these coatings are not known at this time and it is therefore not possible to conclude what the ultimate, total tritium inventory of the coatings would be under prolonged exposure to plasma. This ultimate level will, however, be governed by the surface boundary condition which as discussed will generally be given by the energetic ion flux rather than the  $\sim eV$  atom flux.



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TABLE 1

## X-RAY DIFFRACTION ANALYSIS OF PRE- AND POST-IRRADIATED SAMPLES

THE BOMBARDMENTS WERE PERFORMED WITH ELECTRONS UNDER CONDITIONS INDICATED BELOW

SAMPLE	CONDITION	COATING PROCESS	COATING THICKNESS ( $\mu\text{m}$ )	PRE-IRRADIATION TREATMENT		IRRADIATION PARAMETERS eV      mA	DIFFRACTION LINE IDENTIFICATION	
				BAKE OUT TEMPERATURE [K]	TIME (MIN)		VACUUM (TORR)	PRE-IRRADIATION
<u>JET SAMPLES</u>								
TiC on Inconel (600) (JET-PS-TiC #2)	Virgin	{ PS <sup>(c)</sup>	$10^2-3 \times 10^2$					{ TiC <sup>(d)</sup> , C <sup>(d)</sup> , Ni <sup>(d)</sup> , Mo <sup>(f)</sup>
		{ PS	$10^2-3 \times 10^2$	1200 <sup>(b)</sup>	30	$\sim 10^{-5}$		{ TiC <sup>(d)</sup> , C <sup>(d)</sup> , Ni <sup>(d)</sup>
TiC on Inconel (600) (JET-PS-TiC #1)	Irradiated	PS	$10^2-3 \times 10^2$	1000 <sup>(a)</sup>	5	$\sim 10^{-6}$	1000 0.2-2	TiC <sup>(d)</sup> , Ti <sup>(f)</sup> , C <sup>(e)</sup>
SiC on Inconel (600) with Mo Interlayer (JET-PAVD-SiC #1)	Virgin	{ PAVD <sup>(c)</sup>	5-10					Mo <sup>(d)</sup> , C <sup>(d)</sup> , Si <sup>(f)</sup>
		{ PAVD	11	1200 <sup>(b)</sup>	30	$\sim 10^{-5}$		{ Mo <sup>(d)</sup> , Ni <sup>(e)</sup> , C <sup>(e)</sup> , Si <sup>(f)</sup>
<u>GA SAMPLES</u>								
TiC on POCO graphite (GA-18)	Virgin	{ CVD <sup>(c)</sup>	15-25					TiC <sup>(d,e,f)</sup>
		{ CVD <sup>(c)</sup>	15-25	1200 <sup>(b)</sup>	30	$\sim 10^{-5}$		TiC <sup>(d,e,f)</sup>
TiC on POCO graphite (GA-21)	Irradiated	CVD	15-25	900 <sup>(a)</sup> - 1000	12	$\sim 10^{-6}$	1000 0.3	TiC <sup>(d,e,f)</sup>
C-SiC on POCO graphite (GA-C-SiC #1)	Virgin	{ CVD	$\sim 125$					SiC <sup>(d,e,f)</sup> , C <sup>(d,e,f)</sup>
		{ CVD	$\sim 125$	1200 <sup>(b)</sup>	30	$\sim 10^{-5}$		SiC <sup>(d,e,f)</sup> , C <sup>(d,e,f)</sup>

(a) bake out in situ in target chamber,

(b) bake out in separate chamber,

(c) coating process: PS: Plasma Sprayed; PAVD: Plasma Activated Vapour Deposition; CVD: Chemical Vapour Deposition,

(d) strong line,

(e) intermediate line,

(f) weak line.

Table 2

Comparison of LRA and NRA Retention Results in Graphite Samples

Exposed to  $10^{19}$  D<sup>0</sup>/cm<sup>2</sup>

(The sensitivity of the NRA technique is limited to  $\sim 10^{13}$  D/cm<sup>2</sup>.)

Sample	W Coverage (monolayers)	LRA D/cm <sup>2</sup>	NRA <sup>a)</sup> D/cm <sup>2</sup>	NRA <sup>b)</sup> D/cm <sup>2</sup>	NRA <sup>c)</sup> D/cm <sup>2</sup>
2 SCG	-	$3 \times 10^{13}$	$1.5 \times 10^{13}$	-	$2.6 \times 10^{13}$
3 PG	0.01	$8 \times 10^{14}$	-	$8.1 \times 10^{14}$	$14.8 \times 10^{14}$
4 SCG	10	$3 \times 10^{14}$	-	$2.27 \times 10^{14}$	$4.56 \times 10^{14}$
5 SCG	<0.01	$3.2 \times 10^{13}$	-	$0.8 \times 10^{13}$	$2.9 \times 10^{13}$

a) Laser spot, but no desorption by LRA

b) Laser spot, after desorption by LRA

c) Off laser spot

Table 3

## Gases Released from JET Coatings

Sample	Number of Shots		$\Sigma$ Mass 2,3,4 H/cm <sup>2</sup>	Mass 28 CO/cm <sup>2</sup>	Mass 40 Ar/cm <sup>2</sup>
Si	(1)	5	$7.0 \times 10^{16}$ (0.005)*	$1.2 \times 10^{16}$ (.01)	
	(2)	3	$4.0 \times 10^{15}$ (0.05)	$1.1 \times 10^{15}$ (.004)	
TiC-PS	(1)	5	$6.7 \times 10^{16}$ (0.004)	$3.6 \times 10^{16}$ (.02)	
	(2)	1	$1.5 \times 10^{15}$ -	$2.1 \times 10^{15}$ -	
TiC-SIP	(1)	5	$5.6 \times 10^{16}$ (0.009)	$4.6 \times 10^{15}$ (.03)	$6.5 \times 10^{16}$ (.015)
	(2)	3	$1.3 \times 10^{16}$ (0.015)	$4.7 \times 10^{15}$ (.02)	$3.8 \times 10^{16}$ (.03)
SiC	(1)	7	$1.8 \times 10^{16}$ (0.10)	$1.6 \times 10^{14}$ (.11)	$5.2 \times 10^{14}$ (.13)
	(2)	2	$2.6 \times 10^{15}$ (0.28)	-	$1.7 \times 10^{14}$ (.15)
TiO <sub>2</sub>	(1)	5	$4.5 \times 10^{16}$ (0.08)	$2.0 \times 10^{16}$ (.03)	
	(2)	3	$5.9 \times 10^{15}$ (0.67)	$2.6 \times 10^{15}$ (.04)	
Al <sub>2</sub> O <sub>3</sub>	(1)	7	$3.3 \times 10^{15}$ (0.08)	$3.7 \times 10^{15}$ (.007)	
	(2)	3	$4.4 \times 10^{14}$ (0.06)	$2.1 \times 10^{14}$ (.008)	
MgAl <sub>2</sub> O <sub>4</sub>	(1)	5	$2.9 \times 10^{15}$ (0.28)	$2.6 \times 10^{15}$ (.03)	
	(2)	3	$4.8 \times 10^{14}$ (0.12)	$5.6 \times 10^{14}$ (.01)	

\*The number given in brackets is the ratio of the amount of gas released in the last laser shot to that released with the first laser shot.

(1) Baking at 500K for 24h

(2) Baking at 500K for 40-48h, plus sample heating at 800-900K for 1h

Table 4  
Deuterium Retention in JET Samples

Sample	Loading Temperature	D/cm <sup>2</sup> (Sum of 4 shots)	H/cm <sup>2</sup>	Ratio Shot 4/Shot 1
Si-PS	200°C	2.2×10 <sup>15</sup>	1.9×10 <sup>14</sup>	0.13
TiC-PS	250°C	2.4×10 <sup>15</sup>	2.9×10 <sup>14</sup>	0.10
TiC-SIP	250°C	1.2×10 <sup>16</sup>	-	0.15
SiC-PAVD	200°C	6.9×10 <sup>15</sup>	9.2×10 <sup>15</sup>	0.10
TiO <sub>2</sub> O <sub>3</sub>	200°C	9.8×10 <sup>15</sup>	-	0.53
Al <sub>2</sub> O <sub>3</sub>	200°C	4.8×10 <sup>13</sup>	1.7×10 <sup>13</sup>	0.18
MgAl <sub>2</sub> O <sub>4</sub>	200°C	7.5×10 <sup>13</sup>	-	0.28

Sub-eV D<sup>0</sup> fluence: ~2×10<sup>19</sup> D<sup>0</sup>/cm<sup>2</sup>

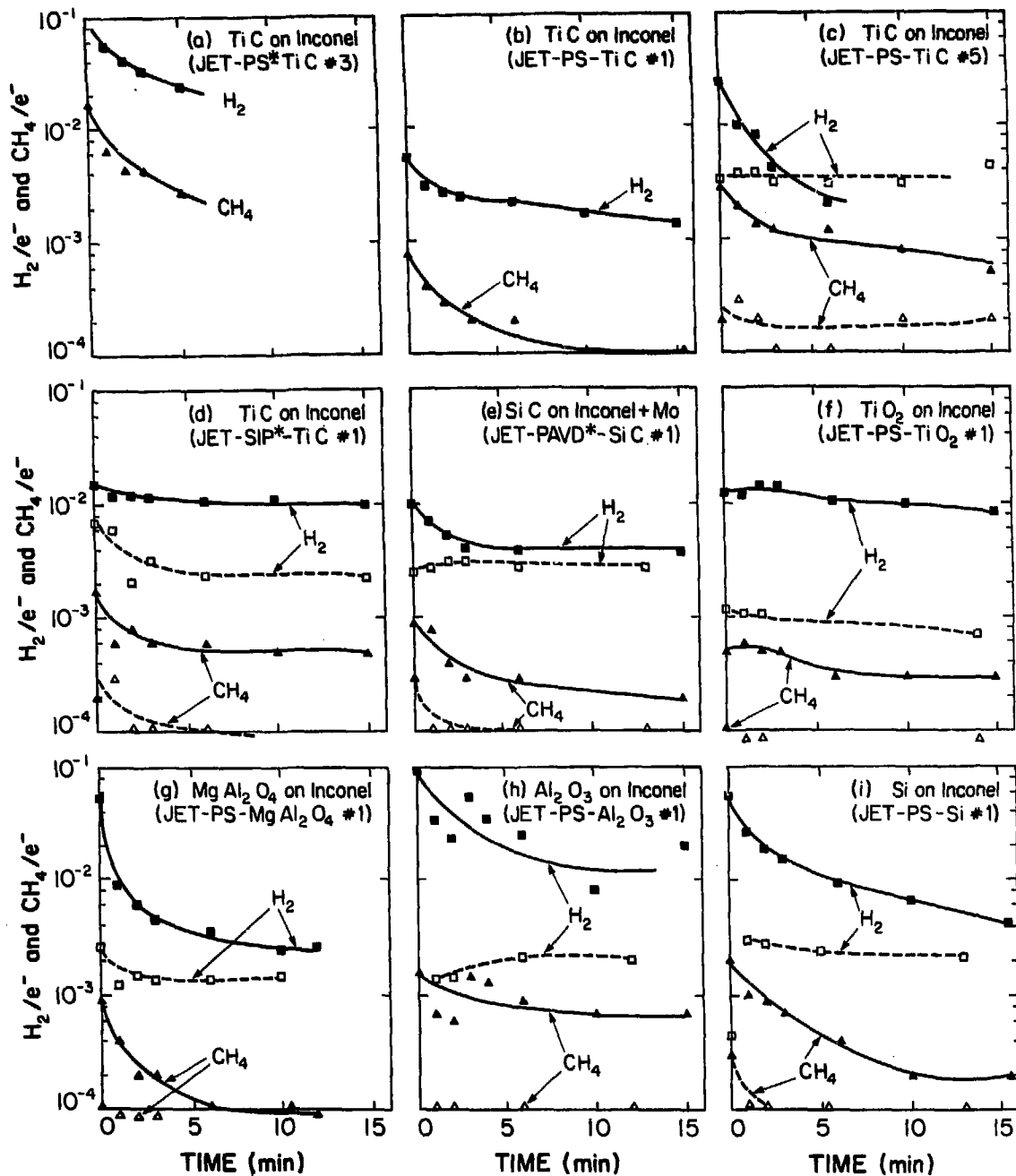


FIG. 1 Electron impact desorption of JET samples. Release of hydrogen and methane is shown as a function of time after electron beam is turned on. In all cases, except (a),  $e^-$  impact tests were performed at pressures of  $\sim 10^{-9} - 10^{-8}$  Torr; for case (a) the pressure was  $\sim 10^{-7}$  Torr. Sample temperatures during tests were maintained at  $\sim 300$  K. Electron energy and current were 300 eV and 300  $\mu$ A, respectively. Comments for the various cases: (a) Sample as received; no system bakeout. (b) Sample previously heated up to 1000 K for 5 min and exposed to 1000 eV electron impact; these previous  $e^-$  tests yielded  $\sim 10^{-4}$   $\text{CH}_4/e^-$ . Current results were obtained after sample exposure to atmosphere for 16 months and subsequent system bakeout for 24h at 450 K. (c)-(i)  $\blacksquare$   $\blacktriangle$  Hydrogen and methane desorption due to  $e^-$  impact test performed after 24h system bakeout at 450 K.  $\square$   $\triangle$  Results obtained after further sample heating for 30 min at 750 K. \*Coating processes: (PS) Plasma sprayed; (SIP) sputter ion plated; (PAVD) plasma activated vapor deposition.

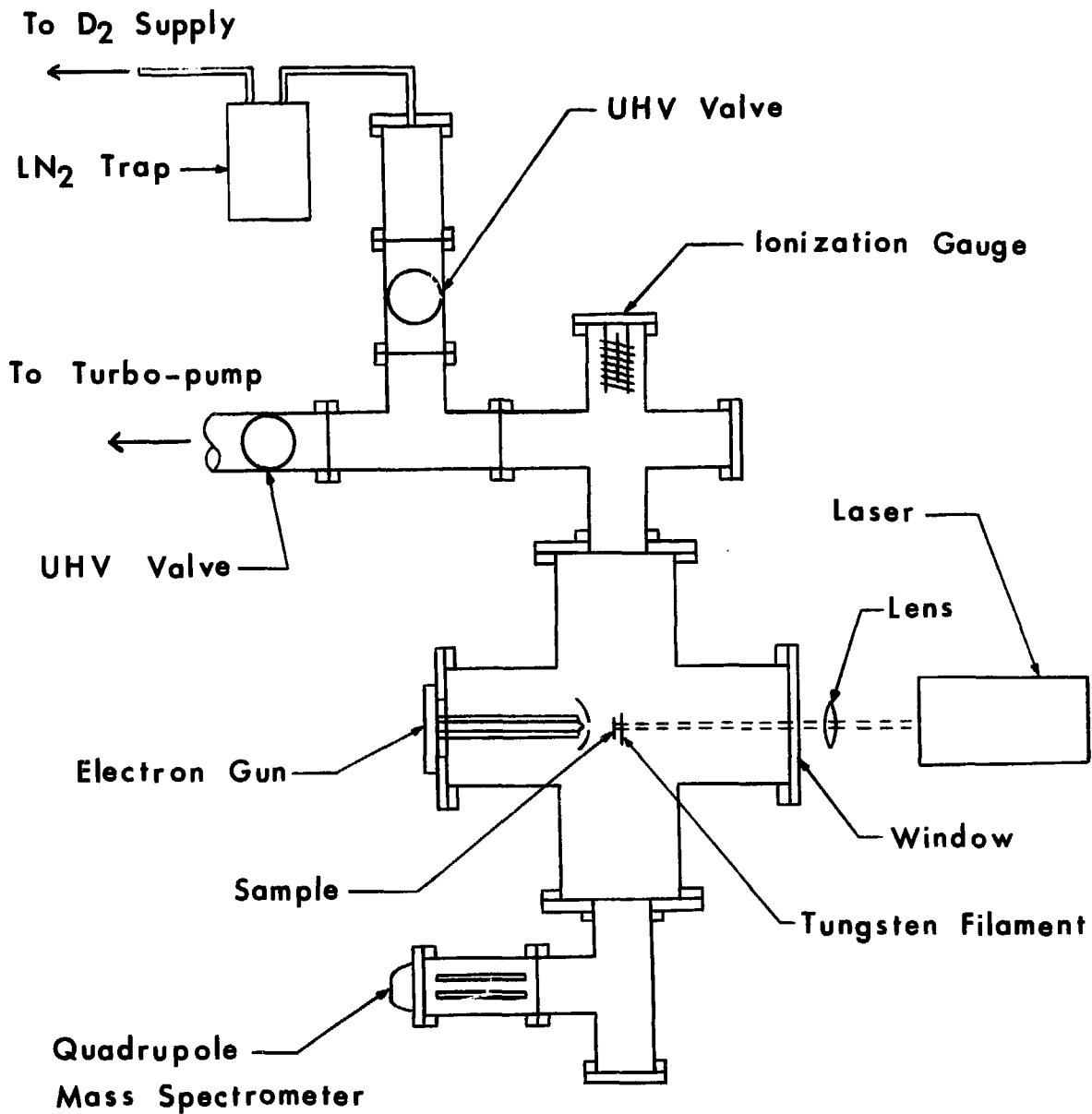


FIG. 2 Schematic of the apparatus for laser release analysis experiments.



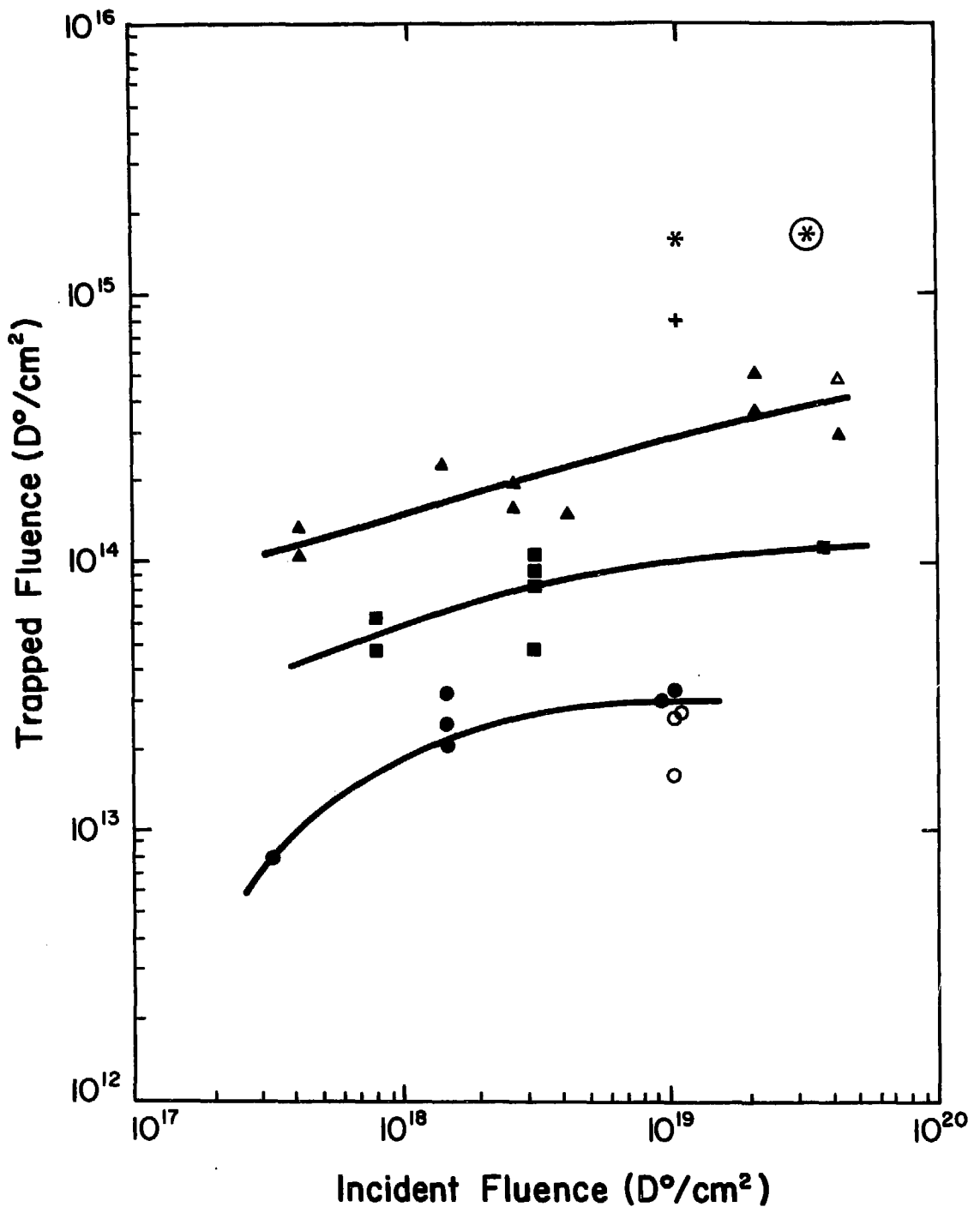


FIG. 3 Experimental retention values of sub-eV atomic deuterium in graphite. The results from LRA experiments are: ● single crystal graphite,  $\theta_w < 0.01$ ; ■ single crystal graphite,  $\theta_w \sim 0.5$ ; ▲ single crystal graphite,  $\theta_w \sim 10$ ; + pyrolytic graphite, one laser shot. Some of the scatter in the LRA results may be due to the use of several different samples. The NRA results are: ○ single crystal graphite,  $\theta_w < 0.01$ ; ▲ single crystal graphite,  $\theta_w \sim 10$ ; \* pyrolytic graphite, present experiment; ⊛ pyrolytic graphite, from Stangeby et al [12].

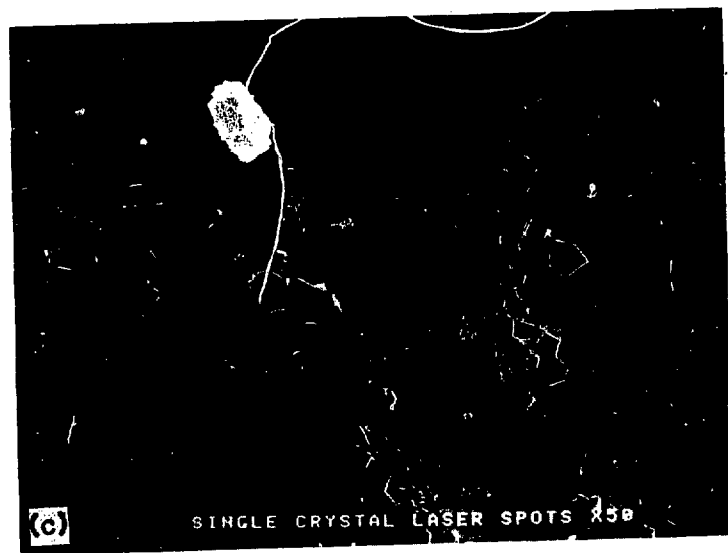
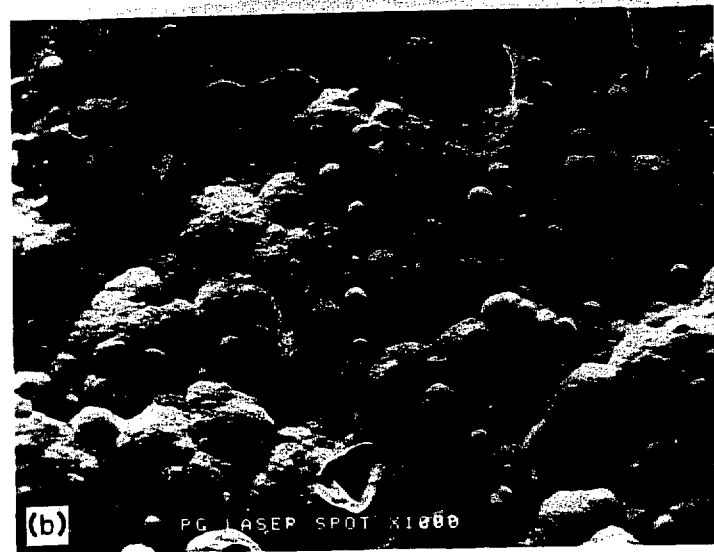
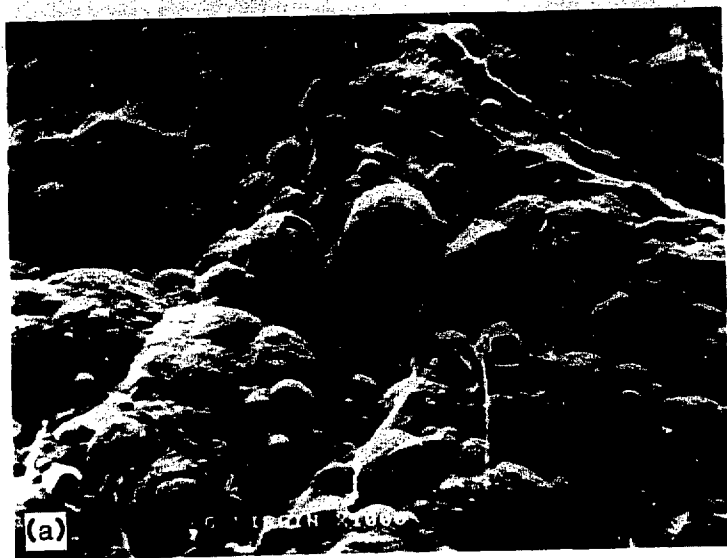


FIG. 4 SEM photographs of the graphite samples studied with LRA. The scale is shown by dashes near the top of the photo; the length of the rightmost line represents  $100\ \mu\text{m}$  if it is preceded by 3 dashes or  $10\ \mu\text{m}$  if it is preceded by 2 dashes.

- (a) Unirradiated pyrolytic graphite surface ( $\times 1000$ )
- (b) Laser irradiated pyrolytic graphite surface ( $\times 1000$ ); some rounding of sharp edges is evident
- (c) Large-scale photograph of the single crystal graphite surface; two laser irradiated spots are partially visible, outlined by blisters.

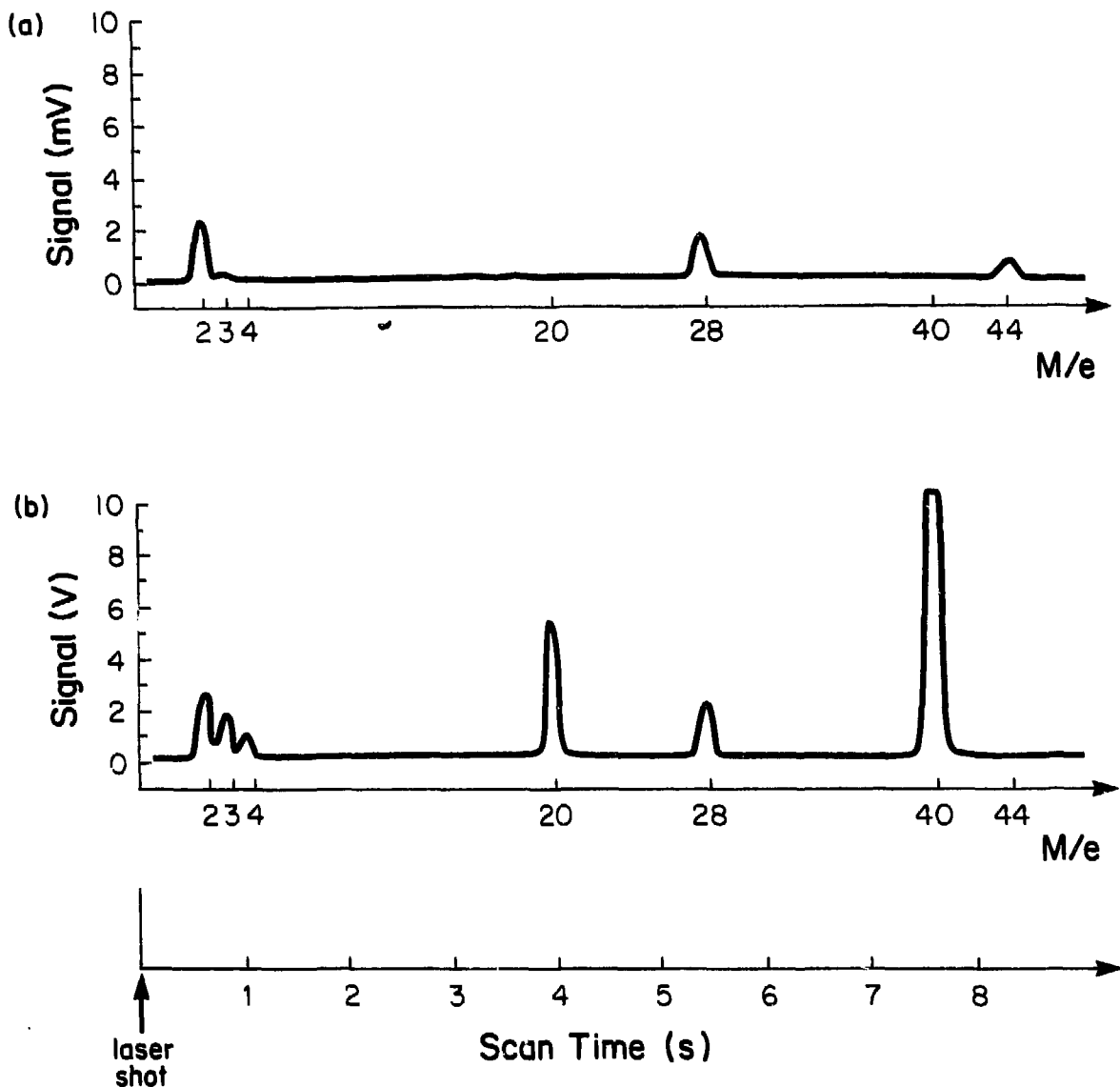


FIG. 5 Example of laser induced release spectrum for TiC-SIP before any exposure to  $D^0$  atoms. (a) Base spectrum in the isolated target chamber, and (b) spectrum immediately following laser shot.

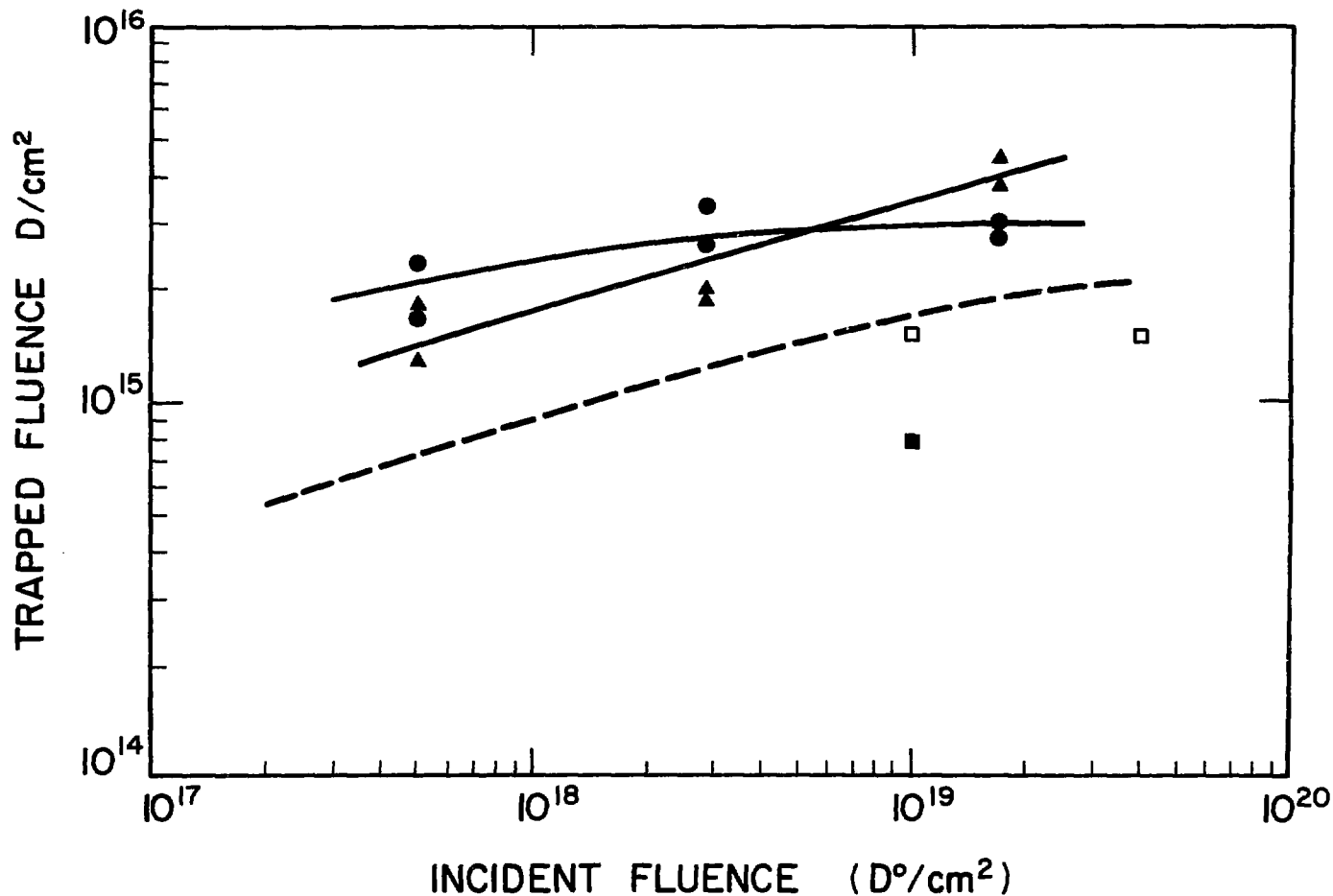


FIG. 6 Experimental retention values of sub-eV  $D^0$ : Results from the present study: ● JET-Si-PS and ▲ JET-TiC-SIP. Previous results on pyrolytic graphite: ■ as measured by LRA (one laser shot only);<sup>14</sup> □ as measured by NRA,<sup>14,18</sup> and --- as measured by resistively heated thermal desorption.<sup>18</sup>

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Haasz, A. A., Davis, J. W., Auciello, O., Stangeby, P. C.

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2. Low-Z coatings
3. Atomic hydrogen
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5. Electron-desorption

I. Haasz, A. A., Davis, J. W., Auciello, O., Stangeby, P. C. II. UTIAS Report No. 303

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