# Hydrophobic Fluorocarbon and Organo-silicon Condenser Tube Coatings Deposited By Plasma Enhanced CVD

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The aim of the work is to investigate coatings which could be applied to utility condenser tubes to promote dropwise condensation (DWC) of steam. This requires durable, hydrophobic coatings with good adhesion and minimal internal stresses. Flat sheet specimens of titanium and 304 stainless steel, some coated with a thin buffer layer of aluminium by thermal evaporation, were coated by plasma polymerisation of octafluorocyclobutane (OFCB), or tetraethylorthosilicate (TEOS). Other substrates were coated with polycrystalline diamond or amorphous silicon alloys. Both parallel plate r.f. and novel microwave plasma sources were used, with in-situ analysis by optical emission spectrometry and mass spectrometry. The coatings were subsequently analysed by optical and electron microscopy, ellipsometry and Dektak profilometry to examine uniformity and surface topography. Structural and compositional analyses confirm that the OFCB and silicon alloy films are amorphous, and that the OFCB films are comprised largely of short chains with both $CF_2$ and $CF_3$ groups.

## 1 INTRODUCTION

Dropwise condensation (DWC) is a complex heat transfer phenomenon which in recent years has received a good deal of attention due to its inherently higher steam to condensing-wall heat transfer coefficients than filmwise condensation (FWC). The advantages of employing DWC in an electric utility condenser could be realised either as a decrease in operating pressure or as a reduction in condenser size.

The promotion of permanent dropwise condensation has presented somewhat of a problem to researchers in the past. In work by Tanner et al, DWC was observed with an organic promoter present in the steam [1]. Various types of electroplating and ion-plating processes have been used [2] as well as fluoroacrylic polymer coatings [3]. The problem with the organic promoter technique is that, after a period condensing dropwise, the surface impurities are washed away, whereupon filmwise condensation is observed. Long term DWC was reported by Marto et al [3]. However concern was expressed over the ability of this type of film to withstand the mechanical stresses associated with condenser manufacture.

Recently a collaborative project between Heriot-Watt University and Dalian University of Technology, China, achieved success with two types of coating, based essentially on Cr with the addition of surface active elements such as F, C, or O by ion implantation [4]. This work recognised the need for low surface energies in the promotion of DWC and noted that metals with their close packed crystal structure generally possess high surface energy. The principle is that these surface active elements reduce surface bonding energies by introducing disorder into the lattice. Two industrial scale condensers with tubes treated by this method have been operated in Dalian power station for almost 6 years with increases in heat transfer of between approximately 70-100%. ESCA analysis of some of the Chinese samples revealed that the surface contained a sizeable amount of Si in addition to F, C, O and Cr. The source of this impurity is thought to be diffusion pump oil but this Si content seemed to play a key role in the promotion of dropwise condensation. Considering these arguments and observations amorphous silicon and organo-silicon polymer coatings should form excellent dropwise surfaces. Amorphous films are known to have low surface energies and thus favour hydrophobic behaviour and previous work on plasma polymerised organo-silicon films has shown them to be non-wettable [5]. Using plasma enhanced CVD, will allow coatings with a range of physical and chemical properties to be deposited.

## 2 EXPERIMENTAL

Initially, work done by Xuehu et al at DUT [6] on fluorocarbon coatings from OFCB (octafluorocyclobutane), which were seen to promote excellent DWC, was repeated. Following this, amorphous silicon, silicon nitride and coatings from the organo-silicon monomer TEOS (tetraethylorthosilicate) were deposited onto test substrates (15mm x 25mm) of 304 stainless steel and titanium. In addition, some thin diamond films from a 2%-$CH_4/H_2$ gas mix have been deposited onto titanium. All of the substrates were mechanically polished to 6$\mu$m as a reference before being ultrasonically cleaned in Decon solution followed by rinsing in de-ionised water.

Film deposition was monitored by mass spectrometry and optical emission spectrometry to observe constituent species of the discharge. Coatings were subsequently analysed by optical and electron microscopy, ellipsometry and surface profilometry to examine topography and uniformity of the coatings. In addition structural and compositional analyses were performed using FTIR and XRD.

Samples are being contact angle screened with water before selection for lifetime testing in a continuous steam condensation cell. Heat transfer performance of coated tube sections will form the final stage of testing.

## 2.1 APPARATUS

The r.f plasma coating system has been used for many years producing hydrogenated amorphous silicon alloy films. It has been modified to use both gaseous and liquid sources for the present program. In addition, a new 2.45GHz microwave power applicator has been designed and constructed in-house, principally for depositing polycrystalline diamond films at higher powers and pressures than are commonly used in 13.56MHz reactors. It is envisaged however that this new deposition technique will be invaluable in coating tube sections later in the project because of the engulfing plasma which it generates and its higher deposition rates. This plasma deposition system can be quickly converted between parallel plate r.f. and microwave plasma configurations depending on requirements.

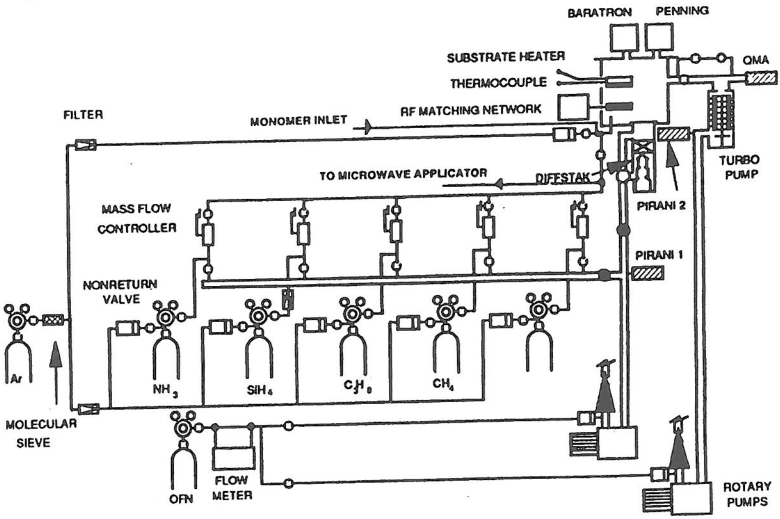


Figure 1. Glow discharge system

Fig. 1 shows the system for 13.56MHz discharge use, capacitively coupled inside a 730mm i.d. stainless steel chamber 440mm high with two viewing ports. The r.f. electrode and the heated substrate electrode are separated by 23-26mm (variable). The samples are grounded along with the rest of the chamber. The chamber is evacuated by 2-stage Edwards rotary and Edwards Diffstack diffusion pumps. A separately pumped quadrupole mass spectrum analyser, evacuable to $10^{-9}$ torr is attached to the main chamber via a sampling valve to monitor concentrations of gaseous impurities and chemical changes in the deposition gases. Process gases flow into the base of the chamber at a rate controlled by electronic mass flow controllers. An alternative input gas line can be connected into the top of the microwave applicator. These lines are wound with electrical heating tape to prevent condensation of the monomer before reaching the chamber.

The plasma reactor used for deposition of thin films utilising microwave enhanced chemical vapour deposition is shown in Figure 2. It was especially designed for high deposition rates sustaining high thin film uniformity across the substrate surface. The monomer gas or gas mixture is fed to the reactor volume through the gas inlet line by means of flow controllers. The gas inlet line is arranged such that it injects the process gases along the vertical axis of symmetry of the reactor towards the centre of a (circular symmetric) substrate. A 2.45 GHz microwave power generator (not shown in Fig. 2) which is connected to the PDR26 flange supplies power of up to several kilowatts to the reactor using an R26 waveguide transmission line. The waveguide is equipped with a tapered single ridge for impedance matching to a coaxial line transition stage which is used to convert the microwave power to radial symmetric TEM waves. The metal pipe of the gas inlet is used as the inner conductor of this low impedance coaxial line which is attached to the top plate of the reactor volume. Subsequently the diameters of both inner and outer conductor are increased so that the diameter of the inner conductor defines the horizontal cross section of the reactor volume (~4 inch). The cylindrical punched metal outer conductor enables the plasma to be seen. The inner conductor consists of a number of coaxial metal blades around the circumference of the reactor volume to form a slotted line. Hence, the microwave power can penetrate the slotted line and, after passing the walls of a fused silica cylinder (air to vacuum interface), sustains a stable and spatially uniform plasma discharge inside the reactor. At present the reactor is limited to a maximum power of 1 kW c/w which allows for operating gas pressures in the range of 0.5 to 60 Torr. Higher power levels require air cooling and water cooling of the mounting flange.

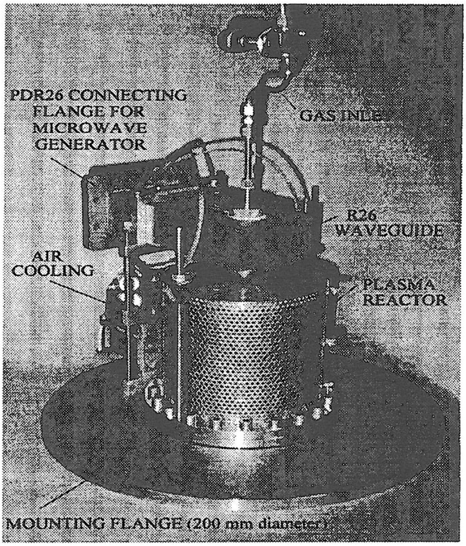


Figure 2. The microwave PECVD reactor

## 2.2 SAMPLE PREPARATION

Stainless steel and titanium samples (other than those used in the deposition of diamond) were coated in batches of up to 6, some of which had previously been coated by thermal evaporation with a thin aluminium buffer layer to observe its effect on film adhesion. In previous work by Peters et al a thin intermediate aluminium layer was seen to increase adhesion of organic-silicon films on stainless steel considerably [7]. After a series of argon pump-purge cycles, samples were cleaned in an argon glow discharge prior to deposition to remove any physically adsorbed material. It has been noted that if film adhesion proves to be insufficient a hydrogen-argon plasma clean may be required to remove surface oxide and enhance chemical bonding between film and substrate.

A range of deposition parameters were used in trying to optimise the process for different precursors. These are detailed in table 1;

| **Precursor** | **Material** | **Substrates** | **Power** (watts) | **Pressure** (torr) | **Flow** (sccm) | **Temp** (°C) | **Deposition time** |
|---|---|---|---|---|---|---|---|
| OFCB | fluorocarbon | 20 x s.s<br>5 x Ti | 100-200 | 0.1-1.0 | 15-30 | 100-<br>200 | 14-18<br>(mins) |
| $SiH_4$ | a-Si:H | 6 x s.s<br>5 x Ti | 20-40 | 0.1 | 30 | 240-<br>250 | ~15 (mins) |
| $NH_3$:$SiH_4$ | a-SiN:H | 6 x s.s<br>6 x Ti | 20-40 | 0.1 | 30:3 | 250-<br>300 | 15-20<br>(mins) |
| $CH_4$-$H_2$<br>(2%) | polycrystalline<br>diamond | 2 x s.s<br>5 x Ti | 500-<br>1000<br>(µwave) | 30-60 | 100 | 600-<br>950 | 2.5-5.5<br>hours |
| TEOS | SixOy:H | 6 x s.s<br>6 x Ti | 50-100 | 0.1 | 30 | 100 | 15-30<br>(mins) |

Table 1. Deposition process parameters

After etching a step profile into the fluorocarbon films a Dektak surface profile showed the deposition rate of this material to be approximately 0.8-1.6µ/hr at the conditions given. At this stage the other deposition rates are unknown but the diamond has been estimated at around 0.6µ/hr. It is intended to make quantitative adhesion measurements on the films but it appears at present that all coatings, other than those diamond films deposited onto stainless steel or at very high pressure, which gave flaky carbon deposits, adhere well.

## 2.3 ANALYSIS

Mass spectra have been taken during each process to monitor the stable by-products of the discharge as well as any impurities which may be present in the precursors or the chamber. This confirmed that all precursors were of high purity and that chamber contamination levels were minimal. The optical emission of the plasma is sensitive to changes in gas mix or fluctuations in energy distribution and can provide a statistical measure of plasma temperature for the $CH_4/H_2$ discharge by taking the ratio of $H_\alpha$ and $H_\beta$ transition lines (Figure 3). Including a correction factor for spectrometer sensitivity, calculations [8] gave a statistical H atom temperature of the order of 4200K.

Films have been analysed after deposition by optical and electron microscopy. Many of the films appear optically uniform and this has been confirmed by ellipsometry and Dektak surface profile measurements. The surface topography has, in most cases,

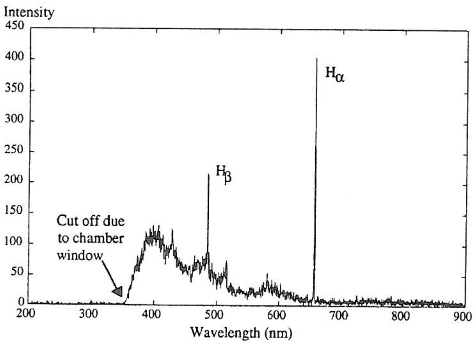

Figure 3. OES of $2\%CH_4/H_2$ plasma

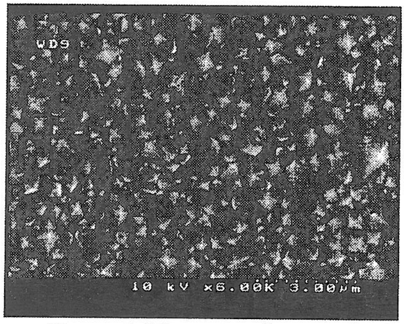

Figure 4. Electron micrograph of polycrystalline diamond

been smooth showing nothing more than fine scratches from the polishing stage. In the case of the polycrystalline diamond however SEM reveals small uniform <100> and <111> mixed crystallites, Fig. 4. This small crystal size is likely to be ideal for our application as less tensile stress will be present inside the film.

FTIR results confirmed the expected amorphous nature of the fluorocarbon and silicon containing compounds and that OFCB films were comprised largely of short chains with both $CF_2$ and $CF_3$ groups.

## 3 CONCLUSION

An investigation into the feasibility of operating utility condensers in the dropwise mode is currently in progress. Films from TEOS, OFCB, silicon alloys and $CH_4/H_2$ precursors have been deposited and seem to be suitable for hydrophobic coatings. It is the authors intention that films which perform well during long-term condensation tests will be laid down onto tube sections for heat transfer performance tests.

## 4 ACKNOWLEDGEMENTS

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