IN SITU THERMOGRAVIMETRY - A TOOL FOR QUANTITATIVE STUDY OF PLASMA-SURFACE INTERACTION

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Keywords: Thermogravimetry, Kinetics

Compounds: Silicon, Carbon

ABSTRACT

An apparatus enabling a continuous measurement of weight changes of a sample immersed into the positive column of a glow discharge will be described. Erosion and deposition rates less than 0.01 monolayer per sec. can be quantitatively followed in a running discharge. Examples of the application of this method to the study of plasma-materials interaction and of the chemical vapour deposition will be presented.

1. INTRODUCTION

The kinetic studies of the reactions between solids and gases are usually performed either by monitoring the mass changes of the sample (e.g. weight; geometrical or optical thickness [1]; resistivity [2]; and others) or by measuring the gaseous reaction products.

Modulated molecular beam mass spectrometry [3, 4] represents the most sophisticated recent development of the latter approach. In principle it allows the elucidation of the mechanism of a reaction $aA(s)+bB(g) \rightarrow A_aB_b(g)$ in terms of reaction probabilities, relaxation times and activation energies. As pointed out by Olander [3] this method has some serious limitations, such as a complicated and expensive instrumentation, limited sensitivity allowing the study of only reactions with reaction probabilities larger or equal to 10^{-4}, and limited primary beam fluxes of less than about 10^{17} particles per cm^2 sec.

The in situ thermogravimetric method described in the present paper uses much cheaper equipment, it can operate with a high sensitivity in a wide pressure range covering the whole spectrum of low pressure plasmas. For example, at a pressure of 0.1 torr reaction probabilities as low as 10^{-7} can be measured. Another obvious advantage of thermogravimetry is the possibility to study the chemical evaporation, $aA(s)+bB(g) \rightarrow A_aB_b(g)$, as well as the deposition $C(g)+D(g) \rightarrow A(s)+B(g)$, and reactions yielding solid products such as nitriding, oxidation, carburization and others.

However, by this method one measures only the overall reaction rates without any possibility of time resolution within the scale of relaxation times of the elementary processes involved. Thus one obtains the overall reaction rates and their dependence on various plasma parameters, but only indirect information on the reaction mechanism.

Quartz-crystal-oscillator-microbalances commonly used in thin film technology for monitoring the thickness of deposited films or for measuring the etching rates (e.g. [5]) possess a very high sensitivity, but their application is limited to a rather narrow temperature range and thin films only.

In contrast, the microbalance used in the present study can handle bulk samples of a total weight up to $\sim$1 g which opens up the way for their additional characterisation by a number of chemical and physical methods. Although the sensitivity of such a microbalance is less than that of the quartz-crystal types, one can - as will be shown below - measure etching or deposition rates as low as ~ 0.01 Å s^{-1} which is more than sufficient for any reactions of preparative and/or technological interests.

2. DESCRIPTION OF THE APPARATUS

There are several types of commercially available microbalances with a sensitivity of 0.1μg which satisfy requirements for operation in high vacuum. We have used an electrically compensated microbalance Cahn-model RG (manufactured in 1966) which was made available to us. Critical for operation of such a microbalance is a constant environmental temperature, mechanical stability of the apparatus and a sufficiently low RF noise. When used for in situ thermogravimetry in the low pressure plasmas it is, in addition, necessary, to provide an adequate stability of the discharge and avoid any ignition of a discharge towards the microbalance itself.

The apparatus is schematically shown in Fig. 1. The microbalance, B, is mounted in a glass vacuum vessel G, which is connected to a quartz discharge tube, Q (i.d. 4.6 cm) and evacuated through a pumping line, P. A mercury diffusion pump with two cold traps in series provide an oil free vacuum of 1×10^{-6} torr. The vacuum vessel G and the electronic unit of the microbalance are housed in a thermostatized screening box D. The output of the electronic unit is connected to a recorder via a very stable chopped amplifier (drift $\lesssim 0.05\,\mu$V per 1°C, recorder range either 1 or 10 mV). To avoid electrostatic charging of the glass housing several sources of α-radiation (americium 241, see α's in Fig. 1) are inserted into the discharge tube, and into the counter weight housing, CW.

In order to maintain a stable DC discharge several precautions were necessary. First of all the whole high voltage circuit including the power supply (4 kV, 4 A), stabilizing resistors, R, and all auxiliary equipment has been carefully insulated with respect to the ground ($> 10^{8}\,\Omega$). Any spurious electric current and oscillations which might develop with respect to the ground were successfully blocked by a permanent magnet, M. The resulting stray magnetic field which would disturb the microbalance was screened by thick iron sheets, E which also served as a heat shield. In addition, the glass tube between the magnet and the microbalance housing was thermostatized (not shown in Fig. 1).

The discharge took place between a cathode, C, and an anode, A, both fixed on metallic flanges. It is well known that the cathode fall of a glow discharge is the source, or an amplification region of many kinds of plasma instabilities. Therefore a thermionic cathode, F_2, (thoriated tungsten) placed into the axis of a nickel cylinder was used. The total voltage applied across the discharge tube of a total length of about 160 cm was only 200-500 V for discharge currents up to 300 mA (hydrogen, 0.1 to 2 torr).

The sample, S, was hanging on a thin quartz fibre, F_1 in the positive column of the glow discharge. The distance from both electrodes (about 80 cm) was sufficient to avoid their influence on the plasma parameters.

H_1 and H_2 (see Fig. 1) denotes auxiliary heating or cooling equipment which allow the control of the temperature of the sample, H_1, or - in the case of the deposition study - of the charge zone, H_2, independent of the discharge current. The temperature was measured with thermometers immersed into the plasma (e.g. T, Fig. 1), and covered with the same material as the sample under study to avoid errors of the measurement due to differences in the catalytic heating of the surfaces (see e.g. [6]).

3. OPERATIONAL PERFORMANCE

Figure 2a illustrates the long term stability of the apparatus without the glow discharge on. One notices that the noise and drift is less than 0.1 μg in 10 hours. Figure 2b shows a typical recorder trace during measurement of the erosion of pyrolytic graphite in a hydrogen plasma at 0.04 torr. The observed noise enhancement of about 0.5 μg (to be compared with Fig. 2a) is due to not completely damped plasma instabilities. The weight difference corresponding to the full scale of the recorder is given by the variable setting of the sensitivity of the microbalance. At any setting, a total weight change of 200 mg can be measured by means of a calibrated compensation circuit. The compensation is adjusted manually when the recorder trace approaches the end of the scale. It is seen in Fig. 2b that this manipulation introduces some additional disturbance. We believe that this can be improved in the future.

Nevertheless, this example demonstrates that erosion rates of the order of $10^{-2}\,\mu$g cm^{-2} s^{-1} which are equivalent to $\sim$0.1 monolayer per sec can be reliably measured in a short term run. Except at the beginning and the end of the recorder trace, the noise is of the order of 0.1 μg but the overall stability allows an easy integration yielding the above mentioned sensitivity.

A particular problem arises from standing striations, which are found in most of the molecular gases and their mixtures at a pressure between 0.1 and several torr and a discharge current from 1 to 100 mA. Any slow movement of these striations causes periodic oscillations of the balance signal due to the electrostatic forces acting on the (negatively charged) sample by the periodically changing local value of the axial field strength. Fast moving striations which represent an even more common phenomena do not cause any significant problems since their frequency is in the kilohertz range or higher.

Figure 2c shows the erosion of silicate glass in an hydrogen plasma at $\sim$ 1 torr, discharge current of 180 mA and sample temperature of 450°C. A cold cathode has been used in this case. One notices an enhanced noise and rather aperiodic oscillations of the recorder trace which are due to the afore mentioned movement of the striations.

In spite of the problems associated with the striations, weight changes as low as $\sim$ 1 μg/hr can be measured in long term runs. The maximum sample surface which can be used without facing any significant problems related to the radial gradients of the plasma parameters is about 2 cm^2.

Thus, erosion and deposition rates as low as ~ 1.5×10^{-4} μg cm^2 s^{-1}, i.e. less than 0.01 monolayer per sec can be measured in this case.

4. EXAMPLES OF APPLICATIONS

In order to demonstrate the application of the microbalance for in situ kinetic studies we shall briefly present two examples.

Figure 3 shows the temperature dependence of the erosion rate of single crystalline silicon in an hydrogen plasma at three different discharge currents [7]. The reactivity displays a pronounced maximum at temperatures below 100°C. It has been suggested that this is due to competition between two processes, i.e. the forward reaction, $Si(s) + xH \rightarrow SiH_x(g)$, and the heterogeneous and homogeneous recombination of H-atoms. Figure 3 further shows that the chemical transport of silicon in a temperature gradient $T_1 \rightarrow T_2$ $(T_1 < T_2)$ and/or in a plasma gradient $\varepsilon_2 \rightarrow \varepsilon_1$ $(\varepsilon_2 > \varepsilon_1$ denotes the internal plasma energy which is, for example, a function of the discharge current density) should take place at significantly lower temperatures than those originally used by Veprek and Mareček [8].

This is demonstrated in Fig. 4. In this case a polycrystalline silicon charge has been introduced into the charge zone (see H_2, Fig. 1) which was kept at ~ 45°C. At this temperature the forward reaction $Si(s) + xH(g) \rightarrow SiH_x(g)$ proceeds at the charge and the gas phase gets more or less saturated with the reaction products $SiH_x(g)$, depending on the gas flow rate. By changing the sample temperature, T_s (H_1 - see Fig. 1) the sample can be either eroded (see Fig. 4, T_s = 110 and 90°C, negative sample weight changes $\Delta W/\Delta \tau$) or silicon deposition on the sample can take place due to decomposition of the SiH_x-species originally formed in the charge zone (T_s = 270°C, Fig. 4). The shaded areas indicate the scattering of the measurements from several runs.

A comparison of the erosion rates given in Fig. 3 with those in Fig. 4 shows that the rates are significantly reduced in the latter case when the gas phase is partially saturated with the reaction products from the charge. This illustrates the validity of the Le Châtelier-Brown principle for chemical equilibria under conditions of non-isothermal low pressure plasmas. Since we want to illustrate here only the application of the microbalance the reader is refered to the original paper for further details concerning this point [7].

As a second example we should like to demonstrate the application of the microbalance for a study of the reactivity changes of carbon due to radiation damage caused by bombardment with energetic ions. This study is related to the material problems arising by plasma-wall interaction in devices for controlled thermonuclear fusion (see e.g. [9]).

Figure 5 shows the dependence of the erosion rate of pyrolytic graphite annealed at 2700°C and irradiated with energetic ions on the total amount of the eroded material, i.e. on the depth. The first four points taken before the sample irradiation show the reactivity of undamaged material. After irradiation the erosion rate of the topmost surface is enhanced by an order of magnitude and it decreases when the damaged surface layer is eroded away. The enhancement of the reactivity is observed up to a depth of $\sim 30 \mu m$ which is much more than the projected range of the 2 MeV-$^4He^+$ ions which amounts $\sim 6 \mu m$. In this way one can study the depth profiles of the radiation damage and their dependence on various parameters such as the energy and dose of the primary ions, irradiation temperature, quality of the graphite used, and others [10].

The measurements indicated in Fig. 5 by solid lines were performed in an R.F. discharge in which the erosion had to be periodically interrupted, the sample removed from the discharge tube and weighed on a conventional microbalance [11]. This procedure is time consuming (e.g. several days for one curve) and the accuracy of the measurement is rather limited, particularly at high erosion rates. Using the in situ gravimetry (see broken line, Fig. 5) reduces the time requirements considerably and improves also the accuracy. The erosion rate is obtained from the slope of the recorder trace in a continuous run without exposing the sample to air.

It should be emphasized that the weight of various solids which were either eroded or deposited in the plasma can significantly change upon exposure to air due to oxidation, and/or absorption of moisture, CO_2, etc. This has been observed for some of the carbon materials and for silicon, under certain conditions for deposited amorphous phosphorus [12] and for boron [13]. For example the weight of $\sim 5 \mu m$ thick boron films deposited at 260°C increases by $\sim 280 \mu g$ within about 43/4 mins which amounts to about 10 % of the total film weight (see Fig. 6). Since such changes occur frequently within a few minutes they can escape the attention of the experimentalist and cause significant errors. In contrast they can be easily measured by means of the in situ gravimetry.

ACKNOWLEDGEMENTS

We should like to thank Professor H.R.Oswald for his generous support of this work and in particular for making the microbalance available to us. We appreciate very much also the help of Dr.M.R.Haque during the initial building of the apparatus, and the financial support by the Swiss National Science Foundation.

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FIGURE CAPTIONS

Fig. 1: Experimental apparatus for in situ thermogravimetry. The sample S is hanging on a quartz fibre F_1 in the positive column of a D.C. discharge. The fibre is attached to a microbalance B. (For details see text).

Fig. 2a: Part of a recorder trace illustrating a long term stability of the apparatus with discharge off.

Fig. 2b: Recorder trace during the erosion of pyrolytic graphite in an hydrogen plasma at 0.04 torr.

Fig. 2c: Recorder trace showing the erosion of silicate glass in an hydrogen plasma at $\sim$ 1 torr and with a cold cathode. A slow movement of the standing striations, which are present in the positive column under these conditions, causes enhanced noise and oscillations of the trace.

Fig. 3: Temperature dependence of the erosion rate of single crystalline silicon in an hydrogen plasma at 0.1 torr and discharge currents of 4, 10 and 360 mA.

Fig. 4: Example showing the transition from sample erosion, $\Delta W / \Delta \tau < 0$, towards deposition, $\Delta W / \Delta \tau > 0$ (see text).

Fig. 5: Effect of radiation damage caused by energetic He$^+$-ions on the reactivity of pyrolytic graphite with an hydrogen plasma. Solid line - R.F. discharge, broken line - D.C. discharge (see text).

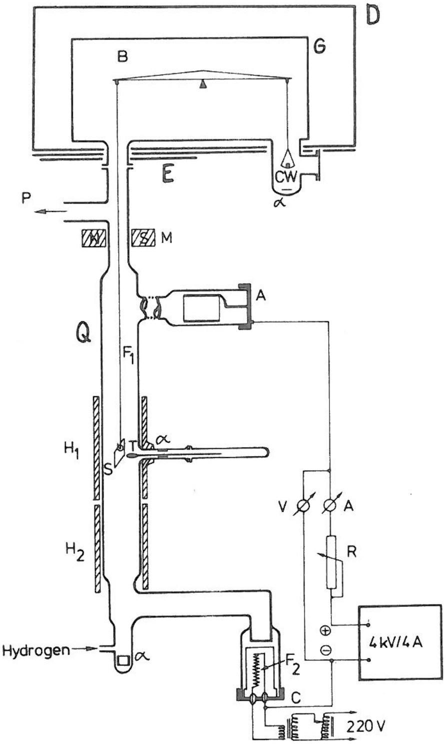

Fig. 1

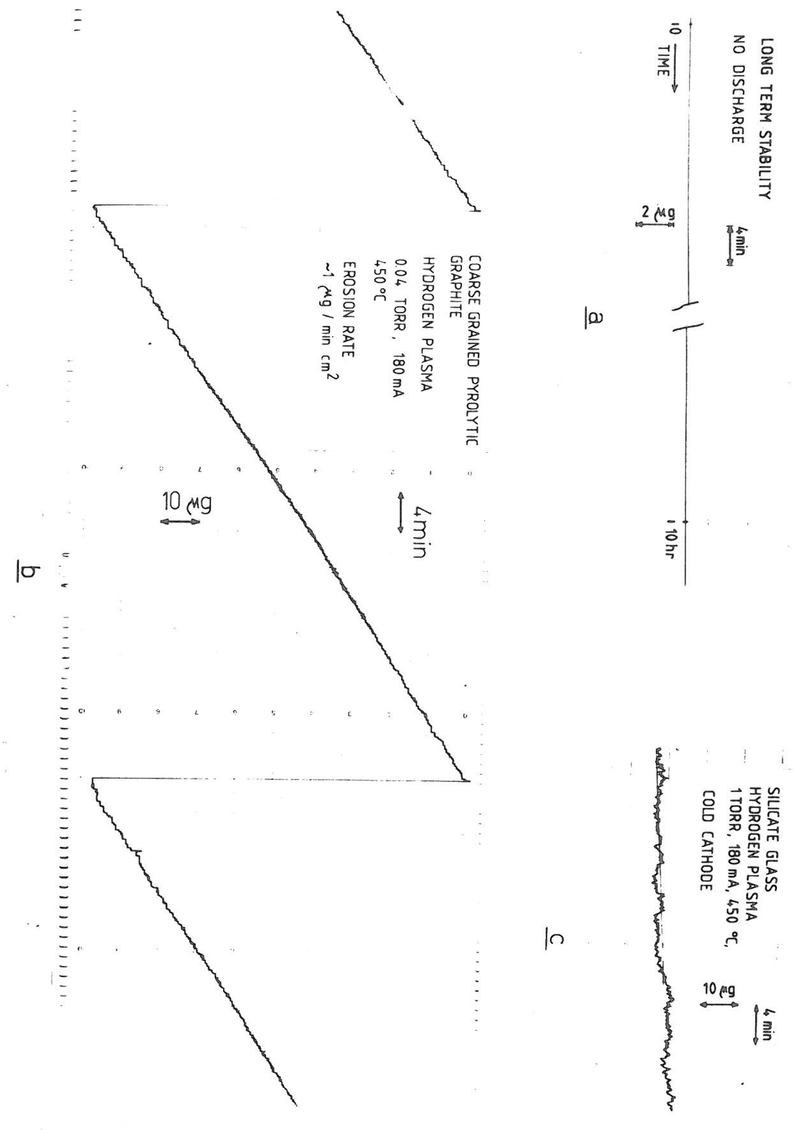
LONG TERM STABILITY
NO DISCHARGE
0
TIME
4min
2 µg
10 hr
a
COARSE GRAINED PYROLYTIC GRAPHITE
HYDROGEN PLASMA
0.04 TORR, 180 mA
450 °C
EROSION RATE
~1 µg / min cm²
4 min
10 µg
b
SILICATE GLASS
HYDROGEN PLASMA
1 TORR, 180 mA, 450 °C,
COLD CATHODE
4 min
10 µg
c

Fig. 2

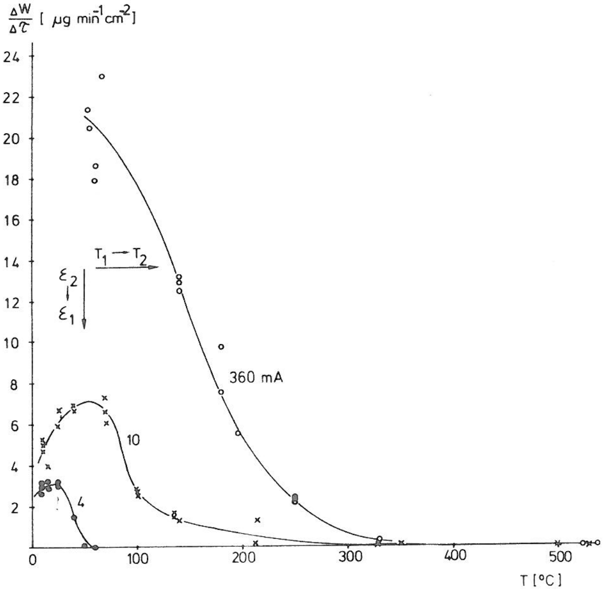
ΔW/Δτ [μg min⁻¹cm⁻²]
24
22
20
18
16
14
12
10
8
6
4
2
0
100
200
300
400
500
T [°C]
T1 → T2
ε2 → ε1
360 mA
10
4

Fig. 3

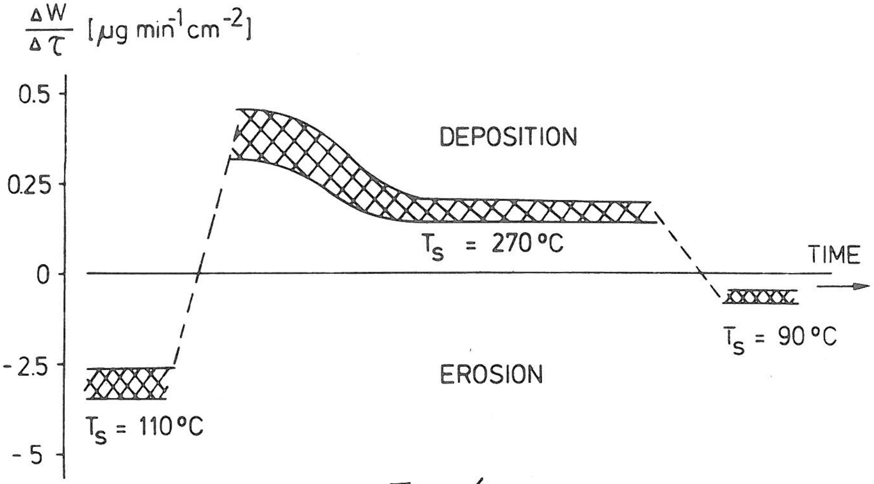
ΔW/Δτ [μg min⁻¹cm⁻²]
0.5
0.25
0
-2.5
-5
DEPOSITION
Ts = 270 °C
TIME
EROSION
Ts = 110 °C
Ts = 90 °C

Fig. 4

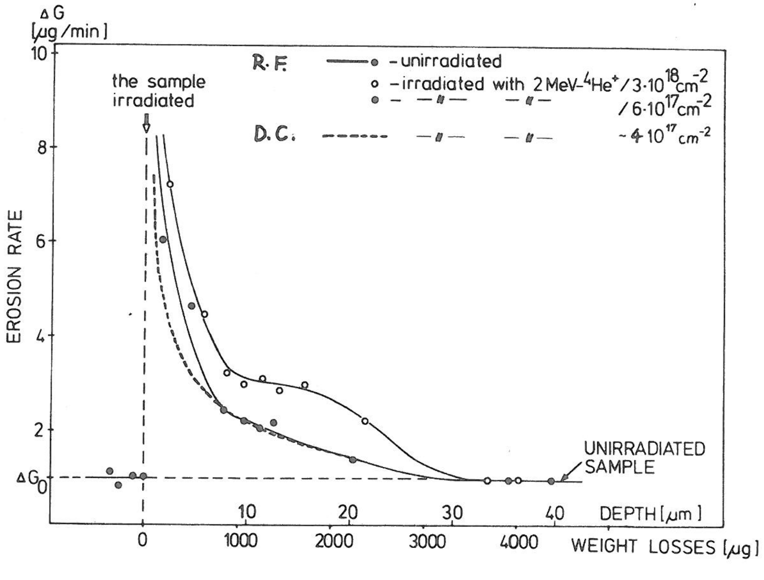
ΔG
[μg/min]
10
8
6
4
2
ΔG0
EROSION RATE
the sample irradiated
R.F.
- unirradiated
- irradiated with 2 MeV-$^4He^+$ / $3\cdot10^{18}cm^{-2}$
— " — — " —
/ $6\cdot10^{17}cm^{-2}$
D.C.
— " — — " —
~ $4\,10^{17}cm^{-2}$
UNIRRADIATED SAMPLE
10
20
30
40
DEPTH [μm]
0
1000
2000
3000
4000
WEIGHT LOSSES [μg]

Fig. 5