Proc. 3rd Int. Symp. Diamond Mater., Honolulu, May 1993. (Electrochem. Soc. Proc. Vol. PV-93-17, Pennington, N.J., eds. J.P. Dismukes & K.V. Ravi)

CVD DIAMOND FILMS PRODUCED IN A PARALLEL-PLATE RF REACTOR

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A parallel-plate radio frequency reactor operating at 13.56 MHz has been used to deposit hard-carbon and diamond films from mixtures of methane and hydrogen. It was found that if the Si substrate was positioned on either of the electrodes, high energy ion bombardment resulted in etching of the Si rather than deposition. Alternatively, with the Si wafer positioned in the glowing plasma region midway between the electrodes, ion bombardment was minimised and net deposition occurred. The type of deposition depended upon the substrate temperature, with hard-carbon bristles being formed at temperatures below about 600°C, and spherical diamond balls above this temperature.

INTRODUCTION

There are a number of reports of radio frequency (RF) plasmas being used to grow diamond films using Plasma Enhanced Chemical Vapour Deposition (PECVD) techniques (1-3). Most of these reports, however, utilise an inductively-coupled electrodeless discharge, where the substrate sits inside a quartz tube, which has a coil wrapped around it and is connected to an RF generator. Well-facetted diamond crystals have been grown by this method, however the reported growth rates are very slow. Moreover, inductively-coupling the RF power into the vacuum chamber necessitates high power (up to 2 kW) RF generators, which are often prohibitively expensive.

To try and overcome some of these problems, we have used a capacitively-coupled parallel-plate RF system. The advantage of such a system is that it is relatively simple. It is also less expensive, since capacitively-coupling the RF to an electrode is a very efficient means of power transfer, allowing a dense, bright plasma to be produced for less RF input power. Despite this however, there are few reports of such parallel-plate reactors being used for diamond film CVD (4,5), although their use for production of diamond-like carbon (DLC) films is well-known (6-9).

Most RF plasma systems used, for example, in plasma deposition or reactive ion etching, typically operate in the 5-500 mTorr pressure range, since at these pressures the mean free path of electrons is large, and so efficient ionisation of the process gas is accomplished over a large volume. Such low pressure RF discharges are characterised by a bright central plasma region, with darker regions (the dark space, or sheath) extending a few mm from each electrode (see fig. 1a). The glowing plasma region is at equipotential, and is where energetic electrons collide with neutral gas species, causing ionisation and excitation, with the resulting emission of light. This region is also relatively cool, having a temperature typically 300-400 K. Any object placed into this region will be electrically floating with respect to the RF, and so will only charge up to the floating potential of a few volts.

Such objects will therefore experience little ion bombardment, remain relatively cool, but be surrounded in a 'sea' of reactive free radicals and atoms.

Conversely, the sheath regions are defined as the areas over which the electrode potential acts. Sheath potentials are typically several hundred volts, and serve to accelerate positive ions towards the electrodes, where they impact with high kinetic energy (10). Any object placed on the electrodes will therefore experience high energy ion bombardment, and this is often cited as the basis for the high rate and directionality of reactive ion etching (11). The sheaths are also darker than the surrounding plasma due to the negative sheath potential excluding electrons (12), and so reducing the electron-impact excitation processes which cause light emission.

For CVD diamond growth, however, process pressures in the range 10-100 Torr have been found to give optimum growth rates in a variety of deposition systems (13). This is because the mechanism of diamond growth requires a very high density of chemically reactive species (such as methyl radicals or hydrogen atoms), with relatively low kinetic energy. Too high a kinetic energy for these species, and the growing diamond lattice is likely to be damaged producing graphitic or amorphous carbon, or in the extreme case, the substrate may be etched. Such high process pressures, however, are rarely seen with RF plasmas, since the reduced electron mean free paths often make the resulting plasmas unstable and localised.

The appearance of a high pressure RF plasma is very different to the more commonly-used lower pressure plasmas, and not as well understood. For example, fig. 1b depicts the 30 Torr methane/hydrogen plasma used for our PECVD process. Extending a few mm around each electrode was a bright glowing region **C**, which is presumably caused as a result of high energy secondary electrons ejected from the electrode impacting with process gas molecules. In the centre of the reactor, directly between the 2 electrodes, was a bright, glowing region **B**, presumably analogous to the plasma glow region seen in low pressure plasmas. We believe that a large proportion of the RF power was being delivered directly to electrons within this central region. Because of their very low mean free path at this pressure, these electrons then lost energy in collisions before being able to travel any great distance. As a result, between region **B** and the electrode glow regions **C**, was a region **D** from which no light emission was observed. Although at first sight, region **D** may appear similar to the dark sheaths **A** of low pressure RF systems, this is misleading. We believe region **D** is not a sheath, *per se*, since no potential is dropped across it; in effect it is just a region of stable, ground state gas molecules bordering the plasma region.

APPARATUS

We have used a purpose-built RF PECVD reactor in order to optimise the process conditions for diamond growth. A schematic diagram of the PECVD reactor is seen in Fig. 2. A mixture of methane (1.44 sccm) and hydrogen (200 sccm) was admitted into a glass bell jar, which was maintained at a process pressure of 30 Torr. Two stainless steel electrodes, one grounded, and one connected via a matching network to the RF supply, were situated within the chamber. In order to obtain stable, dense plasmas at pressures of tens of Torr, we ensured that the electrode sizes were small (typical dimensions being 2 cm diameter) and close together (1 cm). For an input RF power of 500 W, this provides a plasma power density of 160 W cm^{-3}, which is 10^4 times higher than typical low pressure RF plasma systems although, of course, this power was being dissipated into about 10^3 times as many gas molecules. The electrodes were not cooled, and glowed red hot during deposition as a result of ion bombardment.

The substrate was positioned in one of three places (a) on the powered electrode, (b) on the grounded electrode, or (c) electrically floating within the plasma glow region. When the substrate was on either electrode, no extra heating was applied to the substrate, since the hot electrode provided sufficient heating. However with the substrate in the plasma region, additional radiant heating was

supplied by means of a 150 W lightbulb-reflector assembly. This heater unit was placed about 2 cm below the substrate, and focused the light, and therefore also the heat, from the bulb, to a 5 mm-diameter spot on the back side of the substrate. Thermocouple measurements (with plasma off) showed this arrangement was able to maintain the substrate at a temperature of up to 600°C.

The substrate was single-crystal {100} silicon, which was manually abraded prior to deposition using 1-3 μm diamond powder and then cleaned using methanol.

RESULTS

(a) Substrate Positioned on an Electrode

Substrates that were placed upon either electrode were inevitably bombarded by large fluxes of very high energy ions that were accelerated through the sheath potential. For lower pressure systems, such ion bombardment by hydrocarbon ions results in hard, smooth DLC films (6-9). However, in our system the high hydrogen content of the process gas, coupled with extremely high sheath potentials, caused etching of the substrate rather than deposition. This etching was mainly due to direct sputtering, although there may have been a chemical etching component as well, with Si being removed from the substrate surface as SiH_x species.

Figures 3(a) and (b) show scanning electron micrographs (SEM) of the Si surface after 6 hours on the powered electrode. The Si has been etched into rounded cone structures. This is because the inherent directionality of the high energy ions, which would tend to produce a rough, spiky surface (11), has been modified by numerous collisions within the sheath. These collisions cause the ions to lose energy, as well as deflecting them from their normal incidence trajectories (14). Ions striking the substrate at glancing angles produce a smoother surface (11), in this case rounding off the spikes into cones.

Similarly, substrates placed on the grounded electrode also etched into rounded cones, since for equal area electrodes the sheath potentials, and hence the ion bombardment energies, were identical. In order to reduce the sheath potential, it is necessary to make the electrode areas unequal. The smaller electrode (usually the powered one) then develops a DC bias offset voltage, increasing its sheath potential by up to a factor of 2, while the larger electrode has its sheath potential decreased by an equivalent amount (15). Therefore we varied the ratio of the electrode areas (grounded : powered) between 1 : 1, 2 : 1, 5 : 1 and finally 10 : 1, with the Si substrate always being placed on the larger, grounded electrode. In each case, however, we still observed only etching of the Si and never deposition. We believe this was due to the high RF power density used in the reactor. Even with a highly asymmetric electrode arrangement, the sheath potentials on the larger electrode were still too large for deposition to occur.

(b) Substrate in the Plasma Region (with no additional heating)

With the substrate in the centre of the plasma region, there was very little ion bombardment at the substrate surface, and net deposition was observed. Without additional heating, the substrate was only in thermal equilibrium with the bulk gas in the plasma. We estimate therefore, that it reached a temperature only just above ambient, probably around 50-150°C. Such low temperatures are not compatible with diamond growth, which normally requires substrate temperatures in excess of 700°C (13). Consistent with this, we found that the deposited layer was not diamond, but resembled closely-packed bristles or whiskers (see Fig. 4). Transmission electron microscopic (TEM) analysis of these bristles showed them to be composed of hard amorphous carbon, with some graphitic component. No evidence of diamond was found, although dense, nanometer-sized crystallites of unknown composition were detected within the bristles.

(c) Substrate in Plasma Region (with additional heating)

With the heater turned on, the Si substrate was maintained at 600°C (plus any extra heating arising from the RF plasma or radiation from the hot electrodes). Figure 5 is an SEM of the resulting deposition. Instead of bristles, we now obtain roughly spherical balls, whose composition has been determined by electron energy loss spectroscopy (EELS) to be diamond. TEM analysis confirms this result, and reveals that the diamond balls are highly defective, and consist of clumps of crystals with grain sizes on a scale of tens of nm.

The growth rate of the diamond balls is about 0.15 $\mu m\ hr^{-1}$, which is lower than for most hot filament reactors. We believe this is due to the lower deposition temperature, and evidence for this is seen in Fig. 5, where both carbon bristles and diamond balls can be seen to have deposited concurrently. This suggests that our deposition conditions are only just on the border between the bristle and diamond growth regions. Increasing the temperature still further should increase the diamond deposition rate at the expense of the bristles. This work is currently underway.

CONCLUSIONS

We have demonstrated that it is possible to produce CVD diamond using a parallel-plate RF reactor, albeit with slow deposition rates at present. These results are the first to arise from our RF PECVD system, and in the near future we will perform a detailed systematic study of the conditions under which diamond grows in this reactor in order to optimise the process. This will involve increasing the substrate temperature to the more usual values of 700°C+, increasing the applied RF power to boost dissociation rates of gaseous species in the plasma region, and possibly decreasing electrode areas to confine the plasma to a smaller region, thus making it more dense.

ACKNOWLEDGMENTS

We should like to thank the Department of Trade and Industry for the financial support for this project, and C.G. Trevor for performing the TEM and EELS analysis. PWM would also like to thank the Ramsay Memorial Trust and British Gas for financial support. This paper is published with the permission of the Controller of Her Britannic Majesty's Stationery Office, (c) British Crown Copyright 1993/DRA.

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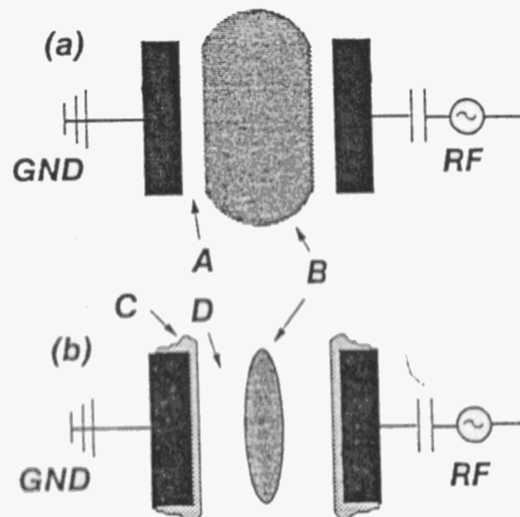


Fig. 1

(a) Appearance of a typical low pressure (5-500 mTorr) RF plasma. One electrode is grounded, while the other is capacitively-coupled to the RF generator. Areas marked **A** are the dark space sheaths extending a few mm above each electrode. **B** is the bright plasma glow region. (b) Appearance of the 30 Torr methane/hydrogen RF plasma used to deposit diamond. **B** is analogous to the plasma glow region seen in lower pressure plasmas, but this now only extends a few mm from the centre of the discharge. Between **B** and the electrodes there is a darker region **D**, from which little or no light is emitted. Surrounding each electrode at a distance of about 1 mm is a very bright glow region, **C**.

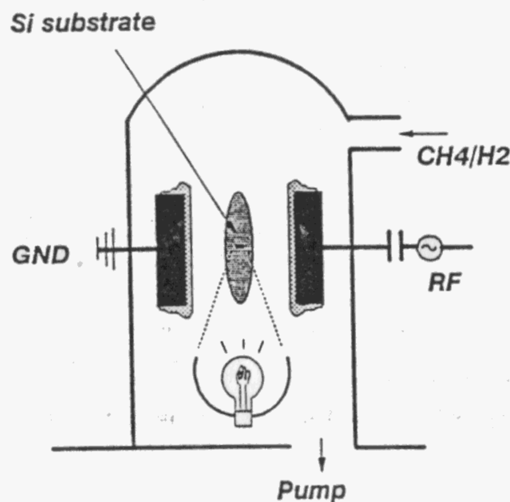


Fig. 2.

Schematic diagram of the RF PECVD reactor. The Si substrate is either clamped to an electrode surface, or supported in the centre of the plasma glow region. A focused lightbulb-reflector assembly is used to heat the substrate.

(a)

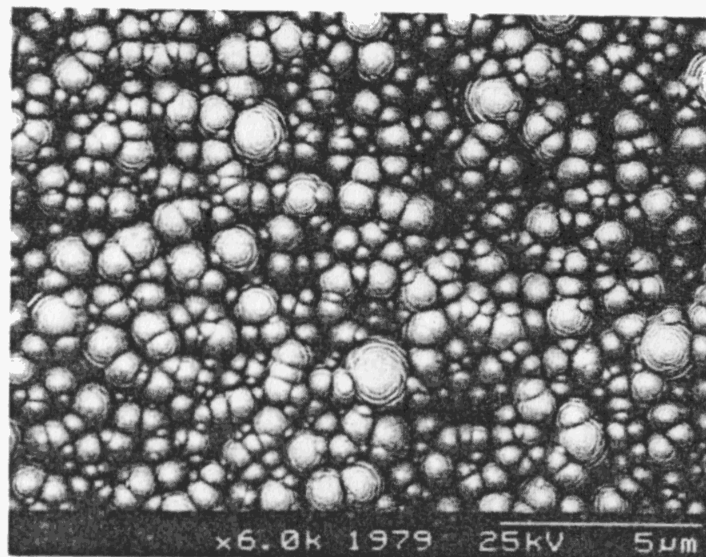
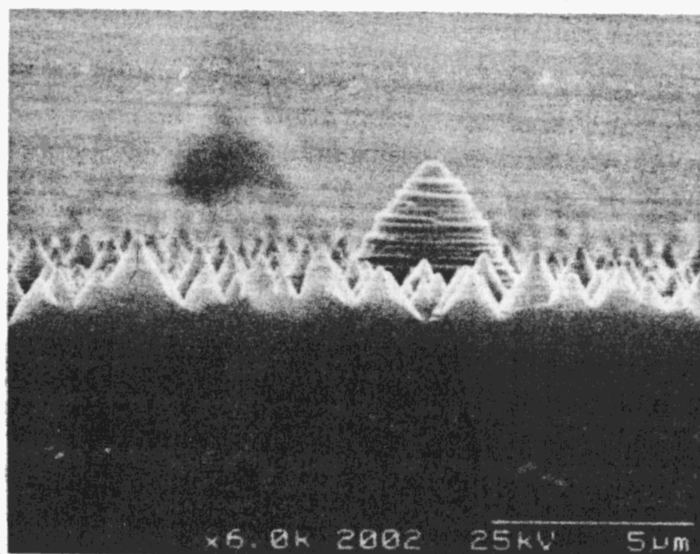


Fig. 3.

SEMs of the surface of the Si surface after 6 hours processing on the powered electrode. Conditions were: pressure 30 Torr, methane flow 1.44 sccm, hydrogen flow 200 sccm, applied RF power 450 W, reflected power 0 W, equal area electrodes, and no additional substrate heating. (a) shows a plan view of the Si surface, while (b) gives a cross-section, showing that the Si has been etched into rounded cones.

(b)



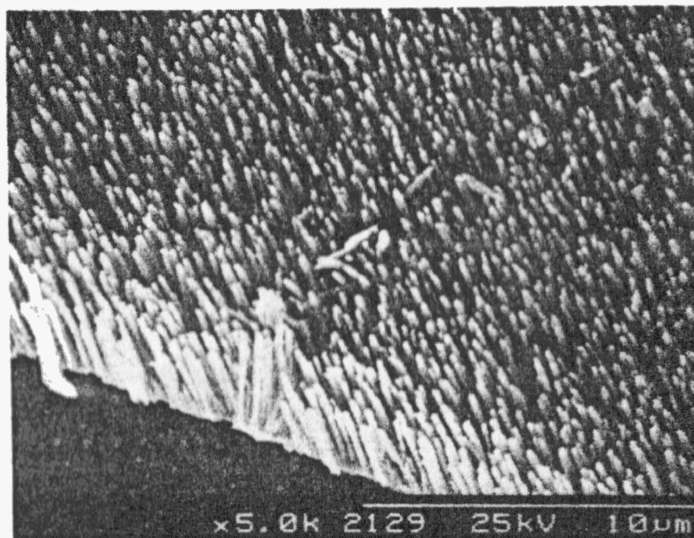


Fig. 4.

SEM of the Si surface after 6 hours between the electrodes (no additional heating). Plasma conditions were the same as in Fig. 3. Etching no longer occurs, and the surface is covered with hard, amorphous-carbon bristles.

Fig. 5.

SEM of the substrate surface after processing under the same conditions as Fig. 4, except with additional radiative heating applied to the substrate to raise it to a temperature of about 600°C. Highly defective diamond balls have now been deposited, along with occasional carbon bristles.