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Inkjet printing of nanodiamond suspensions in ethylene glycol for CVD growth of patterned diamond structures and practical applications

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ABSTRACT

Fabrication of patterned diamond structures in an inexpensive way is desirable for a variety of practical applications. Inkjet printing is a well-developed and inexpensive process by which liquid ink, as well as solid suspensions in a properly formulated solution, can be applied in a precise quantity and at selected locations on a rigid or flexible substrate. In this work, nanodiamond suspensions in ethylene glycol were used as inks for the printing of patterned nanodiamond particles on substrates. By utilizing inks with optimized nanodiamond suspensions, high number density of diamond nanoparticles were laid down directly by inkjet printing to form almost continuous nanodiamond films of designed patterns on a substrate. A brief chemical vapor deposition process that lasted for 15 to 20 min or so was adequate for the further growth of nanodiamond seeds to form a continuous nanocrystalline diamond film. This process allows inexpensive seeding of diamond in selected areas as well as possible formation of 1-D, 2-D, and 3-D nanodiamond structures. Details of the inkjet printing process and its potential applications will be reported.

1. Introduction

Synthetic diamond fabricated using chemical vapor deposition methods has been studied extensively and has become a promising material for various potential applications due to its outstanding physical, mechanical, chemical, and biological compatibility properties [1–3]. Among various diamond deposition methods, including hot filaments, combustion flames, plasmas and others, microwave plasma assisted chemical vapor deposition (MPCVD) has the greatest advantage of being reproducible and possessing precious in-process control for the growth of diamond [4–8]. In the present work, MPCVD was used to deposit nanocrystalline diamond on patterns that were seeded with nanodiamond by inkjet printing using inks containing nanodiamond powder.

Desired diamond patterns with different dimensions for various applications can be achieved by either pre-growth selective seeding or post-growth etching of diamond [9–15]. Pre-growth selective seeding is a relatively cost-effective method. Inkjet printing is a mature and useful technique for direct writing and printing for the printing industry. In the reference [15], water based ink was used for a regular inkjet printer to print diamond seeds on paper-mounted substrates. The number density of printed diamond seeds was low and subsequent diamond CVD for as long as twenty some hours was needed to form polycrystalline diamond films of patterns showing many scattered diamond particles surrounding the patterns due to the splashing of ink. Commercial inkjet printers designed for printing special inks such as those containing carbon and silver nanoparticles for direct printing of conductive micro-patterns [16] are available in the market. When the inkjet printing technique is employed for pre-growth selective nucleation of diamond, nanometer-sized nanodiamond powder is mixed into a solvent with the desired viscosity and used as the ink, which is then used for direct printing of patterns. Nanometer-sized diamond powder mixed with commercially available conductive ink for the selective nucleation process has been demonstrated previously [17]. Expensive lithographic and etching facilities for post-growth patterning for pattern dimensions within the capability of inkjet printing could be replaced with commercially available and relatively inexpensive image software for pre-growth selective seeding.

For large scale production of diamond films with a high demand of precision patterning, the cost of diamond seeding can be further reduced by selectively printing diamond seeds only on patterns that are pre-formed by lithographic processes instead of seeding the whole sample surface. This process yields an easy technique for forming possible 1-D, 2-D. and 3-D nanodiamond structures. In this paper, details on this process and progress in implementing it will be reported, and potential applications will be discussed.

2. Experimental details

Dimatix Materials inkjet printer and cartridges were employed for the selective printing of diamond seeds. This particular printer was

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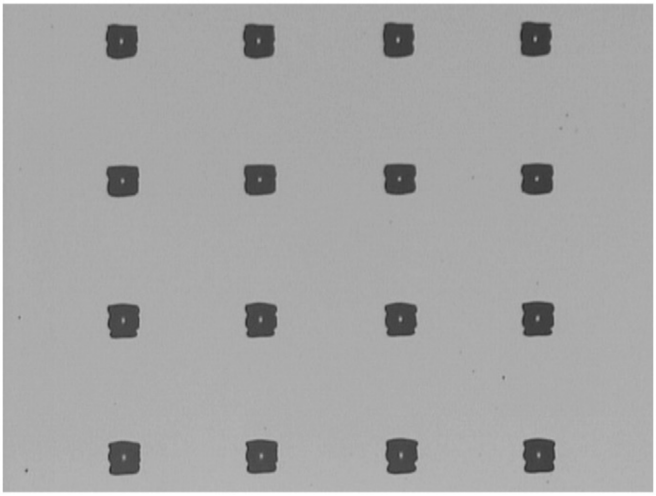

Fig. 1. An inkjet printed array (6×6) of 36 squares of 200 μm×200 μm in dimensions.

originally designed for printing structural patterns with special materials such as carbon and silver. Ink with nanodiamond suspensions was custom-made for our research by International Research Center (ITC) in North Carolina, USA. For this ink, 12 g of 40–50 nm of aggregates with 4–5 nm primary nanodiamond particles was suspended in every 1 Liter of ethylene glycol. The stability is due to the following factors: (i) additional high purification of the initial nanodiamond; (ii) surface groups dissociating in the solvent resulting in high surface charge (so that inter-particle repulsion prevents agglomeration); and (iii) small size of the nanodiamond particles, that prevent undesirable sedimentation. Diamond particles were well-dispersed in the ethylene glycol to form a solution with desirable viscosity and would not precipitate to the bottom for an extended period of time. As a comparison, the cited reference [15] reported the use of water based inks, which didn't provide as high density and uniformly distributed diamond seeds as what is being demonstrated in this work. Besides, water is an unfriendly material for vacuum systems where diamond CVD is done.

The printing process was performed with both the cartridge head and the substrate kept at room temperature in order to minimize vaporization of the solvent during the printing process. Fine patterning was achieved by means of optimizing the drop spacing and firing distance. In this study, drop spacing ranging from 12 μm to 25 μm was examined. Each cartridge reservoir had 16 nozzles linearly spaced at 254 μm for individually controlled printing. For this set of experiments for printing micro-patterns, only a few of these nozzles were used. Furthermore, the effective size of the nozzle opening was 21 μm, which was much larger than the size of the diamond powder.

Nanocrystalline diamond films were deposited in gas mixtures of 1% CH_4+2% H_2+97% Ar with 800 W of microwave power while the gas pressure was kept at 150 Torr and growth temperature was approximately 570–620 °C [8,18]. Because of the excellent nanodiamond suspension, very high surface number density of fine nanodiamond seeds was able to form an almost continuous film on the substrate even before diamond CVD was done. The sizes of nanodiamond seeds were of a narrow distribution which allowed a very smooth diamond film to be grown on the printed seeds. This is in contrast to the large-grained polycrystalline films that were reported by the cited reference [15]. With the uniformly suspended diamond powder in the solution, it took as short as 15 to 20 min of microwave plasma CVD to grow diamond on the diamond nanoparticles to form pinhole-free nanodiamond films of desired patterns with few scattered diamond particles around the printed areas usually due to splashing of inferior inks.

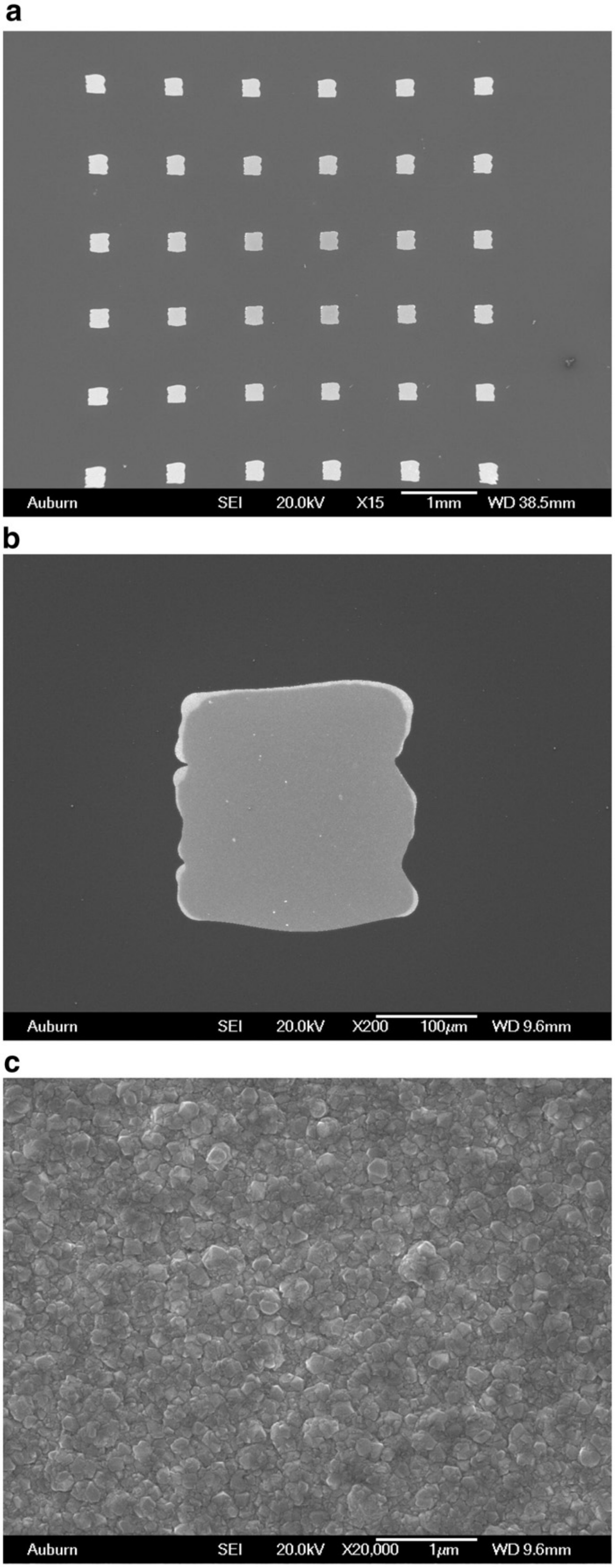

Fig. 2. SEM images of a printed sample, as shown in Fig. 1, after 20 min of diamond growth (a) an array of squares; (b) a continuous film obtained after 20 min of deposition; (c) surface morphology of a deposited diamond film.

Silicon substrates with a 5000 Å thick silicon dioxide layer were utilized as the pre-patterned substrates for the combined selective printing/lift-off process. Patterns and printing sites were designed to ensure that the diamond seeds were only printed on desired areas so that a minimum amount of diamond seeding ink was used. After a short period of growth time, typically less than 10 min, a lift-off process was performed using HF solution that removed the silicon dioxide layer along with diamond on it from the undesired areas outside of the pre-formed pattern. The substrate was subsequently subjected to further diamond growth to realize continuous films. Unlike conventional seeding processes, this technique allows users to economize the use of diamond powder and also obtain sharp pattern edges.

The specimens were characterized by means of scanning electron microscopy (SEM) for surface morphologies, and Raman spectroscopy for crystallinity and defects of diamond or diamond containing films.

3. Results and discussion

Key requirements for high-performance inkjet printing of diamond seeds are, for example, (i) Nano-scaled diamond seeds remain suspended instead of forming large aggregates; (ii) Printed ink remains in the pre-designed printed fine areas on the substrates without splash or unwanted re-flow of the ink; (iii) Diamond seeds don't clog the orifice of the inkjet; and (iv) Multiple printing on the same spot with variable quantity of ink and ink-covered areas can be precisely done. A practical and useful inkjet printing technique for the growth of diamond fine patterns is presented in this paper. Fig. 1 is an optical image of a printed pattern on silicon. The silicon substrate was cleaned by HF solution to remove residual silicon dioxide on the surface, with no other cleaning or preparation performed. This pattern is an array (6×6) of 36 squares in the dimensions of 200 µm×200 µm. After inkjet printing, the actual dimensions became 220 µm×220 µm. The ink utilized for this experiment was a solution with nanodiamond powder suspending in ethylene glycol to achieve a desired viscosity. The solvent used in the ink, i.e., ethylene glycol, is an excellent feedstock for the growth of diamond as well and would not adversely affect the quality of CVD diamond. The splash problem was minimized by optimizing the solution concentration and viscosity, as well as other printing parameters. Undesired diamond seeding in areas surrounding the desired seeded pattern was minimized. The hydrophobic silicon substrate surface caused some blurry edges of the printed patterns. Further work is being undertaken in controlling the wetting of the substrates to improve the quality of printed diamond seeds.

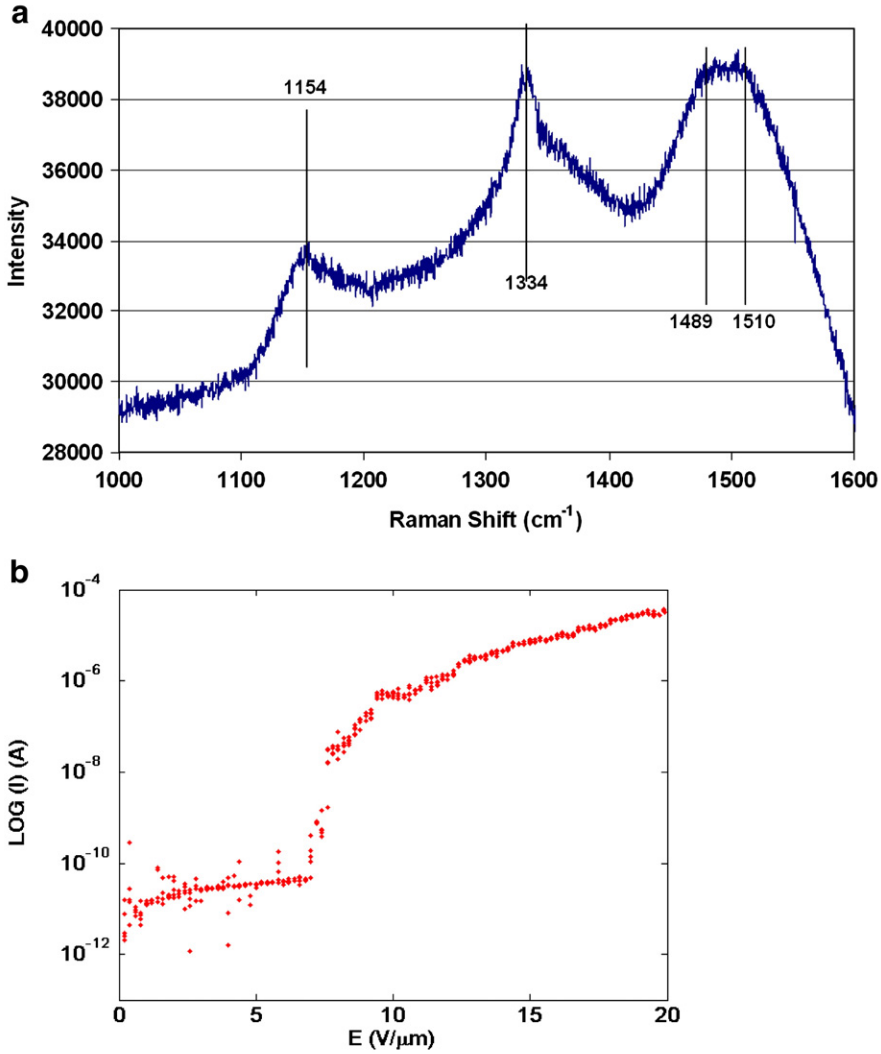

Fig. 3. (a) Raman spectra from the printed square pattern after 20 min of diamond deposition; (b) Electron field emission measurement shows that the sample starts to conduct electron field emission at 7 V/µm.

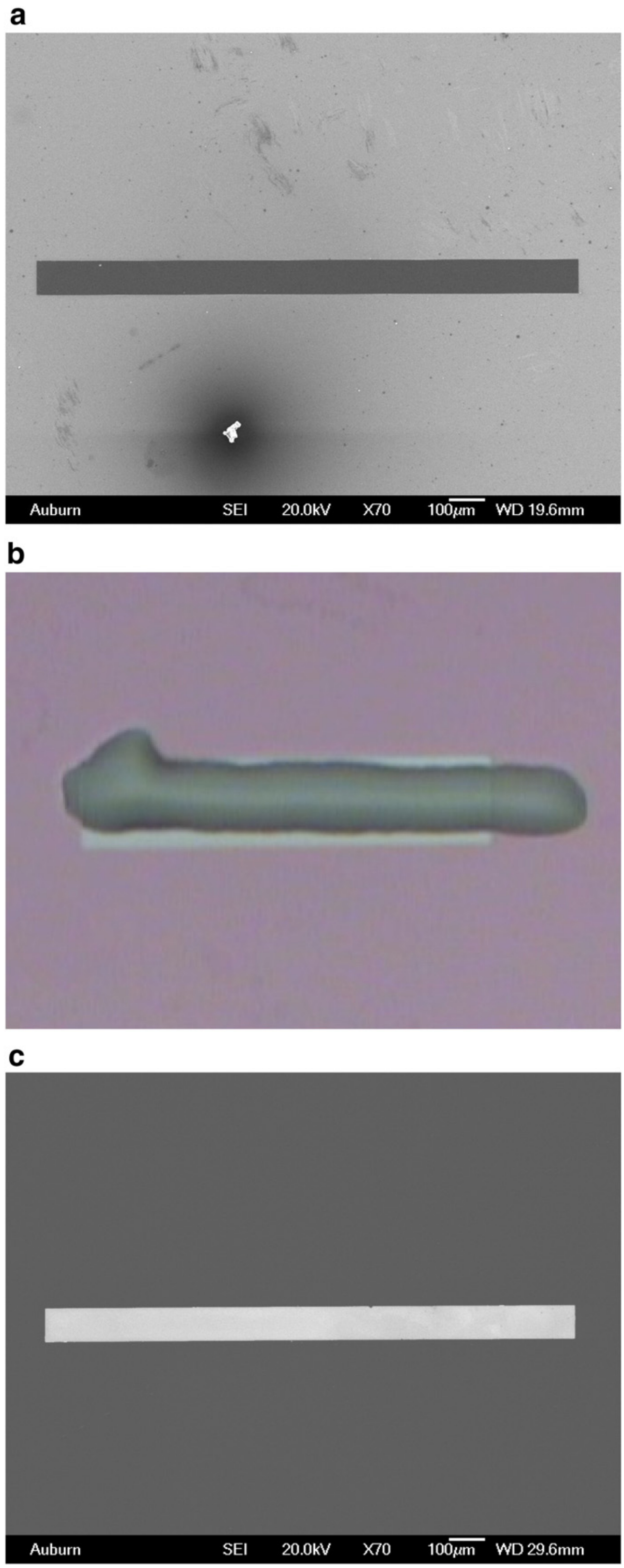

Fig. 4. Sequential steps of the process, (a) a square pattern on silicon dioxide on a silicon substrate is fabricated; (b) selective printing of nanodiamond seeds into the pattern; (c) After diamond pre-deposition, lift-off, and deposition, nanodiamond line pattern is fabricated.

Fig. 2(a) shows the SEM image of the sample shown in Fig. 1 after it was subjected to a brief (20 min) diamond growth. With the uniformly suspended diamond powder in the ink, the required time for obtaining continuous diamond films was significantly reduced. The patterned diamond films had a uniform thickness of 450 nm and good adhesion to the substrate surface as tested by a tape-and-peeling process. Continuous diamond films across the pattern and the surface morphology were shown in Fig. 2(b) and (c), respectively. Raman spectrum obtained from one of the square patterns after diamond deposition shows the sharp diamond peak, 1334 cm^{-1} (Fig. 3). Other features of the Raman spectrum including the peaks located at 1154 cm^{-1} and around the graphite band, 1489 and 1510 cm^{-1} are commonly seen on nanodiamond films [19–24]. With the addition of ethylene glycol as the carrier, SEM and Raman spectrum on printed samples showed no significant differences from nanodiamond films grown without the solvent under similar conditions. Electron field emission measurement of the sample was also carried out. Electron field emission of an as-grown sample started at 7 V/μm is shown in Fig. 3(b) [25,26].

Nanodiamond-containing ink was accurately and selectively jetted onto the patterns, where silicon was exposed, pre-formed in the silicon dioxide layer on a silicon wafer. The optical image shown in Fig. 4 demonstrates the step by step process. By conventional lithography processing, patterns in shapes of “trenches” were defined. In Fig. 4(a), silicon dioxide was patterned on the silicon substrate prior to the inkjet seeding. The jetting sites were precisely designed so that only desired areas would be seeded and jetted ink would be directed to the bottom of the “trench” to fill it up to avoid waste of diamond materials. The top pattern of Fig. 4(b) demonstrates a well-aligned printing of diamond seeding within the pattern. The unwanted structures caused by ink deposited outside the pattern were lifted off by buffer oxide etchant (BOE) after 10 min of CVD growth for the diamond seeds to be desirous to adhere to the exposed silicon areas. After the lift-off, the substrates were subjected to further CVD diamond growth to ensure that continuous films with good adhesion could be obtained. Thus patterns with well-defined edges were formed (Fig. 4(c)). The thickness of the silicon dioxide layer is believed to be a factor in the sharpness of the edges. When it is thicker, the seeding pattern tends to have a larger gap between the seeding within the pattern and outside the pattern, ensuring the performance of the lift-off process.

Raman spectroscopy was also employed for the quality inspection of the specimens (Fig. 5). The peak located at 1156 cm^{-1} is common in CVD nanodiamond films. The pronounced sp^3 diamond peak located at 1335 cm^{-1} was observed. There appeared to be a broad line within the range of 1480–1507 cm^{-1}, usually accompanying the 1156 cm^{-1} peak, indicating the existence of trans-polyacetylene [19–24].

4. Conclusions

This paper demonstrates a significant progress towards a number of new practical applications of inexpensive and rapid patterning of thin and/or smooth nanodiamond films. By utilizing the inkjet printing technique with an ink containing nanodiamond powder in ethylene glycol, selective-area and patterned diamond seeding has been successfully demonstrated. Continuous diamond films of desired patterns are formed on printed diamond seeds following a brief MPCVD diamond growth process. Fabrication of patterned diamond films is further improved by combining a conventional lithographic process with inkjet printing assisted diamond seeding. Minimum diamond growth time for obtaining continuous diamond films is adjusted and improved by varying the amount of applied ink and the concentration of diamond powder of the size of 40–50 nm uniformly suspended in the ink. This technique allows a cost-effective method for selective seeding and patterning of diamond

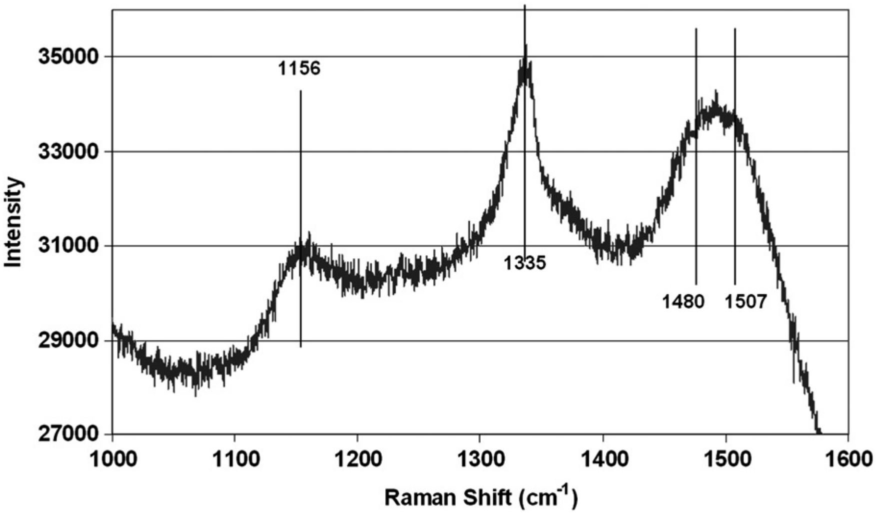

Fig. 5. Raman spectra for films grown on printed diamond seeds after the sequential seed printing, growth, lift-off, and growth procedure.

coatings. Future applications employing 3-D diamond structures can be obtained by sequential and repeated printing and deposition.

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