CLM-P228

CLM-P228

United Kingdom Atomic Energy Authority

RESEARCH GROUP

Preprint

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1970

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(To be submitted for publication in Journal of Vacuum Science and Technology)

A B S T R A C T

The efficiency of glow discharges in He, Ne and Ar for the removal of H_2O, CO and CO_2 from the surfaces of vacuum systems has been demonstrated. However, re-emission of the rare gas and of hydrogen atoms trapped in the surface during the discharge cause the total outgassing rate not to be significantly reduced. In general, as the pressure of the discharge increases the efficiency of cleaning decreases, and this has been correlated with a decrease in the number of energetic ions hitting the surfaces.

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March, 1970

C O N T E N T S

Introduction

The slow desorption of adsorbed gases from the surfaces of vacuum vessels usually necessitates baking to high temperatures to produce ultra-high vacuum, and this severely limits the materials and techniques which can be used. The main outgassing species of unbaked surfaces is normally water vapour with lesser quantities of CO and CO_2, and it has been shown (Barton and Govier[1]) that there appears to be no cleaning process in atmosphere which can remove them.

Adsorbed gas on walls can also be a serious disadvantage in plasma physics experiments where ultra high vacuum is not necessarily required but where particle bombardment can desorb the adsorbed species and contaminate the plasma. This problem can frequently be overcome by "conditioning" i.e. running the discharge until the contamination is removed (e.g. Lewin[2]). The "conditioning" process suggests a method of removing adsorbed gas and allowing better vacua to be obtained without baking. The cleaning of glass by glow discharges has been investigated by Holland[3] and is used regularly in the cleaning of substrates for the deposition of thin films[4]. Isler and Bullis[5] have measured the energy deposition in the surface and have shown that for a given discharge current, the lower the pressure of the discharge and the smaller the electrode dimensions, the larger is the energy deposition. However, the physical mechanisms for these effects are still not clear.

The clean up, or pumping, of gases in a discharge has been known for many years, and a summary of early experimental data was given by Brodetsky and Hodgson[6]. Later work has been described by Vanderslice[7]. A number of mechanisms are responsible for pumping including ion trapping in surfaces, the formation of atomic species

and radicals which increase the probability of chemical reactions and gettering, and the burial of thermal atoms by sputtered metal. However, most investigations of gas clean up have been concerned with the principal gas which formed the discharge. In order to clean up adsorbed gas it is probably necessary to desorb it by energetic particle bombardment. It would be very difficult to maintain such bombardment over all surfaces of a practical vacuum system using ion or electron beams. On the other hand a glow discharge tends to spread in such a way that all surfaces do get fairly uniform bombardment. In the present paper we discuss the effect of glow discharges in rare gases on the outgassing behaviour of stainless steel.

I Experimental

The experiments have been carried out in a cylindrical stainless steel (EN58B/AISI321) discharge tube 15·7 cm diam × 75 cm long, with an axial stainless steel electrode (Fig.1). This tube is pumped by a turbomolecular pump when it is being initially evacuated and also during the discharge. After the discharge when the sample tube has been evacuated to less than 10^{-6} Torr the outgassing from the tube is measured with a 60^{o} sector magnetic mass spectrometer. This minimizes the contamination of the mass spectrometer and helps to maintain a low background. The whole system is bakeable.

The gas inlet system was designed for removal of the desorbed gas species using continuous gas flow. This puts stringent conditions on the purity of the discharge gas used. After the discharge ends the time taken to pump away the discharge gas will allow re-contamination of the surfaces. A water vapour impurity concentration < 0·001% is necessary to keep contamination down to ~ 0·1% monolayer under typical conditions. This is achieved with a pre-evacuated inlet

line and a liquid nitrogen cooled trap. The purity is checked directly with the mass spectrometer.

The discharge tube and mass spectrometer were first baked under vacuum to 450°C for 20 hours to remove as far as possible the effects of dissolved gas in the metal. The experiments were carried out by exposing the sample to atmosphere for a fixed time, re-evacuating and then measuring the outgassing rate of all gas species as a function of time.

II Results

Without any discharge it was found that the outgassing rates of the principal gas species were reproducible to within a factor 2 on successive runs, and typical results are shown in Fig.2(a). The effect of the discharge was then determined by following the identical procedure except that after evacuation to 10^{-7} Torr a rare gas was introduced to a pressure of 10^{-2} to 10^{-1} Torr, and a glow discharge produced between the centre electrode and the vacuum wall. The conditions of the discharge in the geometry used were an applied potential of 400-600 V and a discharge current of 0·5 A. In the majority of experiments an ac discharge was used although no difference in the effects produced were observed using dc. The discharge was normally operated dynamically pumped, with a gas flow rate of 10^{-2} to 10^{-1} Torr litres/sec. However, the outgassing behaviour observed after a discharge in a static system was the same as the dynamic indicating that the adsorbed gas removed from the wall is permanently trapped within the discharge tube itself.

After the discharge the rare gas was pumped away and the outgassing rate was measured as a function of time as before. The results obtained for helium, neon and argon under the best conditions for

clean up are shown in Figs.2(b), 2(c) and 2(d). It is seen that a very marked reduction in the three original outgassing components is observed while in all cases there is a considerable increase in the hydrogen outgassing rate and the appearance of the discharge gas in the outgassing spectrum. Thermal effects due to heating of the tube during the discharge were shown to be negligible by water cooling the tube in some experiments.

The pressure maintained during the discharge was found to have a marked effect on the efficiency with which the adsorbed gases were removed. In general the higher the pressure the less effective was the cleaning. The outgassing observed after a discharge in argon at 100 mTorr is shown in Fig.2(e) and this can be compared with the effect of a similar discharge at 25 mTorr shown in Fig.2(d).

To illustrate the pressure dependency the effectiveness of the discharge cleaning has been measured arbitrarily from the quantity of water vapour desorbed in the 20 hours immediately following the discharge, obtained by integration of the outgassing rate over time. The discharges were maintained for the same length of time and with the same discharge current in all cases. The applied potential varied with pressure and with the gas used within the range 400-600 V. The results, shown in Fig.3, indicate that all three gases can clean effectively if a suitable pressure is chosen. As expected, argon with a lower ionization potential can maintain a discharge at lower pressures than the other two gases, but at pressures above 150 mTorr in argon sparking occurs and the discharge is unstable.

The variation of the effectiveness of cleaning with discharge time was measured in a similar way. With a current density of 100 $\mu A/cm^{-2}$ the minimum time for effective cleaning at optimum

pressure was about 15 minutes for all three gases. Runs with current densities up to 1 mA/cm^{-2} had shorter cleaning times indicating, as expected, that the total ion dose to the surface was the important factor. The dose required was $\sim 10^{18}$ $ions/cm^{-2}$. It was, however, difficult to maintain the higher current densities without serious heating of the electrode and a tendency to arc.

III Energy Distribution of Ions

The variation in cleaning efficiency with discharge pressure was interpreted as being due to the variation of energy of ions hitting the walls with pressure, because of variation in the mean free path and the width of the cathode dark space. Direct measurements of the ion energy distribution were therefore made by sampling ions through a hole 0·23 mm diam in a section of the wall in the middle of the tube thinned down to 0·05 mm. Measurements were made with a Faraday cup using a retarding potential technique, and with a 67^{0} radial electric field energy analyser.

The results from the Faraday cup measurements, Fig.4, showed that the total current at low pressures approached about half the value of $4{\cdot}8 \times 10^{-8}$ A estimated from the total discharge current. As the pressure increases the total current collected decreases. No simple explanation can be put forward for this effect but the results are in quite good agreement with those of Brewer and Miller[8] taken in glow discharges in helium and argon with plane parallel electrodes. Retarding field measurements were also made with the Faraday cup and the results (Fig.4) show that the number of ions with higher energies decrease even more rapidly with increasing pressure than the total current.

The lower number of energetic ions at high pressures explains qualitatively the reduction in cleaning efficiency. There are, however, inconsistencies. In neon, for example, at 200 mTorr the total current has dropped to 7% of the value at 30 mTorr and the current of ions greater than 100 eV energy to less than 2%, whereas the cleaning efficiency from Fig.3 is as effective as at low pressures.

The energy distributions measured with the radial field analyser are shown in Fig.5. At low pressures, Fig.5(b) there is a well defined energy peak confirming that the ions reaching the wall are accelerated by the cathode fall, and at higher pressure, Fig.5(a), the number of ions in this peak drops drastically. The results are consistent with the integrated current measurements made with the Faraday cup.

IV Discussion

Although the principal adsorbed gas species are removed by the discharge the increase in the outgassing of the hydrogen and the appearance of the discharge gas are such that the total outgassing rates observed are not very much different from the case with no discharge. Because of the change in composition of the outgassing species the total pressure in the system can be as much as a factor 4 less, due to the higher pumping speed for light gases (assuming conductance limited pumping). The results are summarized in Table I, outgassing rates and pressures having been corrected for gauge sensitivity.

The re-emission of the discharge gas from the surfaces after the discharge can readily be explained in terms of ion trapping. The trapping efficiency for argon and neon, for the energies observed, have been experimentally shown to be $\sim 0{\cdot}1$ in many metals (cf.

TABLE I

OUTGASSING RATE OF DIFFERENT GAS SPECIES

20 HOURS AFTER DISCHARGE CLEANING (10^{-10} Torr/litre/sec^{-1}/cm^{-2})

	No Discharge	He Discharge	Ne Discharge	Ar Discharge
Rare Gas	-	1·4	0·02	0·03
H_2O	0·87	-	-	-
CO_2	0·09	-	-	-
CO	0·06	-	-	-
H_2	0·25	0·6	0·83	1·5
Total	1·3	2·0	0·9	1·5
Total Pressure (10^{-8} Torr)	3·1	2·3	0·8	1·4

Carter and Colligon[9]), and the trapping efficiency for helium is probably higher. Thus during the discharge the concentration of these ions will build up in the surface, to be slowly released into the vacuum when the vessel is re-evacuated. The fact that the release rate after the discharge, for a given gas, is constant, independent of pressure or discharge time, indicates that saturation has been reached. This is to be expected since the total ion dose is $\sim 10^{18}$ ions/cm^{-2} whereas Kornelsen[10] has shown that for argon ions saturation begins at $\sim 10^{15}$ ions/cm^2.

The hydrogen re-emission has been observed to be almost independent of discharge gas provided efficient clean up has taken place, but to be lower the less efficient the clean up process is. This supports the obvious hypothesis that the hydrogen is produced by break-up of

the water molecule. Hydrogen ions produced would be accelerated into the wall and trapped, to desorb slowly later. The oxygen ions or atoms are likely to be chemically gettered and permanently bound to the metal surface since with the ion energies observed a considerable number of freshly sputtered atoms will be produced.

Since hydrogen and the rare gas are the two main outgassing components after all discharges, one way of reducing outgassing which suggested itself was to run the discharge in hydrogen. When this was done, however, no clean up of water vapour at all was observed. A discharge was then tried in deuterium (Fig.6) to see whether break-up in the water molecule occurred. Again no clean-up of water vapour was observed and in fact a major constituent was now D_2O. This could be produced by the break-up of H_2O followed by the reaction of the oxygen with deuterium since it has been shown (Morruzi and Phelps[11]) that the reaction

$$O^- + H_2 \rightarrow H_2O + e^-$$

has a high cross section, ($\sim 10^{-13}$ cm^{-2}). On the other hand the D_2O could have been formed independently of the H_2O by reactions with metal oxides on the surface in a similar way to that observed by Blauth and Meyer[12] on glass surfaces.

V Cleaning In Other Geometries

It was of interest to see whether discharge cleaning would be effective in more complex geometries than a straight tube. A first test was to shorten the centre electrode to 10 cm and repeat the cleaning experiments. This gave very similar cleaning results and the ion energy distributions were also similar.

A crosspiece 15·7 cm bore with two arms 27 cm long and two arms 18 cm long was then set up. Electrodes 10 cm long were mounted in the

ends of the two long arms and one short arm. A 30 minute discharge using one electrode had only a very slight cleaning effect in this system, but two 15 minute discharges run one hour apart were better (Fig.7). Two 60 minute discharges four hours apart using all electrodes were sufficient to clean the crosspiece as efficiently as the simple tube.

The slow rise in the water vapour outgassing rate after an inadequate discharge cleaning (Fig.2(e) and Fig.7) might be explained by only part of the tube being properly cleaned. These clean areas would pump gas from the less well cleaned parts, causing the total gas released from the tube to be low, until they became partially re-contaminated. Then their sticking coefficients would decrease so that the net gas flow from the tube increases again. This is consistent with the results obtained with two 15 minute discharges one hour apart. During the period between the discharges the clean surfaces pump those not reached by the discharge and are then re-cleaned themselves during the second discharge. Thus it should be possible to clean complex structures provided the area not exposed to the discharge is a small fraction of the total area.

VI Conclusions

Effective removal of adsorbed gases from vacuum surfaces can be achieved by running a rare gas glow discharge in the system provided the surfaces receive a sufficient dose of energetic ions. The mechanism of removal appears to be the break-up of the adsorbed gas molecules, followed in the case of water by burial of the hydrogen ions in the wall. The fate of the oxygen atoms is not clear, but the most obvious explanation is that they are chemically bound to the surface metal atoms.

The result of the discharge, however, is to bury the rare gas ions and the hydrogen ions in the wall of the vessel, so that after the discharge is over these gases slowly desorb. As a consequence the total outgassing rate is not reduced very much although the composition of the gas released is radically altered. This could have advantages in vacuum systems where an inert or reducing atmosphere is required, or in cases where the atomic number of the residual gases are important.

Although the glow discharge has the effect of allowing a relatively high current density to be achieved over a large surface area it is difficult to attain effective cleaning except in fairly simple geometries.

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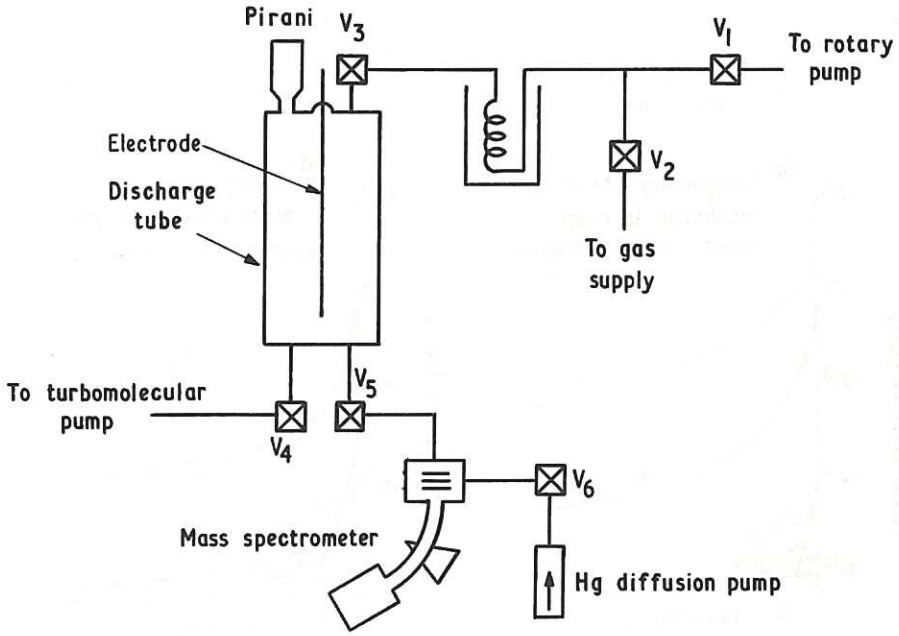

Fig.1 Schematic diagram of experimental apparatus.

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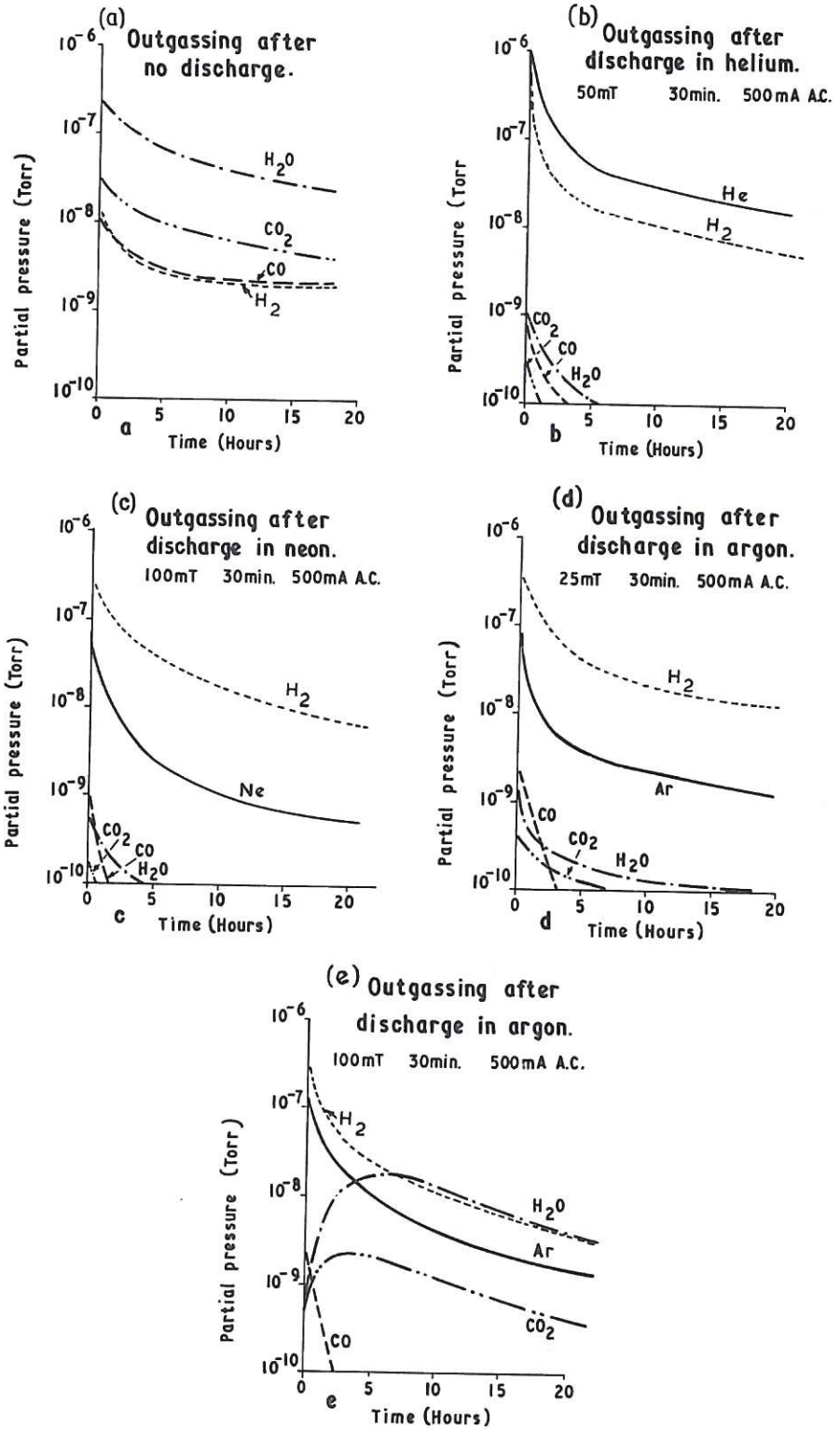

Fig.2 System partial pressures measured as a function of time immediately after discharge cleaning. Pumping speed 13litre/sec for nitrogen.

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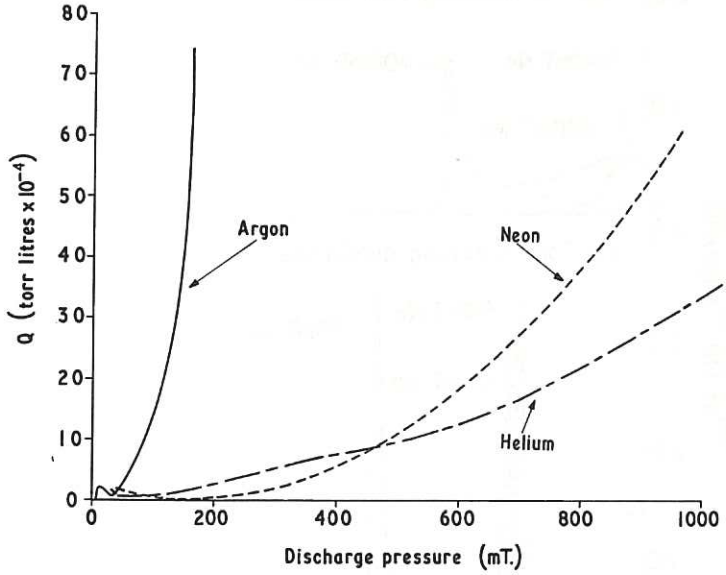

Fig.3 The effect of discharge cleaning for 30mins at 500mA ac as a function of discharge pressure. The effect of the discharge is arbitrarily measured in terms of the amount of water vapour Q which is released in 20 hours immediately after the discharge.

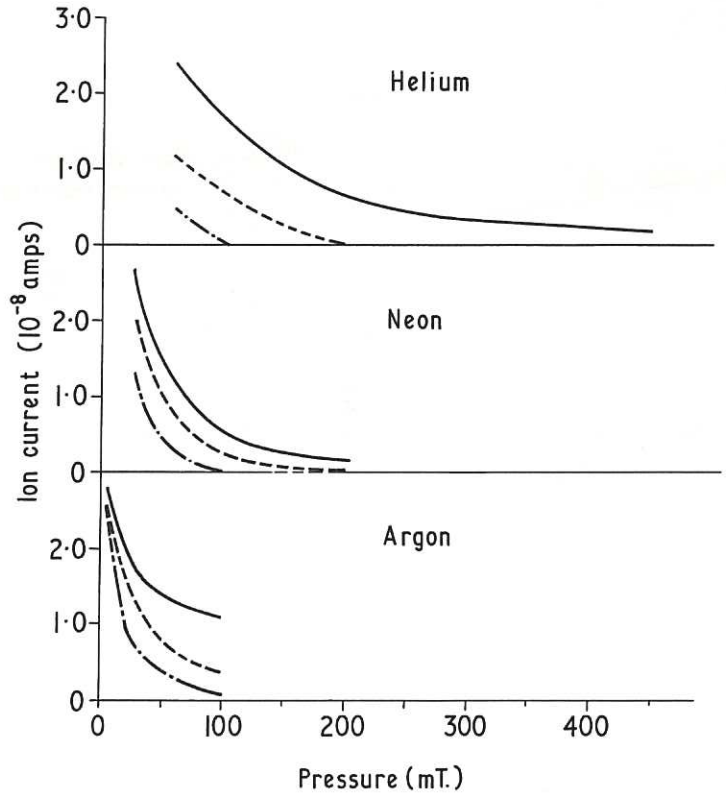

Fig.4 Integral measurements of ion current reaching the walls of the discharge tube, measured with a Faraday amp.

——— 0 retarding V
--------- + 100 retarding V
- - - - - + 200 retarding V

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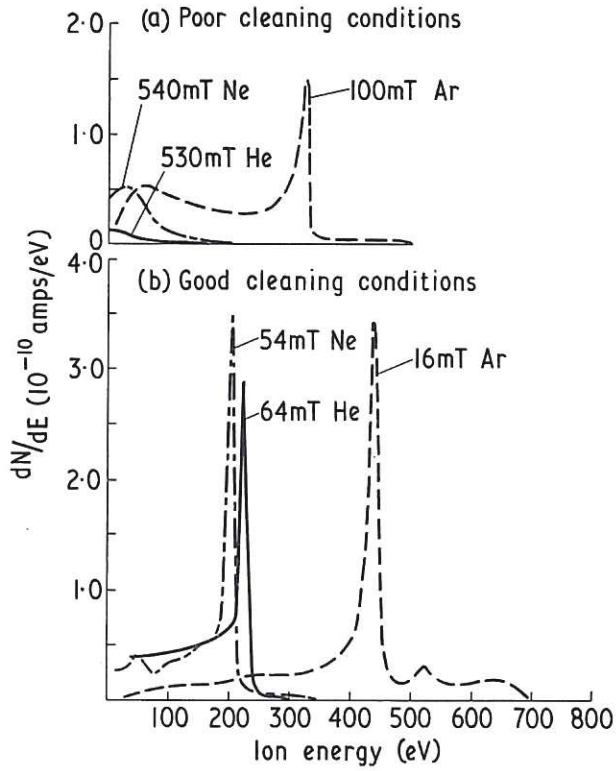

Fig.5 Energy distribution of the ions reaching the walls of the discharge tube under various cleaning conditions.

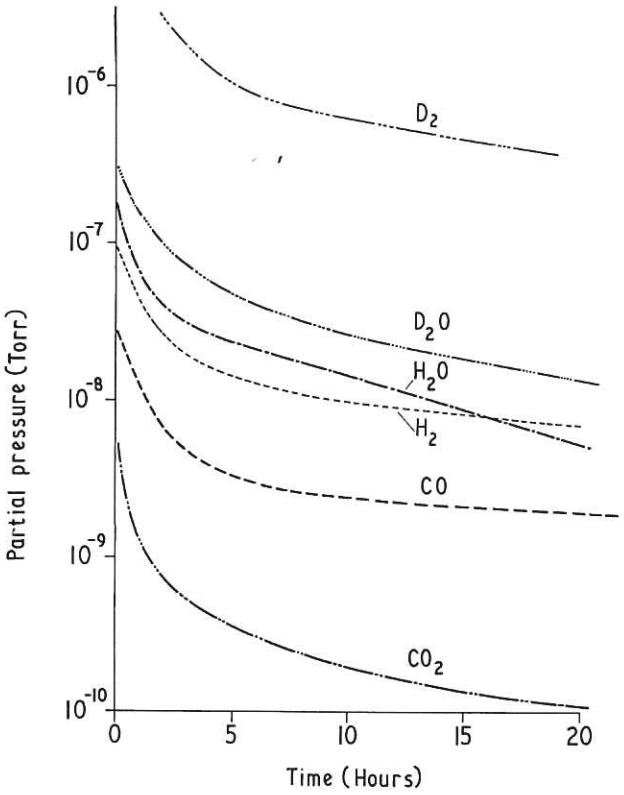

Fig.6 System partial pressures after a 30 min. discharge in deuterium at 35mTorr and 500mA ac. Pumping speed 13 litre/sec for nitrogen.

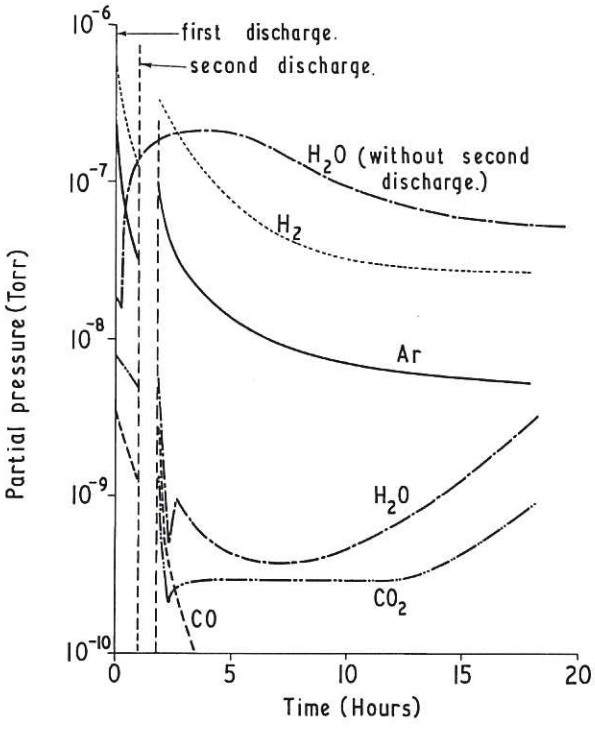

Fig.7 System partial pressures after two 15 min discharges in a cross piece with argon at 10mTorr and 500mA dc.

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