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Electrospray deposition of diamond nanoparticle nucleation layers for subsequent CVD diamond growth

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ABSTRACT

Nucleation is the rate-determining step in the initial stages of most chemical vapour deposition processes. In order to achieve uniform deposition of diamond thin films it is necessary to seed non-diamond substrates. Here we discuss a simple electrospray deposition technique for application of 5 nm diamond seed particles onto substrates of various sizes. The influence of selected parameters, such as experimental spatial arrangement and colloidal properties, are analysed in optimizing the method by optical and electron microscopy, both before and after nanocrystalline diamond deposition on the seed layer. The advantages and limitations of the electrospray method are highlighted in relation to other commonly exploited nucleation techniques.

INTRODUCTION

The nucleation of non-diamond substrates prior to chemical vapour deposition (CVD) of nanocrystalline (NCD) and ultra-nanocrystalline diamond (UNCD) films is crucial for creating smooth, homogenous and uniform thin films. Substrates can be treated to promote surface nucleation in a variety of ways [1-3] including mechanical or ultrasonic abrasion [4-5], bias-enhanced nucleation [6-7] and diamond-containing-photoresist coating [8].

Mechanical abrasion can be efficient at nucleating substrates for microcrystalline diamond (MCD) deposition, but the low surface roughness of NCD and UNCD films often demands a less aggressive nucleation technique. In previous studies, it has been shown that spraying diamond seed particles directly onto substrates can achieve nucleation densities of around 10^{11} cm^{-2} [9-10]. The electrostatic spray (“electrospray”) deposition technique uses a large potential difference to ionize nucleating particles (or droplets containing the particles) via the corona effect and accelerates them towards a grounded substrate. The technology has found many applications in the materials industry for application of particulates, paints and powders onto a variety of complex substrate forms and materials [11]. The technique has been employed successfully to seed silicon substrates prior to diamond CVD [12-13] using diamond powders suspended in water. In this case, the particles were forced through drying media (removing the majority of the liquid) by application of 30 psi pressure into an electrostatic spray gun (with an ionizing electrode at 80 kV) where they became charged and were then applied to the substrate.

Here we describe a variation on this simple yet versatile electrospray deposition method for coating substrates with a nucleation layer comprised of 5 nm diamond particles. The main difference is that both the dispersion medium and the diamond particles exit through the electrode nozzle but the volatile liquid then evaporates before reaching the substrate, resulting in a uniform but dense coating of diamond particles. The potential difference pulls the suspension through the capillary, removing the need to apply a driving pressure, while charging prevents the droplets coalescing.

Subsequent NCD or MCD growth by microwave (MW) plasma enhanced CVD allowed optimization of this method, indicating where seeding uniformity could be improved. Scaling up the technique allowed uniform coverage of planar substrates with diameters up to 2 inches and provided a novel means of seeding more complex three-dimensional substrates.

EXPERIMENT

The application of colloidal particles onto a substrate surface requires only a simple experimental setup which is detailed in Fig.1. Approximately 1 ml of the colloidal suspension (i.e. nanodiamond particles in the chosen dispersion medium) is placed in a plastic syringe located on the outside of an insulating box. The 21G syringe needle (outside diameter = 0.81 mm) passes through the wall of the box by turning through 90° and once inside the box bends through an angle θ to point upwards. The angle θ was varied during the optimization of the apparatus to achieve the best substrate coverage. A 35 kV bias was applied to the metal tip of the nozzle which was sufficient to ionize the droplets without becoming unstable and arcing. The substrate (silicon, unless otherwise stated) was positioned ~50 mm away from the nozzle tip on a moveable, conducting mount which could be adjusted through three axes of freedom. The mount was well grounded, ensuring that ionized aerosols emanating from the nozzle would be attracted along electric field lines towards the substrate.

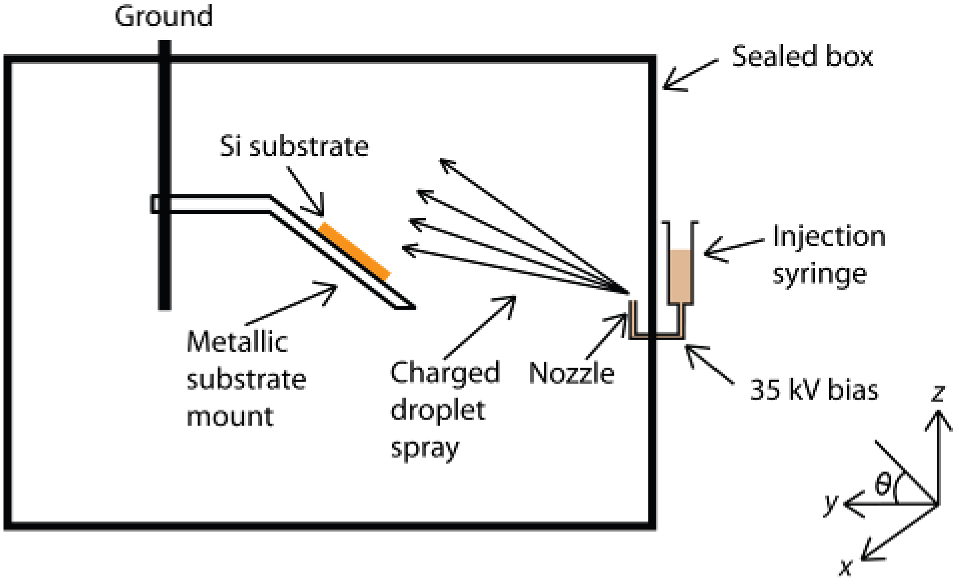

Figure 1. Schematic diagram detailing the electrostatic spray deposition apparatus. Coordinates are used to define the angle of the nozzle relative to the substrate.

When using substrates with diameters greater than ~10 mm the seeding layer was found to be significantly improved by spinning the substrate, thus combining two techniques commonly utilized in the materials industry. Rotating the substrates on the mount at up to 1500 r.p.m. enabled uniform layers to be deposited onto substrates up to 2 inches in diameter. The deposition took just 3 minutes to complete, but could also be repeated to achieve a thicker layer of seed particles if required, although this risked clustering seeds on top of each other.

After seeding, NCD or MCD films were grown at Bristol using an Astex-type 2.45 GHz MWCVD reactor, and by Advanced Diamond Technologies Ltd., USA (ADT) by hot filament

(HF) CVD to get an indication of the nucleation density and uniformity of the subsequent film coverage. These diamond thin films were analyzed by scanning electron (JEOL JSM 6330F) and optical microscopy, and with laser Raman spectroscopy at room temperature and excitation wavelengths of both 325 nm (UV, HeCd) and 514 nm (green, Ar^+) using a Renishaw 2000 spectrometer.

DISCUSSION

In addition to the experimental hardware described above, the following two parameters were investigated to optimize the coverage of diamond nanoparticle seed layers on Si substrates. These were assessed using optical and electron microscopy both before and after growth of CVD diamond films.

Spatial arrangement of nozzle and substrate

The dimensions of the substrate determine its positioning within the electrospray apparatus. Small substrates, less than 10 mm in diameter, could be mounted on the underside of a plate positioned in the *xy* plane (as defined in Fig.1) but ~20 mm higher (i.e. along *z*) than the nozzle tip. For larger substrates, and those requiring simultaneous spin coating, a larger mount was prepared as shown in Fig.1 with the surface to be coated at $\theta = 50°$.

Similarly, the orientation of the nozzle in relation to the substrate was also a key factor in guaranteeing an even coating of nanodiamond. The optimal angle was found to be $\theta = 90°$ (i.e. the nozzle pointing along the *z* axis and, therefore, at 40° to the substrate surface). At angles θ <90°, residual ‘splash marks’ were visible on the substrate where the liquid had not completely evaporated in flight. This highlights another variable: the nozzle-to-substrate distance, which was adjusted to be sufficiently large that all the liquid evaporated from the droplets before reaching the substrate.

Properties of the colloidal suspension of nanodiamond particles

The successful transfer of nanodiamond to, and coating of, substrates depended primarily on the physical properties, such as viscosity, dielectric constant and surface tension, of the colloidal suspension exiting from the nozzle. Studies with similar nozzles have suggested that the primary droplets were generally monodisperse with sizes in the order of 1 µm although this is strongly dependent on the flow rate through the nozzle [11]. Increasing the concentration of the suspension had the effect of reducing the droplet size while also inducing agglomeration of particles. The presence of such agglomerates on the substrate increased the surface roughness of the subsequent film.

Maintaining a suspension of diamond nanoparticles with a narrow size distribution was vital for the homogenous coating of the substrates and depended on treatment of both the raw material and the suspension. The nanodiamond used in this study was formed by detonation synthesis in an oxygen-deficient atmosphere and had the smallest sizes (4 to 5 nm) of all synthetic particulate diamond [14-15]. These nanoparticles, as supplied, are clustered into tightly bound secondary agglomerates which dramatically increase the average particle size and need to be broken up before being dispersed into the suspension for electrospraying. Recent advances have enabled de-agglomeration of these secondary particles to produce clear, monodisperse nanodiamond colloids. The technique, outlined by Ozawa *et al.* [16], combines two processes (stirred-media-milling using zirconia beads and high-power ultrasonication) into a method termed bead-assisted sonic disintegration (BASD). The BASD technique achieves the required ~5 nm particulate size in about 30 minutes and is, therefore, much quicker than previous bead milling techniques. The presence of agglomerates sprayed onto the substrates may well be attributable to incomplete dispersion of the nanodiamond particles.

Perhaps the most crucial parameter in the electrospray techique described here is the liquid used to disperse the nanodiamond. Several criteria influence the choice of dispersion media. The boiling point and viscosity of the liquid determines how quickly it evaporates from the droplet when travelling between the nozzle and the substrate. Generally, a low boiling point/low viscosity liquid, such as methanol, is favoured because this should help ensure only the diamond nanoparticles deposit on the substrate. Using more viscous liquids than methanol, such as water and cyclohexane, causes unwanted splashing of liquid onto the substrate, leaving 'drying marks' in the seed layer. In the case of cyclohexane, the nozzle-to-substrate distance can be increased to counteract this problem. The high surface tension forces of water also have to be overcome as the droplets emerge from the nozzle tip. Related to this property, the polarity of OH bonds in water and alcohol molecules can be used to stabilize the charged nanodiamond particles. In this regard, water is the best liquid for nanodiamond particles but, as shown previously [13], it is not suited to the electrospray apparatus unless the liquid is removed from the particle stream before the ionization stage. Combining sufficient bond polarity and low boiling point, we found that alcohols provide the most suitable dispersion media for the deagglomerated nanodiamond particles. The OH bond polarity allows formation of hydrogen bonds to the charged diamond particles thereby decreasing the propensity to flocculation.

A variety of liquids were tested, including isopropyl alcohol, ethanol, methanol, cyclohexane and deionised water. The optimal bond polarity and viscosity was achieved using methanol, which became the dispersion medium of choice in this experimental setup. In many other cases, the addition of diamond nanoparticles to the liquid resulted in spontaneous flocculation into large clusters of particles, as revealed by the change from a clear to cloudy colloidal suspension.

To stabilize the 5 nm diamond particles in liquids less polar than water, we investigated addition of a polymer to coat the primary particles and prevent their aggregation. Polyvinylpyrrolidone (PVP) is sufficiently polar, due to the carboxyl group on the pyrrole ring, to adsorb onto the charged surface of the nanodiamond particles. This generates a steric layer that prevents the particles getting sufficiently close to agglomerate via van der Waals forces. However, despite successfully dispersing the colloid in almost all the liquids (except for the non-polar cyclohexane where significant flocculation was observed), the use of PVP polymer was abandoned following analysis of the seed layers by optical microscopy and of the grown films by electron microscopy. The polymer increased the viscosity of the droplets and was also found to transfer to the substrate. As this polymer layer dried it formed a cracked pattern on the substrate which was still visible in the diamond films post-growth. It was thought that the extreme conditions of the MWCVD plasma might reduce the influence of this patterning. To some extent this was true, as the nanocrystalline films deposited in the microwave reactor were more uniform than the UNCD films grown in the hot-filament reactors at ADT.

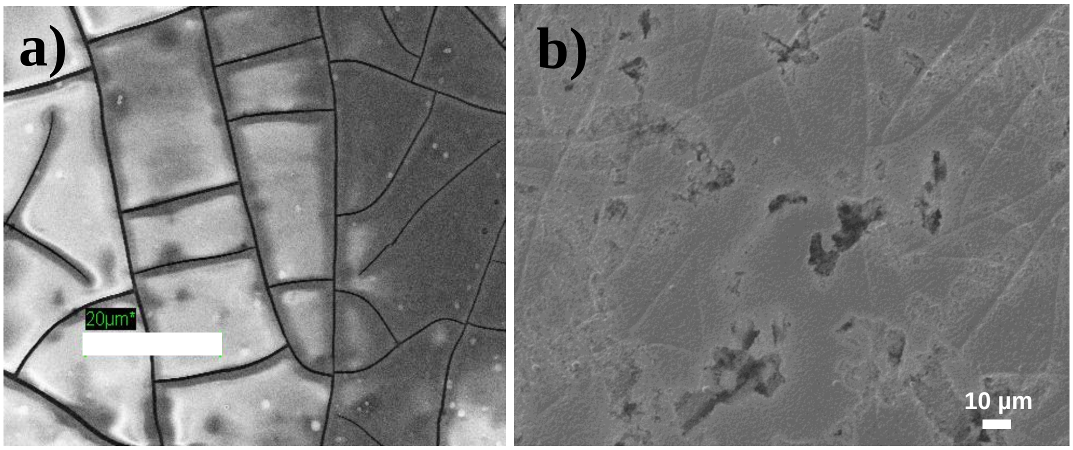

Figure 2. Patterning of substrates due to the PVP polymer drying and cracking, observed a) prior to diamond deposition by optical microscopy (×20) and b) following HFCVD of a UNCD layer by electron microscopy (used with permission from ADT, Ltd.)

The patterning can be seen in Fig.2a, which shows a seeded film prior to diamond deposition. The severity of this problem precludes the use of PVP to stabilize the suspension, limiting the types of liquid which can be used in electrospray deposition. De-agglomeration of the detonation nanodiamond by BASD in methanol, the dispersion medium to be used in this electrospray technique, minimized flocculation and thus removed the need for polymer stabilization.

Analysis of films following diamond deposition

The success of a nucleation layer is best established by growing a thin film, and two methods were employed in this study. The original optimization of the electrospray apparatus involved growing a nanocrystalline diamond layer by MWCVD using an argon rich plasma ($95\%Ar/1\%CH_4/4\%H_2$) and later testing by growing UNCD films on 2-inch Si wafers at ADT by HFCVD. The latter study enabled comparison with ADT's standard ultrasonic nucleation technique. An example of an UNCD film grown by HFCVD on a nanodiamond/PVP coated substrate is shown in Fig.2b.

The cracked patterning due to the dried PVP polymer is still present in the HFCVD grown UNCD film, whereas NCD films grown at Bristol by MWCVD using the same seeding technique are uniform and do not exhibit the lined pattern (Fig.3a). The difference is likely to be due to two important factors. First, the ADT films are much thinner (1.15-1.25 μm for the UNCD films compared with >5 μm for the Bristol NCD films), so inhomogeneities in the seed layer are more likely to be observed in the UNCD layer. Secondly, the higher growth rates, substrate temperatures and atomic hydrogen density associated with the MWCVD technique will reduce the influence of non-uniform areas of the seed layer and 'burn off' any remaining polymer.

Analysis of the surface roughness of HFCVD grown UNCD films using a stylus profilometer over a 2 mm scan shows considerably higher values for the electrospray seeded films compared to the ADT seeding method. However, Raman analysis (not shown) confirms that the quality of the diamond (the ratio of sp^3-to-sp^2 carbon content) is not influenced by the nucleation method chosen having similar spectra for both electrospray and ADT seeded films.

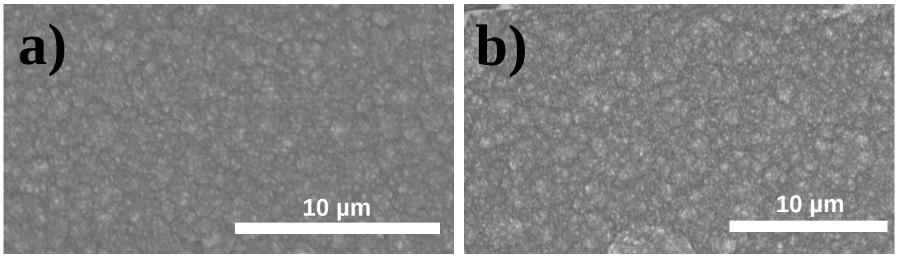

Figure 3. NCD films grown by MWCVD on a) a nanodiamond/PVP seeded substrate showing good uniformity and no evidence of polymer influencing the diamond layer, and b) a diamond film seeded with a PVP-free nanodiamond/methanol dispersion – showing almost identical surface roughness.

After seeding with the BASD nanodiamond in methanol, removing the need for PVP stabilization, another set of NCD films were grown by MWCVD and an example is shown in Fig.3b (UNCD deposition has not been carried out on these substrates at the present time). The NCD films grown with and without PVP in the seed layer display very similar surface roughness.

A major advantage of this electrospray technique over photoresist spin-coating or other abrasive seeding methods is the ability to nucleate more complex shapes other than planar substrates. To this end, we have demonstrated successful seeding of a variety of three dimensional substrates, including 10 mm^3 tungsten carbide cubes and patterned Si wafers (examples of which are shown in Fig.4a and 4b).

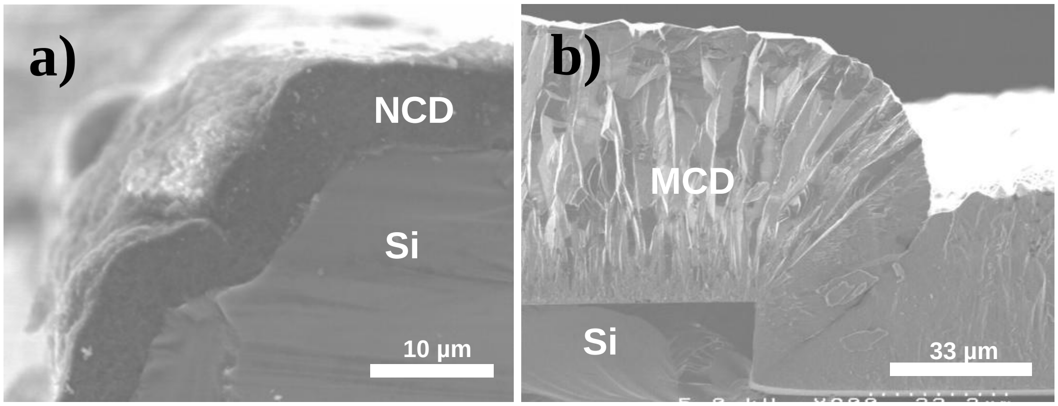

Figure 4. Examples of electrospray seeding using nanodiamond in methanol and subsequent diamond growth on patterned silicon substrates: a) section through thick NCD film and Si substrate showing successful seeding and subsequent growth around substrate edge and b) section of thick MCD film on patterned Si substrate containing recessed areas.

CONCLUSIONS

We have demonstrated a quick, simple and versatile electrospray technique for seeding substrates with a nucleating layer of nanodiamond particles. The addition of a colloid stabilizing polymer in the seed suspension was investigated but rejected as it can cause unwanted patterning of the seed layer which is particularly apparent in thin UNCD films grown by HFCVD. Deagglomerating the nanoparticles by the BASD method in methanol removed the need for addition of any polymer and allowed the colloid to be directly sprayed onto a range of substrate sizes and materials. This seed layer has been shown to be very suitable for subsequent growth of uniform, homogenous films of both nano- and microcrystalline diamond. Any modification of the nanodiamond structure due to the experimental parameters has not been studied but appears not to influence the seed layer or subsequent film growth whereas it could be problematic for more diverse applications.

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