# PPT ($10^{-9}$mbar) Sensor for Trace Detection of Organic Contamination in Vacuum Environments

Robert B Grant, Fred Tapp Philip Pakianathan - BOC Edwards;
Richard M Lambert, David Davis, Georgios Kyriakou - Chemistry Department Cambridge University

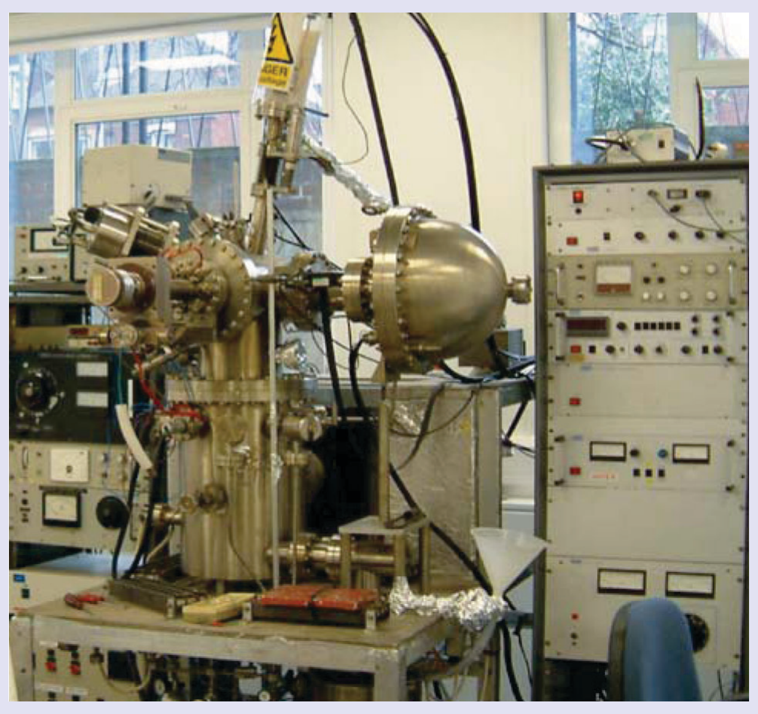
## 1 Introduction

Hydrocarbon contamination of process environments can cause detrimental effects. In particular, Multilayer Mirrors (MLMs) as used in EUV lithography are susceptible to the build up of carbonaceous material when exposed to EUV radiation in the presence of hydrocarbon contamination. Significant losses in mirror reflectivity have been observed even for ppt levels ($10^{-7}$Pascal range) of hydrocarbon contamination. Such contamination can originate from the outgassing of system components or process wafers or from the introduction of contaminated purge gases.

Conventionally, levels of total organic compounds (TOC) in vacuum and UHP process gas would be monitored using mass spectrometry or gas chromatography. Whilst these techniques have the required sensitivity, they are expensive, delicate, difficult to use and not able to operate inside the process tool at the Point of Use (PoU). What is required is a small, low cost PoU sensor that can be integrated into the process tool and qualify the process environment for active hydrocarbon contamination i.e. those species which cause reflectivity losses.

We have previously reported on activities at BOC Edwards to develop solid state electrochemical sensor technologies which will enable PoU hydrocarbon monitoring of Next Generation Lithography, NGL, process tools at sub ppt levels. In this presentation we will present further enhancements to the sensor technologies to deliver practical solutions and improvements in sensitivity as well as recent XPS results from our collaboration with Cambridge University Chemistry Department which demonstrate that the sensor technology used is indeed highly sensitive to the active (unsaturated) hydrocarbon species and relatively insensitive to the un-reactive (saturated) hydrocarbon species.

## 2 Experimental



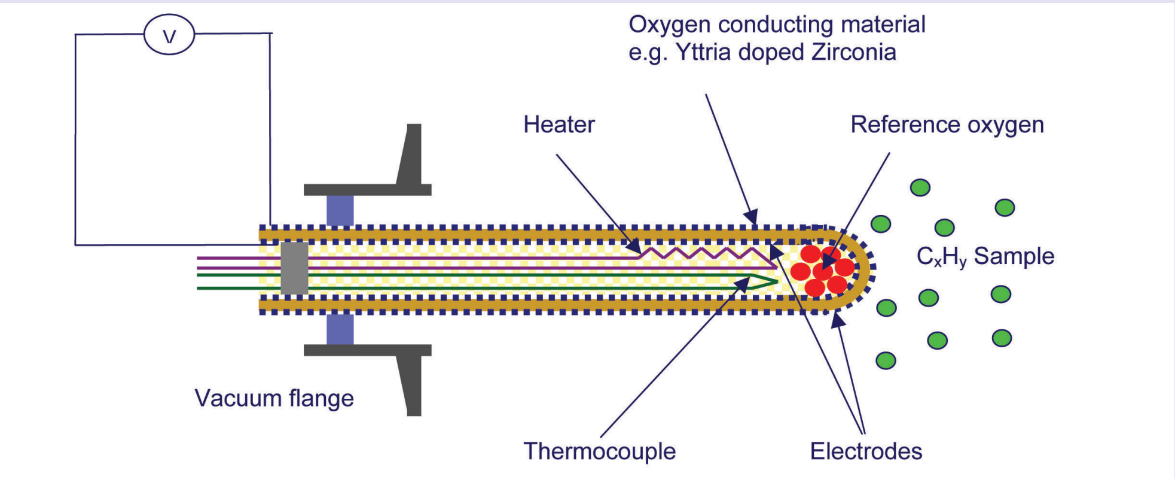
The BOC Edwards sensor test rig has been explained before ref. [1]. Surface science measurements were carried out in a UHV chamber, shown opposite, operated at a base pressure of $2x10^{-8}$ Pascal and is equipped with:-

- A VSW100 hemispherical analyzer,
- A dual (Mg/Al) X-ray source
- A VG SensorLab quadrupole mass spectrometer.

A Platinum polycrystalline model electrode could be resistively heated to 1300 K and cooled to 180 K. Initial cleaning of the sample was achieved by cycles of $Ar^+$ sputtering (Ar 99.999% Messer) (1 kV, 4 (A) followed by annealing at 1100 K for 10 min until no impurities were detected by XPS. Routine cleaning of the sample after experiment was achieved by oxygen treatment at $10^{-5}$ Pascal at 800 K followed by annealing at 1300K. XPS measurements were performed using Al K$\alpha$ radiation.

## 3 Sensor Construction

The solid state electrochemical sensor is constructed from an 8% molar Yttria Stabilised Zirconia (YSZ) oxygen anion, $O^{2-}$, electrolyte 'thimble' coated with platinum to form the electrodes. The YSZ "thimble" is mounted into a vacuum flange and sealed using a glass seal (He leak rate $<10^{-9}$ mbar l $s^{-1}$) and utilises an atmospheric oxygen reference environment. The sensor is temperature controlled at 630° C using a conventional thermal controller and a nichrome wound heater assembly. A Keithly source meter, model 2400, was connected to the cell to allow control of the cell current with simultaneous voltage measurement.



## 4 Sensor - Principle of Operation

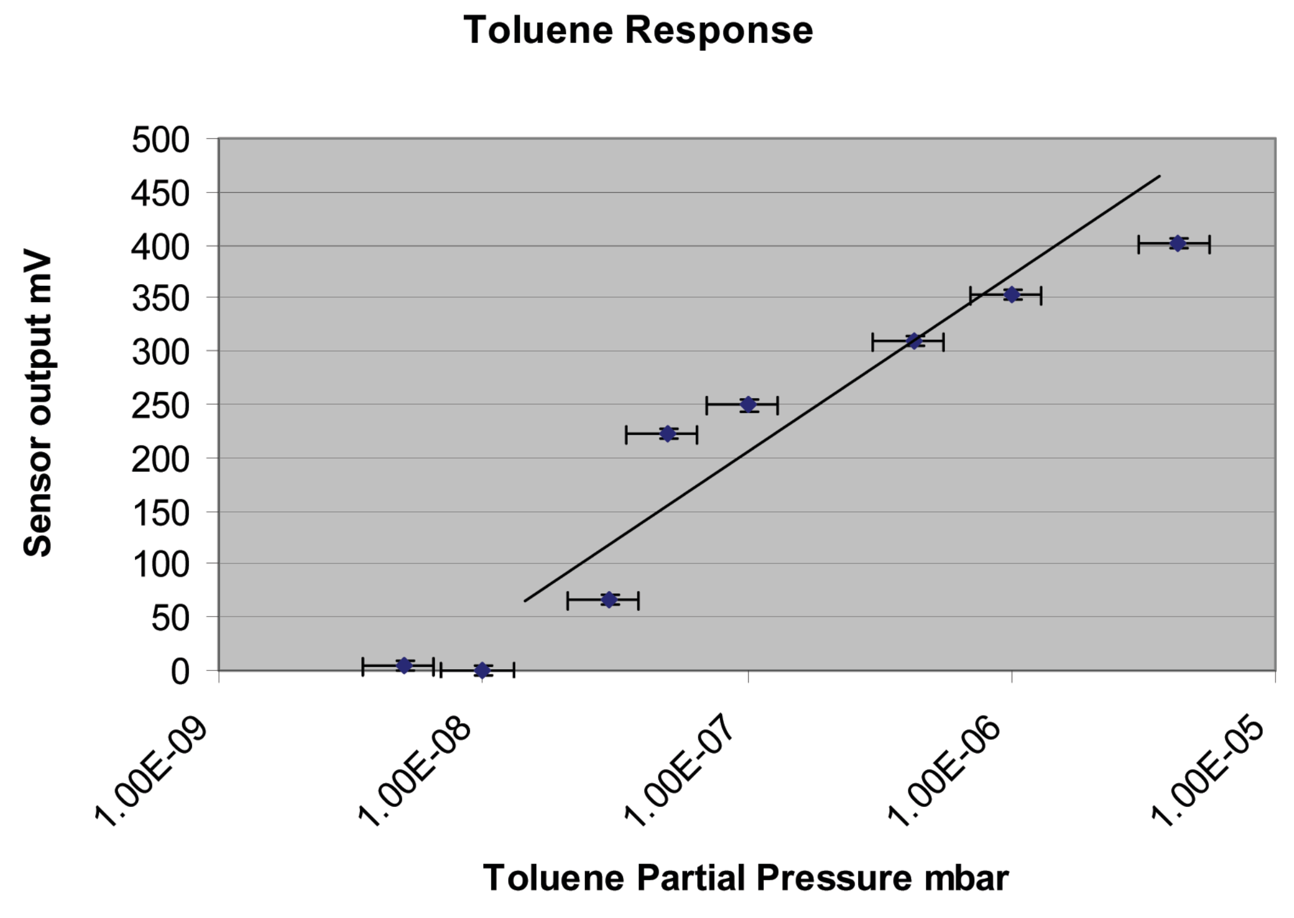
$$E = \frac{RT}{4F} \ln\left(\frac{P_{O_2\,(ref)}}{[O]^2}\right)$$

The cell voltage (E) is given by the modified Nernst equation (see insert). At the reference electrode the concentration of oxygen is constant and determined by the oxygen partial pressure in the atmosphere. At the sensing electrode, in the absence of hydrocarbon contaminants, the concentration of surface oxygen depends on the partial pressure of oxygen in the gas phase and the constant rate of oxygen electrochemical semi-permeation through the YSZ electrolyte. For gas phase oxygen partial pressures below $10^{-4}$ Pascal electrochemical semi-permeation is dominant and a steady "vacuum level" output is observed from the cell of approximately 370mV.
Assuming a Langmuir-Hinshelwood mechanism for the combustion of hydrocarbon contamination to carbon dioxide and water we would expect that the surface oxygen concentration would be inversely proportional to the amount of adsorbed hydrocarbon. In the low pressure limit Langmuir adsorption kinetics (see insert) predict that the concentration of adsorbed hydrocarbon contaminents will be proportional to their partial pressure. Combining the two equations predicts that the sensor response should vary as the logorithm of the hydrocarbon partial pressure.

$$[C_XH_Y] = \frac{P_{C_XH_Y}\,S}{K_d\,(2\pi mKT)^{1/2}}\,Exp(-\Delta H/RT)$$

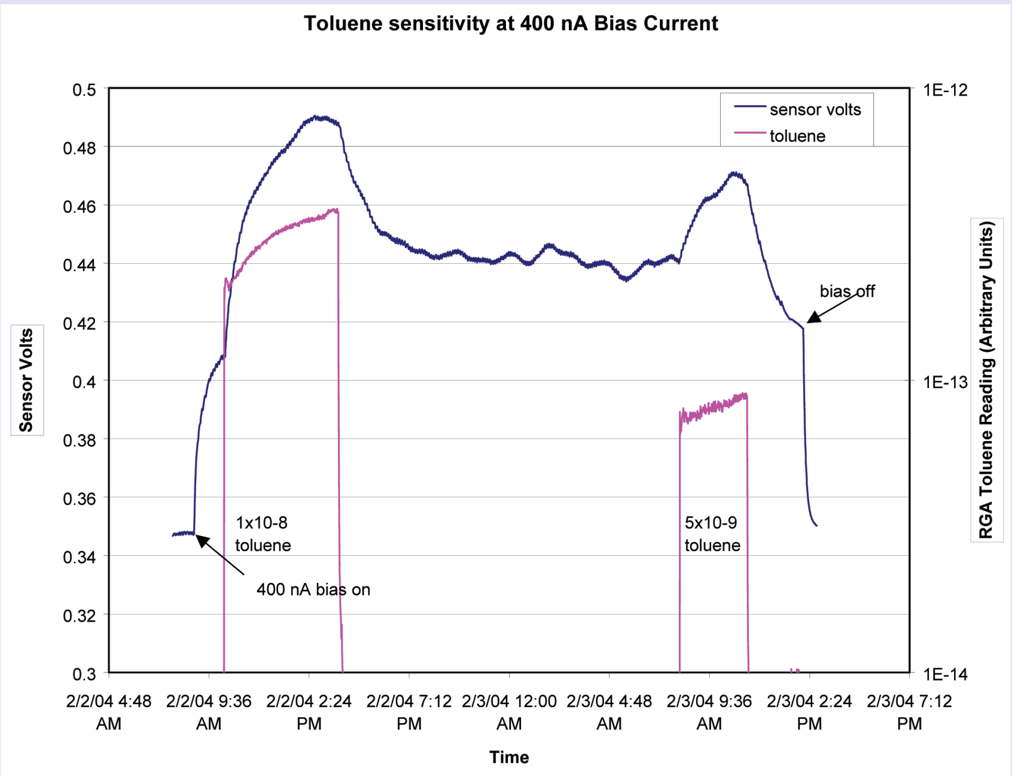
## 5 Sensor response to Toluene

The sensor response to various partial pressures of toluene is shown to be approximately log / linear, as predicted, with a sensitivity of approximately 250mv per decade of Toluene partial pressure and a lower detection limit of approximately 2 $10^{-6}$ Pascal.



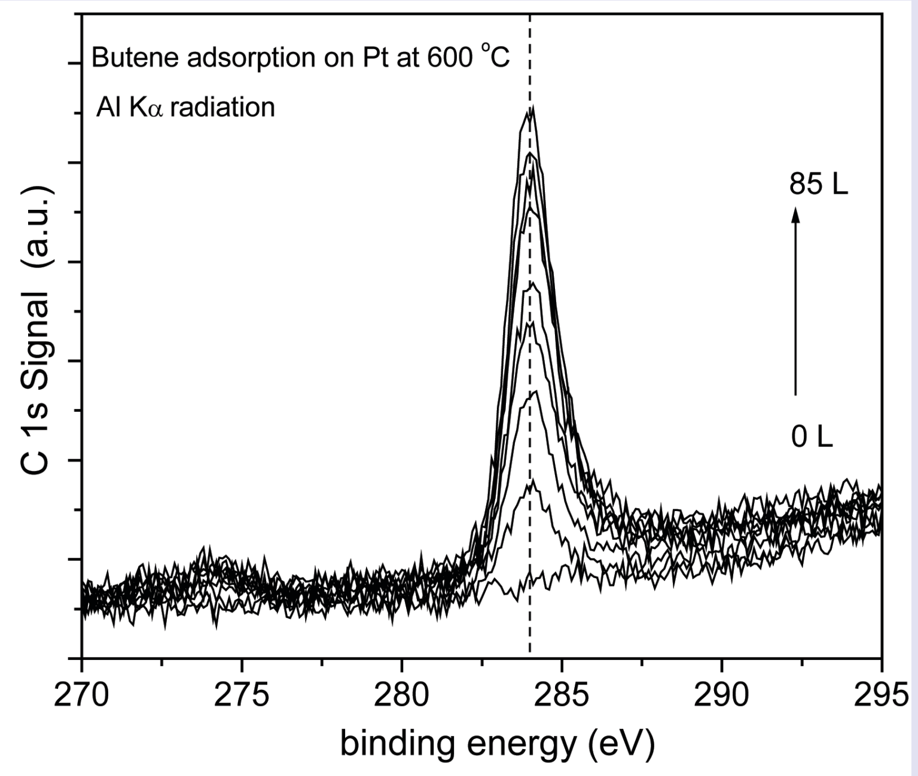
## 6 Increasing the Lower Detection Limit

Electrochemical pumping of oxygen, against the semi permeation flux, reduces the surface oxygen concentration and establishes a new "vacuum" level for the cell of approximately 410mV.
Addition of toluene, at partial pressures below the detection limit of the standard cell, now gives a response as shown below. The lower detection limit is improved by up to a factor of 10



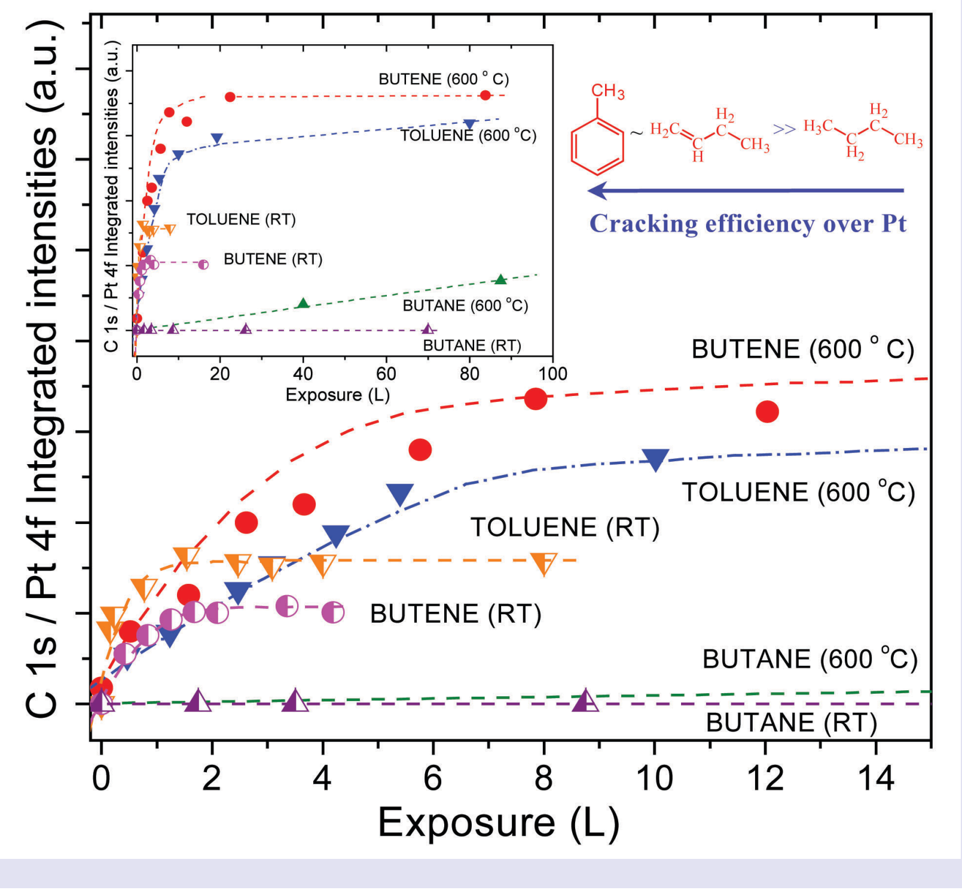
## 7 Experiments on Model Electrode Surfaces

In order to further understand the surface chemistry occurring at the sensing electrode and to determine the expected selectivity of the sensor to the hydrocarbon species which deposit carbon onto the MLMs X-ray photoelectron spectroscopy, XPS, was employed to measure the uptake of carbon species onto the surface at both ambient temperature and the sensor operating temperature of approx. 600°C.



## 8 Expected sensitivity to Saturates and Unsaturates

The model electrode surface clearly distinguishes between saturated and unsaturated hydrocarbon species as shown by the uptakes curves below.
The cracking efficiency is observed to increase in line with the degree of unsaturation of the hydrocarbon.
It is expected that this behaviour will be replicated by the sensor



## 9 Conclusions

We have clearly demonstrated the routine detection of hydrocarbon species in vacuum at levels down to the $10^{-6}$ Pascal (10s ppt) range using a simple solid state electrochemical sensor. By manipulating the concentration of surface oxygen at the sensing electrode through electrochemical pumping of oxygen anions, the lower detection limit can be improved by up to a factor of 10. Surface science investigations suggest that the sensor should have minimal sensitivity to light saturated species and high sensitivity to the species most likely to cause damage to the multilayer mirrors i.e. unsaturated hydrocarbons.

## 10 Further work

Extension of the work already completed for toluene to other organic compounds to understand the effects of the size and structure of the contaminating species together with a broadening the surface science studies to include an electrochemical cell to correlate the actual surface concentrations and reactions with the observed cell responses. This will also include an investigation of other electrode materials to fine tune the sensor response to the application.

Contact details: rob.grant@BOCEdwards.com
REFERENCES[1] R B Grant et al - Contamination Poster #2, 2nd EUVL Symposium, Antwerp Oct. 2003

For more information about BOC Edwards Lithography Subsystems visit the Lithography Subsystems website at www.bocedwards.com