PLASMA ENHANCED CVD OF MATERIALS FOR ENERGY CONVERTERS: NANO-SILICON FOR SOLAR CELLS AND NANO-DIAMOND FOR FUSION REACTORS*

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Received January 24, 2011

Our plasma materials research has been a significant influence in developing microwave plasma enhanced chemical vapour deposition (MPECVD) of diamond and in a similar process for nanocrystalline silicon. These contrasting materials will be presented, together with techniques for determining their structure and quality, including X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy. For instance, Raman spectra clearly show the dependence on deposition parameters of the crystallinity of MPECVD Si films deposited at temperatures below 200^{o}C on to glass, aluminium and polyester. By using mixtures of silane with argon and/or hydrogen, these films are designed to have amorphous or nanocrystalline structure. Photosensitive P-I-N diodes have been produced on conductor-coated, polyester fabric as a step towards manufacturing flexible solar cells on textiles.

In contrast, the higher temperature synthesis of diamond and its unique properties (*e.g.* resistance to high heat flux and chemical erosion) has led to the first experiments on microcrystalline and nanocrystalline CVD diamond as a candidate coating for plasma-facing components in tokamaks. Our exposure results show that diamond coatings do not delaminate, undergo only slight surface amorphisation, retain only small amounts of deuterium in the surface and erode in hydrogen or deuterium plasma ~40% slower than graphite.

Key words: plasma chemical vapour deposition, amorphous silicon, nanocrystalline silicon, solar cells, diamond, graphite, plasma-facing components, tokamak, plasma etching, deuterium, Raman spectroscopy, XPS.

1. INTRODUCTION

Plasma processing of materials encompasses both deposition and removal of material as well as surface modification: sometimes these processes are desirable

* Paper presented at the 15th International Conference on Plasma Physics and Applications, 1–4 July 2010, Iasi, Romania.

Rom. Journ. Phys., Vol. 56, Supplement, P. 15–22, Bucharest, 2011

and sometimes they are an unwanted by-product of an application in which plasmas are used. Materials research at Heriot-Watt University (Fig. 1), over a period of more than 30 years, started with the development of amorphous silicon solar cells by RF plasma enhanced chemical vapour deposition (PECVD) following pioneering work at nearby Dundee University [1]. This technique eventually enabled successful world-wide commercialisation of thin-film silicon solar cells and other devices, by providing low temperature synthesis of a new class of semiconductor alloys, hydrogenated amorphous silicon (a-Si:H) being the first of these. The key to this science was the involvement of atomic hydrogen in the plasma decomposition of silane and other hydride gases, and its subsequent inclusion as a passivating element in amorphous lattices [*e.g.* 2]. More recently we have increased the plasma power frequency to the microwave region to enable production of nanocrystalline silicon (nc-Si:H).

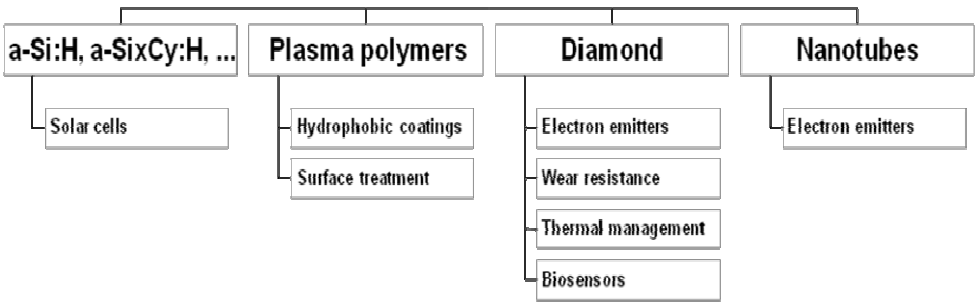

Fig.1 – Plasma Materials Research Topics.

In a contrasting materials research area there were reports from USSR and USA [3, 4] of the successful chemical vapour deposition of diamond, afterwards to be somewhat upstaged by Japanese reports of a plasma-assisted process for diamond synthesis [5]. Later many other methods were also reported across the world. All of these techniques enabled the usual high temperature, high pressure conditions for diamond synthesis to be avoided by including active atomic hydrogen as a constituent in the gas phase chemistry that etched away undesirable sp^2 carbon much faster than the required diamond sp^3 carbon. Hydrogen also passivated the final diamond surface although its action as a network modifier in amorphous silicon was not significant in the case of diamond. More than 20 years work at Heriot-Watt University has contributed to our understanding of PECVD diamond synthesis and to technical enhancements that have enabled orientated films on Si wafers [6], selective area growth of discrete micro-crystals [7], coating of biomedical materials [8], chemical functionalisation of diamond surfaces [9], and effective characterization techniques. Recent work has turned to examining the

plasma etching of CVD diamond [10] and the comparative properties of nanocrystalline and microcrystalline CVD diamond.

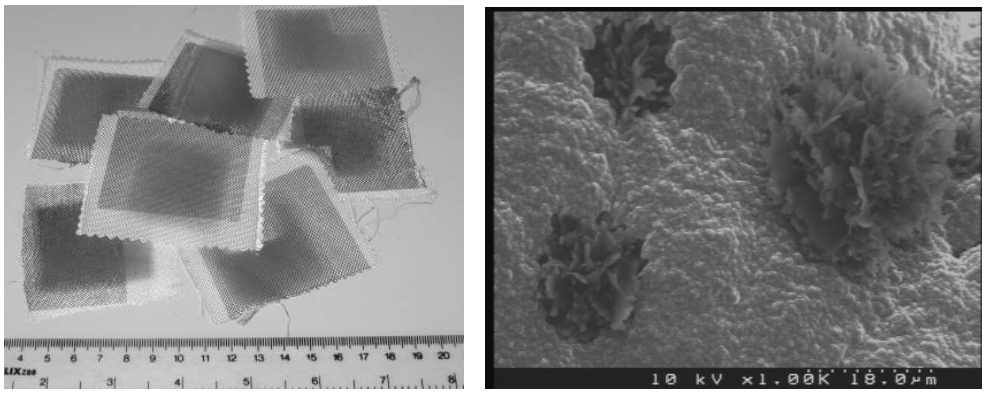

Fig. 2 – (a) Thin-film Si on woven polyester fabric. (b) Thin-film diamond on graphite.

This paper discusses the two areas of thin-film materials research introduced above: namely the application of microwave PECVD thin-film Si for flexible solar cells on textiles and the application of CVD diamond on metal or graphite for plasma-facing components (PFC's) in tokamaks (Fig. 2). Each of these relies on the addition of hydrogen or argon to the gaseous precursor mix to alter the degree of crystallinity of the deposited coating, and in the later application involves the inverse process of material alteration by exposure to hydrogen (deuterium) plasma. Characterisation of the as-grown materials and the plasma-exposed diamond has been mainly through Raman spectroscopy and x-ray photoelectron spectroscopy [11].

2. PECVD SILICON FOR FLEXIBLE SOLAR CELLS

Solar cell economics require consideration of the power conversion efficiency of a cell together with its production cost and energy pay-back period. Thin film cells will generally be of lower efficiency than their bulk crystalline counterparts but have considerably less energy invested in them and are lower cost. Thin-film silicon has a large market share despite its lower efficiency than crystalline Si but also addresses different applications. Our decision to attempt making thin-film Si cells on polyester was driven by the potential low cost of the whole cell, including the replacement of glass or metal substrates by a commodity textile, with the goal of the ultimate flexible device [12]. In addition we can suggest new uses of solar cells in disaster relief shelters, agriculture and horticulture, architecture.

The challenges to making polyester based solar cells include:

- Conducting layer continuity on a textured flexible surface;
- Si microstructure for photovoltaic response (photo-carrier generation and collection);
- Encapsulation;
- Integrating fabrication stages (roll-to-roll coating);
- Up-scaling from laboratory to production.

The first of these has been addressed by a combination of two layers of a flexible conducting polymer and an evaporated or sputtered aluminium film. The Si PIN diode structure has then been added by PECVD, using 500-800 W of microwave power in ~0.15 mBar mixtures of silane, hydrogen, argon, and a dopant of diborane or phosphine diluted in hydrogen, on to substrates held at 200^{o}C. The cell is completed by a layer of sputtered indium tin oxide and then a first hermetic barrier layer of plasma polymer. All of these processes have been scaled up individually by manufacturers of other devices or are believed to be capable of large area processing.

Raman spectroscopy using 514 nm laser illumination reveals that the Si may be amorphous or may have some amount of crystallinity, according to the preparative conditions. It is known that hydrogen dilution of silane tends to produce a microcrystalline film but at very low growth rates for RF PECVD. By using microwave PECVD and including Ar in the mixture, we are able to produce mixed amorphous/crystalline phase material having Raman spectra (Fig. 3) that suggest Si is hexagonal phase. This is not unexpected since there is only a small energy difference between the stacking sequences of cubic zinc blende and hexagonal wurtzite structures for Si [13], especially if the sample volume is small (*i.e.* nano-wires or nanocrystals). Thus we obtain three Raman components under the measured envelope: ~520 cm^{-1} for crystalline Si, ~505 cm^{-1} for nanocrystalline (hexagonal) Si, and ~480 cm^{-1} for amorphous Si; hexagonal Si also shows a small Raman peak at ~420 cm^{-1} [14]. The nanocrystalline peak at ~505 cm^{-1} is seen to shift to lower wavenumber as the nanocrystallite size decreases.

Although the photo-response of thin-film Si diodes on polyester is still rather weak, photoconductive diodes have been produced on woven polyester by this technique, having 200 nm of undoped nc-Si:H between 50 nm n- and p-type Si. Research is continuing into improving the photovoltaic response and solving the other challenges of solar cell son flexible materials.

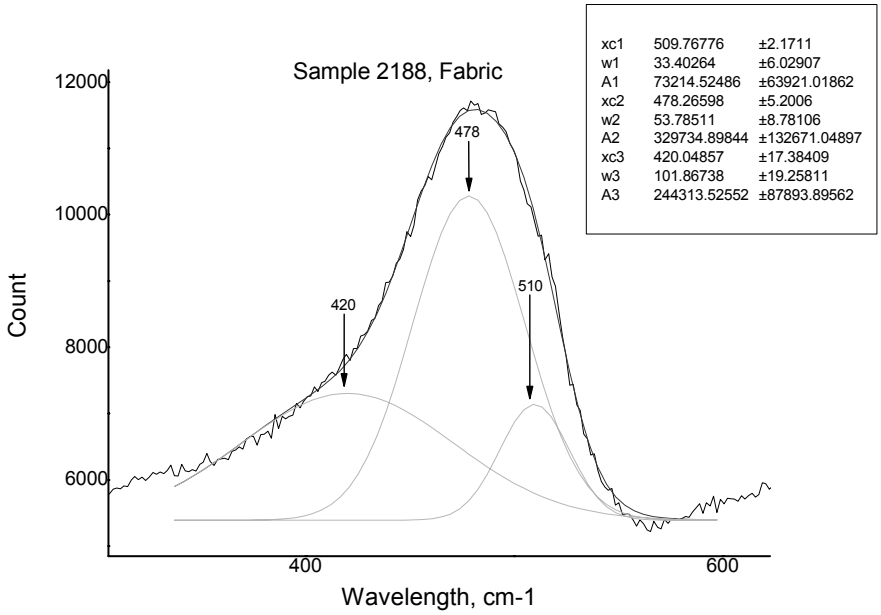

Fig. 3 – Example of a Raman spectrum from thin-film Si on polyester.

3. PECVD DIAMOND ON GRAPHITE

Turning now to CVD diamond for fusion reactors, we have space to explain only briefly why we proposed this solution to the tokamak materials problem. The diverter is especially challenging because of the high flux of heat, energetic particles and radiation load: carbon should be able to handle high thermal fluxes and being a low Z element will not cool the plasma, but it does undergo chemical and physical erosion in this environment and may trap too much tritium [15]. Graphite etching in H or D has a complicated dependence on temperature, flux and ion energy but in low temperature H plasmas, diamond is known to etch at least 100x slower.

The first requested step in testing our diamond as a PFC coating was to use graphite substrates. We were able to confound general belief that this was impossible for the PECVD process (excessive H-etching of graphite could perhaps prevent nucleation of diamond), provided we used particular nucleating techniques prior to growth. The most successful of these have involved mechanical scratching with diamond powder and heating in air [16]. Various morphologies were produced in our 5 kW PECVD system, from micro- to nano-diamond, confirmed by XPS and Raman to be diamond. Subsequent exposure to H plasma produced complex step/terrace etch patterns or dramatic whisker growth.

4. HFCVD DIAMOND FOR PFC'S

However, only a few cm^2 could be coated by PECVD and so we used a large area hot filament reactor (HFCVD) from sp^3 Diamond Technology to coat much larger tiles of Mo or carbon fibre composite (CFC). In this manner we supplied nano- and micro-crystalline diamond-coated tiles to several tokamaks and large plasma facilities, including MAST, DIII-D, Pilot-PSI, PISCES-B for the world's first experiments on diamond in fusion-type plasma [17-19].

Initial exposures of diamond were coated mid-plane probes inserted into the MAST tokamak at Culham for ~1 s [17]. These survived the abrupt rise in temperature to >1000^{o}C in ~100 ms: the diamond remained on the Mo substrate but where there had been incomplete coverage, the uncoated Mo melted. Nanocrystalline diamond (NCD) had small changes in the Raman spectrum after exposure, but microcrystalline diamond (MCD) showed no change. Deuterium retention measurements showed that D was retained only in the upper 250 nm and amounted to <1% of the incident flux on MCD.

Chemical erosion was detected by CH emission during 600 s exposure of NCD or MCD on Mo or graphite to tokamak-like, high density, low temperature D plasmas in Pilot-PSI [18, 19]. After exposure some samples were coated by sputtered metal from the plasma source but again, Raman spectra showed only minor changes due to surface amorphisation. This was confirmed by XPS. Erosion rates for MCD were determined to be ~50% lower than graphite but NCD behaved similarly to graphite. Similar results were obtained from PISCES-B exposures: although NCD behaved similarly to graphite within experimental tolerances, boron-doped MCD showed a factor 2.2 lower erosion than graphite.

Further tests in the DIII-D tokamak provided both outer strike point, detached L-mode "ITER-Like" conditions and attached ELM H-mode conditions (Fig. 4). The former gave no arcing, delamination or graphitization of the diamond coating, but the more extreme latter condition gave greater erosion. High resolution TEM of a section through the coating showed a layer of ~10 nm of amorphous carbon had been formed, but the plasmon peaks in the carbon electron energy loss spectrum suggested this was still sp^3 and not sp^2 bonded. Raman spectra continued to show the diamond signature at ~1320 cm^{-1}.

In conclusion, CVD diamond is still a contender for plasma-facing components that will not erode rapidly in hydrogen plasma but further assessment is needed to ensure it will withstand the high neutron flux in fusion conditions and to establish a working lifetime.

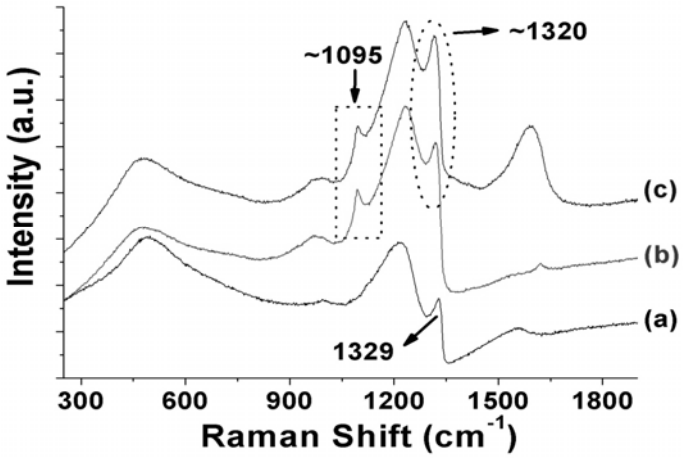

Fig. 4 – Boron-doped diamond on Si (a) before exposure in DIII-D; (b) after 300°C exposure to detached L-mode plasma; (c) after room temperature exposure to attached H-mode plasma.

Acknowledgements. Funding for these research programmes has been provided by UK EPSRC and has benefitted from expertise within several universities and organizations, including: UKAEA Fusion, Culham (S. Lisgo and G. De Temmerman); FOM, The Netherlands; PISCES-B, UC San Diego; D-III-D, GA San Diego (D. L. Rudakov); KTH, Sweden (P. Petersson & M. Rubel); University of Basel (L. Marot); University of Glasgow (D. A. MacLaren & W. Smith); sp^3 Diamond Technologies; NCESS, Daresbury.

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