

Polymer-based nucleation for chemical vapour deposition of diamond

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ABSTRACT: Chemical vapour deposition of diamond on foreign substrates is hindered due to its high surface energy. Therefore, nucleation treatment has to be employed to initialize the formation of diamond crystals. This article deals with diamond growth on silicon substrates coated with three types of polymers: (i) polystyrene (PS), (ii) polylactic-*co*-glycolic acid (PLGA), and (iii) polyvinyl alcohol (PVA) were applied in different forms, i.e., microspheres (PS, PLGA), monolayers (PLGA), multilayers (PLGA, PLGA/PS), and composites with embedded diamond nanoparticles (PLGA, PVA). Thin polymers and microsphere monolayers did not contribute to the diamond nucleation and/or growth. A thicker continuous polymer film (>750 nm) or thin polymer/microsphere layer led to a homogeneous and dense formation of diamond grains. In the case of nucleation using polymer composites, where the thin polymer film serves as a 3D carrier matrix for embedded diamond nanoparticles, a comparable nucleation density to the well-established ultrasonic seeding method was achieved. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43688.

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INTRODUCTION

Due to their extraordinary properties, diamond thin films are suitable for a wide range of applications including optics,¹ photonics,² electronics,³ sensorics,⁴ biomedicine,⁵ etc. However, the synthesis of large area, fully closed and homogeneous thin films on nondiamond substrates (such as metal, Si, glass) is still a challenge because of the high surface energy of diamond.⁶ The crucial step in diamond deposition is the nucleation process, which initializes the surface conditions and creates nucleation centres necessary for the formation of diamond crystals. The used nucleation method controls the properties of the final diamond film (such as adhesion, grain size, and morphology), thus, it directly determines its industrial uses. For example, smooth and homogeneous diamond films with small grains and low surface roughness are required for optical^{1,7} and MEMS⁸ applications, while thick films with large grains are needed for heat spreading.⁹

The most commonly used nucleation (or surface pretreatment) methods are scratching or mechanical abrasion, bias enhanced nucleation (BEN)^{10,11} and ultrasonic seeding with diamond nanoparticles (DNPs).^{12,13} Presently, these methods are becoming routinely used. However, they are limited in treating specific substrates such as polymers, ultrathin metal layers, optical mirrors, membranes, or electrically insulating substrates (glass or

ceramics). In such cases, applying a liquid dispersion of diamond nanoparticles onto the soft substrate by inkjet printing or dip coating has proven a viable alternative.¹⁴

Recently, great effort has been dedicated to innovative polymer-based nucleation methods, where the polymer acts as a carrier matrix for embedded diamond nanoparticles^{15–17} or as a primary carbon source for the sp² to sp³ transformation.^{18–20} Using polymer composites it is possible to achieve a very high density of diamond nanoparticles on the substrate and the subsequent growth of a fully closed ultrathin diamond film (below 100 nm). Polymer coatings have also been shown to be suitable for the nucleation of substrates with complex 3D geometry. Girard *et al.*²¹ provided seeding of 3D substrates with high aspect ratio. This method is based on the electrostatic interactions between the oxygen terminated nanodiamonds (characterized by a negative zeta potential) and the cationic polymer coated sample. Opposite charges caused grafting of particles to the substrate surface via the thin polymer layer, which is then immediately removed during the first seconds of the chemical vapour deposition.

Polymer composites were also used in the form of nonwoven textiles containing diamond nanoparticles.^{22,23} These nanofibre composites were produced by needle-less electrospinning²⁴ and were found to be effective for coating copper rods with

Table I. Materials Used for Study of Diamond Nucleation Process from Polymer Coatings

Material	Molecular formula	Specification	Dispersion composition	Form on the sample
PS	(C ₈ H ₈) _n	Aqueous dispersion (5 wt %) of PS with diameter of 940 nm (microParticles GmbH, Germany)	PS:methanol 1:2	Monolayer of microspheres
PLGA	(C ₆ H ₈ O ₄ *C ₄ H ₄ O ₄) _n	Degradex, Plain Microspheres PLGA with diameter of 1 μm, Freeze Dried (Phosphorex, Inc., USA)	1.2 mg of PLGA in 80 μL DI ^a (15 wt %)	Monolayer of microspheres
PLGA	(C ₆ H ₈ O ₄ *C ₄ H ₄ O ₄) _n	PLG 8531 grade copolymer granules of L-lactide and Glycolide in a 85/15 molar ratio (Purasorb)	20 mg of PLGA in 1 mL DCM ^b (20 wt %)	Thin film (mono- or multilayer)
PVA	(C ₆ H ₄ O) _n or [-CH ₂ CHOH-] _n	Poly(vinyl alcohol) hydrolyzed powder, mol wt 89,000-98,000 (Sigma Aldrich, Germany)	150 mg of PVA in 30 mL DI ^a (5 wt %)	Thin film
DNPs ^c	-	Ultra-dispersed detonation diamond powder, grain size 5 nm, 98.8 wt % (NanoAmando, New Metals and Chemicals Corp. Ltd., Kyobashi)	~10 wt % of diamond nanoparticles dispersed in DI ^a)	Thin film with nanoparticles

^aDeionized water.^bDichloromethane.^cDiamond nanoparticles.

diamond thin film. In this case, nanofiber composites also contributed to the inhibition or suppression of carbon diffusion into copper as well as to the lateral stress compensation.²³ Another study has shown that DNPs dispersed in the PVA matrix led to the formation of long fiber-like diamond structures. This effect was attributed to the combined effect of seeding by DNPs, the GPa pressure difference across the fiber interface and local nanocracks. The highest concentration of DNPs resulted in the growth of a nearly continuous diamond film on Si substrates. For low DNP concentration in the PVA polymer matrix, shortening of the fiber-like structures and the lowering of surface coverage was observed.²² All these results confirm that utilizing PVA polymer nanofibers with diamond nanoparticles is a quick, easy and economical method to nucleate different substrate materials with 3D geometry on a large scale.

In the abovementioned strategies, diamond growth is primarily initialized by the diamond nanoparticles. However, there is also a possibility of transformation of polymers into diamond structures or films. Recently, polycarbynes [such as poly(methylcarbyne), poly(phenylcarbyne) or poly(hydridocarbyne)]²⁵ have aroused interest among researchers for their potential use as polymeric precursors to promote diamond growth. Poly(phenylcarbyne), as a carbon based random network polymer, was transformed into diamond-like carbon or diamond phases at atmospheric pressure by thermal decomposition (at 1000–1600 °C for 7 h in argon ambient).²⁶ Successful transformation of poly(methylcarbyne) to diamond was achieved by Nur *et al.*¹⁹ via sintering under atmospheric pressure of nitrogen at 1000 °C for 24 h. Early studies about poly(phenylcarbyne) as a seeding layer on silicon substrates exposed to hot filament CVD revealed enhanced nucleation densities^{18,27} and growth of isolated diamond crystals in size ranging from nanometers up to

micrometers was observed. However, applying other polymers (phenolic resin, polyethylene, pump oil, etc.) as precursors did not result in diamond growth at lower substrate temperatures (400–500 °C).

In the present study we focused on and investigated the influence of another group of polymer coatings on the nucleation and growth of diamond films deposited by microwave plasma enhanced chemical vapour deposition. Silicon substrates were coated with three types of polymer: polystyrene (PS), poly(lactic-*co*-glycolic acid) (PLGA) and polyvinyl alcohol (PVA). All these polymers are widely used and easily commercially available in different forms (e.g., nano/microspheres, granules, fibers, etc.). In this study we used PS in the form of microspheres, PVA in the form of thin films and PLGA in the form of microspheres as well as thin films (mono- and multilayers). Besides these experiments, the diamond growth from PLGA and PVA polymer composites containing diamond nanoparticles was also studied. The obtained results were compared with reference samples: (i) clean and (ii) ultrasonically seeded Si substrates.

EXPERIMENTAL

Materials and Sample Preparation

Silicon (100) wafers of size 1 × 1 cm² were used as substrates. First, the substrates were ultrasonically cleaned in isopropyl alcohol and deionized water for 10 and 5 min, respectively, followed by drying in nitrogen blow. Then, the substrates were treated in oxygen plasma to achieve hydrophilic surfaces.

Three types of polymers were used: (i) poly(1-phenylethene) (commonly known as polystyrene), (ii) poly(lactic-*co*-glycolic acid), and (iii) poly(vinyl alcohol) in different forms including microspheres, polymer films and polymer composites

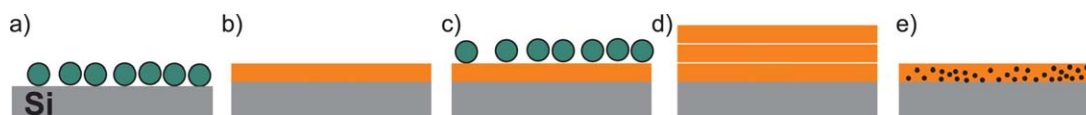


Figure 1. Schematic illustration of polymer coatings used for diamond nucleation: (a) monolayer of microspheres, (b) polymer monolayer, (c) combination of monolayer and microsphere array, (d) multilayer and (e) polymer composite monolayer containing diamond nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing diamond nanoparticles. The complex description of used materials is summarized in Tables I and II.

Note to the data in Table I, the aqueous dispersion of PS microspheres was diluted in Triton X-100/methanol solution (1:400) at a ratio of 1:2. The PLGA granules were dissolved in dichloromethane and the PVA granules in deionized water using magnetic stirring for 1 h.

The polymers (both microspheres and thin films) were applied onto the Si substrates using spin-coating (model Laurell WS-650). Approximately 50 μL of polymer dispersion was dropped onto the substrate surface. The parameters for spin-coating were optimized for specific polymer dispersions (i.e., for microspheres to obtain hexagonal-close-packed monolayer and for thin polymer layers to achieve homogeneous coverage over the whole substrate surface). The rotation speed was varied in the range 1000–8000 rpm and process time in the range 1–3 min. The following combinations of polymers were studied: monolayer of polymer microspheres, bilayer (i.e., combination of microspheres and thin polymer layers) and multilayers (i.e., thicker polymer film) obtained by multistep spin-coating. The applied polymer coatings are schematically illustrated in Figure 1.

In the case of polymer composites, two strategies were employed. In the first strategy (labeled as I. in Table II) diamond nanoparticles were directly dispersed in polymer solution (PLGA or PVA). In the second strategy (labeled as II.) DNPs were first dispersed in deionized water and then mixed with a PVA polymer solution at different ratios (3:1, 1:1, and 1:3). PVA was chosen because it is water-soluble, and has excellent film forming and emulsifying adhesive properties. For PLGA experiments it was not possible to use water-based DNP dispersion, because the solvent (DCM) of PLGA is not miscible with water. Furthermore, PLGA degrades in the presence of water.

Simultaneously with the diamond growth on polymer coated Si substrates, reference samples were used as well: (i) clean Si substrates (i.e., ultrasonically cleaned and oxygen plasma treated substrates) and (ii) Si substrates standardly nucleated using ultrasonic seeding with diamond nanoparticles.¹²

Table II. Polymer Composites Used for Diamond Nucleation

Nucleation method	Polymer	Dispersion composition
I. Polymer + DNPs	PLGA or PVA	3 mL of polymer solution (5 wt %) + 5 mg of dry DNPs
II. Polymer + (DNPs in DI)	PVA	5 wt % of polymer solution (PVA in DI) + 10 wt % of DNPs in DI by different ratio (3:1, 1:1, 1:3)

Diamond CVD and Characterization Methods

The diamond growth process (labelled as “diamond CVD”) was carried out using microwave plasma enhanced chemical vapour deposition (MWCVD) in a focused ellipsoidal cavity reactor.²⁸ The deposition process parameters for the experiments with microspheres and polymer layers were as follows: gas mixture 1% of CH_4 in H_2 , total gas pressure of 5 kPa, MW power of 2.5 kW, deposition time up to 1 h and temperature $\sim 800^\circ\text{C}$ and $\sim 650^\circ\text{C}$ (for set 2 and set 3, respectively). Deposition parameters for the experiments with polymer composites were as follows: total gas pressure of 3 kPa, MW power of 2.5 kW, process time 2 h and substrate temperature about 300°C .

The surface morphology of the samples was characterized using scanning electron microscopy (SEM, Tescan MAIA3 FE-SEM). The chemical composition (i.e., diamond character) was evaluated using Raman spectroscopy (Renishaw In Via Reflex Raman spectrometer) with an excitation wavelength of 442 nm. Statistical analysis of diamond clusters (e.g., surface coverage, distribution) was determined from low magnification (5–20 kx) SEM images using image processing and analysis software (Atlas, Tescan, Ltd.).

RESULTS AND DISCUSSION

Microspheres and Polymer Layers

In the first set of experiments, monolayers of PS or PLGA microspheres were studied. Figure 2(a) shows the surface morphology of a Si substrate covered by a hexagonal-close-packed monolayer of PS microspheres with a diameter of 940 nm.

After diamond CVD, the PS microspheres were etched away, only fingerprints of the original microspheres were observed, which preserved the periodicity of their initial ordering [Figure 2(b)]. Diamond growth was not observed, even when deposition parameters were varied (the temperature varied from 400°C to 900°C and methane concentrations from 0.5% to 5%). Similar results were obtained for PLGA microspheres with a diameter of 1 μm . In comparison, for the ultrasonically seeded Si substrate, standard deposition parameters (2% CH_4 in H_2 , 900°C , 30 min) resulted in the growth of a thin fully closed polycrystalline diamond film consisting of very small grains [<100 nm, Figure 2(c)].²⁹

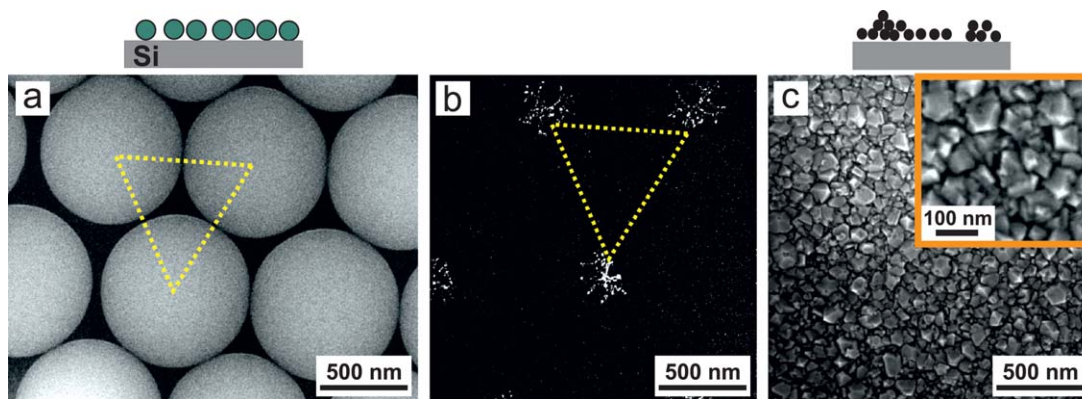


Figure 2. SEM images of a monolayer of PS microspheres with a diameter of 940 nm (a) before and (b) after the diamond CVD. The yellow triangles illustrate the initial and preserved periodicity of the microspheres before and after the diamond CVD. (c) Surface morphology of diamond film grown on the reference sample, i.e., the Si substrate ultrasonically seeded with diamond nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These results reveal that the etching of polymer microspheres is too fast and PS does not promote the diamond growth. As soon as the deposition process starts, the diameter of the spheres is reduced and the close-packed monolayer becomes loosely packed. Then reactive species from plasma penetrate into the gaps between the spheres and their etching further accelerates because the etching occurs in all directions. In the next set of experiments, polymer films were studied, which seem to be more resistant to plasma etching.

First, a 250 nm thin PLGA polymer layer was employed. After the diamond CVD, randomly distributed diamond clusters with a diameter of ~ 300 nm were observed on the Si surface. However, the surface coverage was nearly the same as for the clean Si substrate ($\sim 12\%$) [Figure 3(a,b)]. For the clean Si, the appearance of isolated diamond crystallites is attributed to spontaneous nucleation which is described in more detail in refs. 6 and 30.

For all the samples, the diamond character of deposited clusters was confirmed using Raman measurements, which exhibited a sharp diamond peak located at ~ 1331 cm^{-1} and a broad

G-band located at ~ 1520 cm^{-1} [Figure 3(d)]. The peak at ~ 1331 cm^{-1} is a characteristic line for the phonon mode of the sp^3 crystalline diamond phase and the G-band (or graphite-band) is attributed to sp^2 carbon bonds and represents graphitic phases present at grain boundaries.³¹

Surface coverage increased nearly five times (up to $\sim 61\%$) when the thin PLGA polymer layer (250 nm) was covered by an additional layer of PLGA microspheres [Figure 3(c)]. This observation indicates that applying thicker PLGA layers increases the number of active centres, while thicker PLGA layers could promote diamond growth either as a source of carbon or via the transformation of polymer to sp^3 carbon phases. Moreover, a thicker polymer film equalizes the ratio between two competitive processes, i.e., polymer etching and diamond growth. Therefore, the next set of experiments focused on investigating the dependence of nucleation on the polymer film thickness. In addition, to minimize the spontaneous nucleation observed in the first experiments [Figure 3(a)], the deposition temperature was decreased to 650 $^{\circ}\text{C}$.

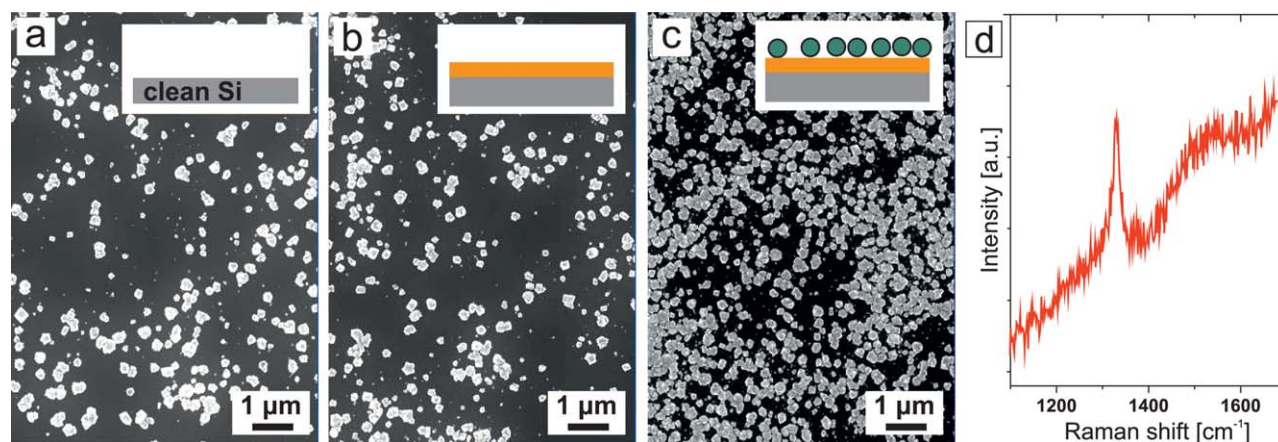


Figure 3. Surface morphology of samples after the diamond CVD of (a) clean Si substrate, (b) Si sample covered by thin PLGA layer and (c) Si sample covered by thin PLGA layer and PLGA microspheres. (d) Representative Raman spectrum of diamond grains grown on sample covered by thin PLGA layer. (Deposition parameters were as follows: 1% CH_4 in H_2 , 800 $^{\circ}\text{C}$, 1 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

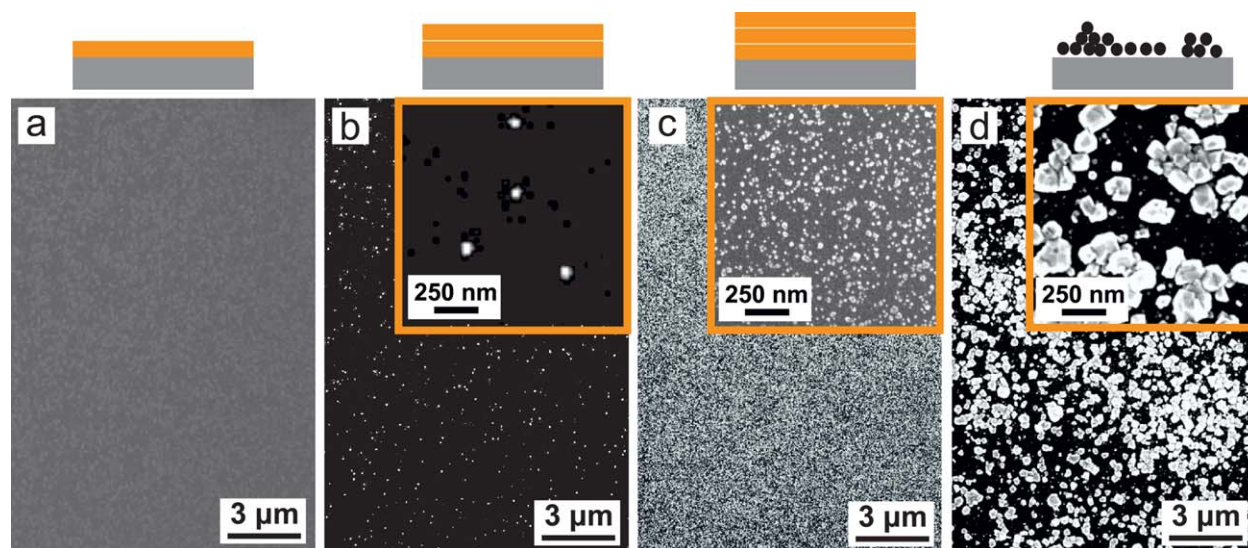


Figure 4. Surface morphology of samples coated with polymer layers of different thicknesses after the diamond CVD. Si substrate covered by (a) one, (b) two and (c) three PLGA polymer layers. (d) reference Si substrate nucleated using ultrasonic seeding with diamond nanoparticles after the diamond CVD. (Deposition parameters were as follows: 1% CH₄ in H₂, 650 °C, 1 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 shows the surface morphology of Si substrates coated with one, two and three PLGA layers and a reference sample, after the diamond CVD. The thickness of polymer films was evaluated to ~ 250 nm, ~ 500 nm, and ~ 750 nm for one, two, and three layers, respectively. After the diamond CVD, the surface of the clean Si substrate (not shown here) and the Si substrate coated with the polymer monolayer [Figure 4(a)] remained nearly featureless. For both these samples the spontaneous nucleation was suppressed and the thin polymer layer did not promote any diamond nucleation and/or growth.

The two times thicker PLGA film resulted in the growth of rarely distributed and isolated diamond clusters ~ 70 nm in size [Figure 4(b)]. Further increase of the PLGA film thickness to ~ 750 nm (i.e., three layers) led to the formation of the most densely distributed diamond clusters [Figure 4(c)]. The size of the clusters was ~ 30 nm, which is much smaller than in the case of the reference sample [Figure 4(d)]. The reason for this size difference is probably the longer incubation period, which precedes the nucleation process for the sample covered with PLGA polymer. The diamond character of formed clusters was confirmed using Raman spectroscopy (not shown here). Raman spectra revealed features similar to the previous experiments [Figure 3(d)].

Diamond growth from a polymer layer is a complex issue which generally involves two competing processes—(i) diamond growth from the additional source of carbon and (ii) polymer melting, decomposing and full etching by atomic hydrogen. It was demonstrated that the equilibrium between these processes is sensitive to the diamond deposition parameters. During the early stage of growth the concentration of carbon in the close vicinity of the Si substrate surface is higher (from polymer as the solid source), which can enhance the formation of diamond nuclei or polymer transformation into the sp^3 bonded carbon phase (i.e., diamond phase). A similar transformation was observed for polycarbonyl polymers.^{18–20}

Additionally, the polymer film thickness plays a crucial role. An adequately thick polymer layer (750 nm for PLGA) provided a denser distribution of diamond clusters (i.e., nucleation centers) than typically used ultrasonic seeding with diamond nanoparticles. Finally, such densely packed clusters with small diameter allowed the deposition of fully closed ultrathin diamond coatings (<100 nm) suitable for optical applications.²¹

Polymer Composites

In the last set of experiments, Si substrates were covered with PLGA and PVA polymer composites containing diamond nanoparticles (see Figure 5).

The direct dispersion of diamond nanoparticles in a polymer solution (first strategy) resulted in the formation of large and rarely distributed diamond clusters. For the PLGA polymer composite, the size of clusters varied from 400 to 800 nm in diameter [Figure 5(a)]. For the PVA composite the clusters were smaller [100–500 nm, Figure 5(b)]. The higher degree of agglomeration of DNPs in PLGA than in PVA dispersion is mainly attributed to a different solvent being used (see Table I). In the second strategy, the PVA granules were first dispersed in deionized water and only then mixed with the polymer solution. In this case the formed diamond clusters were smaller (30–50 nm) and they became more homogeneously distributed [Figure 5(c,d)]. During the initial phases of the diamond growth from polymer composites, some processes taking place could be the same as in the case of the previously discussed pure polymer layers. However, in this case, the polymer acts as the carrier matrix for the diamond nanoparticles which primarily promote the diamond growth.

Further, it was observed that the morphology and density of grown crystals is influenced by the mixing ratio of the polymer solution and deionised water with diamond nanoparticles (labeled as “DNPs in DI”). By decreasing the mixing ratio of PVA to “DNPs in DI” the agglomeration of nanoparticles was lower and the dispersion led to

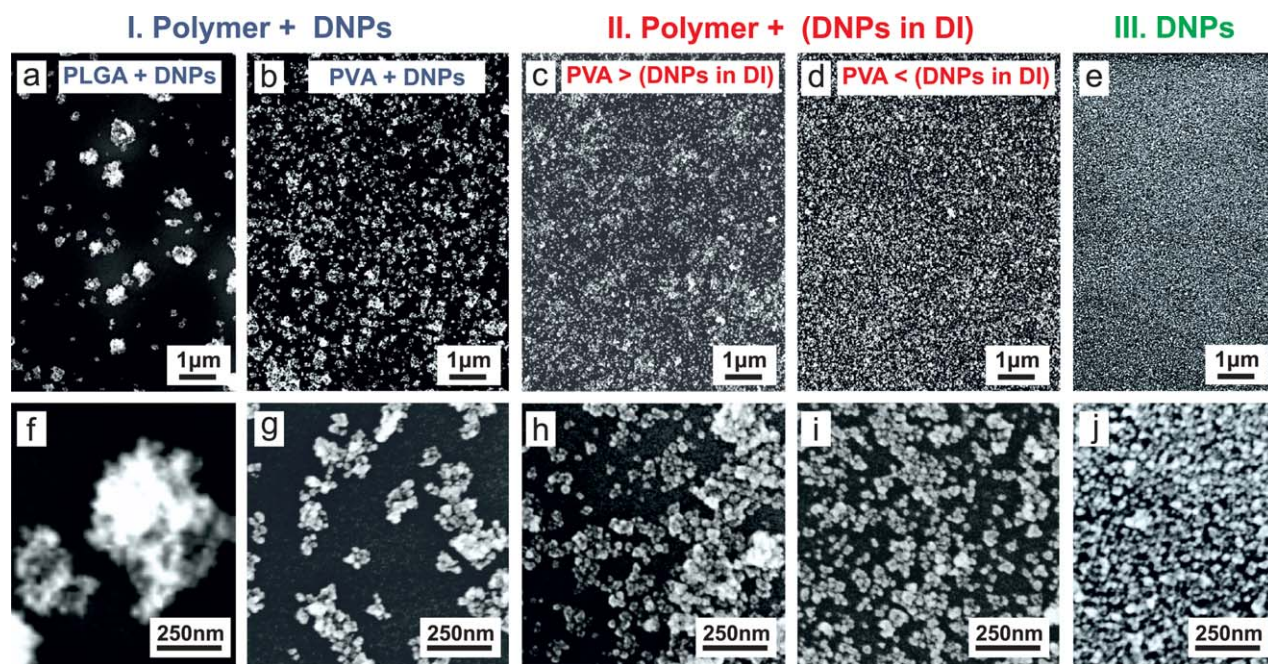


Figure 5. Surface morphology of samples covered by polymer composites after diamond CVD: (a,b) PLGA and PVA solution mixed with diamond nanoparticles; (c,d) PVA solution mixed with diamond nanoparticles dispersed in deionized water at a ratio of (c) 3:1 and (d) 1:3; (e) reference Si substrate nucleated by ultrasonic seeding with DNPs. Bottom row (f–j) shows SEM images taken at higher magnification for the corresponding substrates. (Deposition parameters were as follows: 1% CH₄ in H₂, 300 °C, 2 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a more homogeneous distribution of diamond on the substrate. The ratio of 3:1 PVA to “DNPs in DI” resulted in a less homogeneous distribution of diamond clusters and the agglomerates were larger in size up to 200 nm [Figure 5(c)]. For the opposite ratio (i.e., 1:3), the diamond CVD led to the formation of more homogeneously distributed diamond clusters on the Si surface without any larger agglomerates [Figure 5(d)]. This surface morphology is similar to the reference sample nucleated using ultrasonic seeding with diamond nanoparticles [Figure 5(e)]. The nucleation method based on the PVA composites with diamond nanoparticles has been already successfully utilized for diamond growth on a fragile 3D GaN membranes.³²

CONCLUSIONS

We presented a simple and low cost polymer-based nucleation process as an alternative to the standard nucleation methods used for initializing diamond growth. Three different forms and three types of polymers [polystyrene, poly(lactic-co-glycolic acid) and polyvinyl alcohol] were studied including microspheres, thin films and composites. It was shown that thin polymer layers (<250 nm) or microsphere (diameter of ~1 μm) monolayers did not contribute to diamond nucleation and/or growth in a broad window of process parameters. However, using thicker continuous polymer films (>750 nm) or a combination of thin film/microsphere arrays unambiguously led to a homogeneous diamond growth. In the case of polymer/DNPs composites, the PLGA resulted in a high degree of DNPs clustering. On the other hand, the PVA-based composite enabled a better distribution of DNPs with a comparable nucleation density to the standard ultrasonic seeding. In summary, we showed

that the optimized polymer-based nucleation process has a high enough nucleation density and is usable for deposition of fully closed ultrathin diamond coatings (<100 nm) on mechanically soft, fragile or unstable substrates.

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