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STRUCTURING OF DIAMOND FILMS USING MICROSPHERE LITHOGRAPHY

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Abstract. In this study, the structuring of micro- and nanocrystalline diamond thin films is demonstrated. The diamond films are structured using the technique of microsphere lithography followed by reactive ion etching. Specifically, this paper presents a four-step fabrication process: diamond deposition (microwave plasma assisted chemical vapor deposition), mask preparation (by the standard Langmuir-Blodgett method), mask modification and diamond etching. A self-assembled monolayer of monodisperse polystyrene (PS) microspheres with close-packed ordering is used as the primary template. Then the PS microspheres and the diamond films are processed in capacitively coupled radiofrequency plasma using various plasma chemistries. This fabrication method illustrates the preparation of large arrays of periodic and homogeneous hillock-like structures. The surface morphology of the processed diamond films is characterized by scanning electron microscopy and with the use of an atomic force microscope. The potential applications of these diamond structures in various fields of nanotechnology are also briefly discussed.

Keywords: nanostructuring, diamond thin films, polystyrene microspheres, reactive ion etching, scanning electron microscopy.

1. Introduction

1.1. Diamond and its applications

The most commonly used methods for synthesizing diamond are high-pressure, high temperature (HPHT) [1] and chemical vapour deposition methods (CVD) [2]. Other methods include explosive formation (forming detonation nanodiamonds), sonication of graphite solutions (ultrasound cavitation), laser ablation, etc. Due to a unique combination of properties (e.g. extreme hardness, high thermal conductivity, wide band gap, negative electron affinity, high mechanical strength, chemical inertness, resistance to particle bombardment, and biocompatibility) diamond is a promising material for applications in various fields of electronics, bioelectronics, sensorics, etc. [3].

The potential applications of diamond depend not only on its intrinsic physical and chemical properties, but also on its surface geometry. The defined surface structuring allows these unique properties to be tuned and exploited for a wider range of applications. For example, structuring of films enhances the surface-to-volume ratio and therefore increases the sensitivity and other performances of fabricated devices [4]. For example, increasing the surface area-to-volume ratio of diamond films improves the field-emission properties by introducing the enhancement effect of the local field near the tips [5]. Generally, various nanostructures can be fabricated from diamond films known as nanowires, nanorods, nanoneedles, etc. Therefore, there is still great interest in developing methods for obtaining diamond nanostructures with high area density, high aspect ratio (depth/width), good uniformity and controlled geometry over large areas [6].

1.2. Structuring of diamond films

On the basis of the fabrication or structuring method, two basic concepts can be defined as: a) the bottom-up strategy and b) the top-down strategy. For structuring diamond films, the bottom-up strategy (e.g. selective area deposition [7]) is rarely used because of the greater complexity and low process reliability. Wet chemical etching is not applicable due to the high-temperature stability, super hardness and chemical inertness of diamond. Among the top-down strategies, only dry reactive ion plasma etching through a mask can be used. The advantages are greater reliability, greater reproducibility, and a broad family of possible masking materials (metals, polymers, oxides or nitrides) than when the bottom-up strategy is used. The mask, which defines the required geometrical patterns, is formed using standard lithographic processes (photolithography, electron beam lithogra-

Steps	Process parameters	
1a) MCD deposition	MW power	3000 W
	total gas pressure	7000 Pa
	CH_4/H_2	5 %
	CO_2/H_2	1.5 %
	temperature	800 °C
	process time	4 h
(pre-deposition: 2 % of $CH_4/H_2$2 without CO_2 for 10 min)		
1b) NCD deposition	MW power	3000 W
	total gas pressure	7000 Pa
	CH_4/H_2	5 %
	CO_2/H_2	1.5 %
	temperature	800 °C
	process time	3 h
(pre-deposition: 2 % of CH_4/H_2 without N_2 for 10 min)		
2a) RIE process (O_2-plasma)	RF power	100 W
	total pressure	12 Pa
	O_2 flow rate	50 sccm (for 7 min)
	self-bias voltage	−57 V
2b) RIE process (CF_4/O_2-plasma)	RF power	100 W
	total pressure	12 Pa
	(1.) O_2 flow rate	50 sccm (for 2 min)
	(2.) O_2/CH_4 flow rate	40/10 sccm (for 8 min)
	self-bias voltage	−57 V

TABLE 1. Process parameters for CVD diamond deposition and diamond etching using the PS template as a direct mask (for PS1500).

phy, nanoimprinting, etc.). However, these processes are expensive or time-consuming. A possible mask preparation process would involve utilizing a monolayer of plasma-treated microspheres with controllable size and gap. In this study, we present structuring of diamond thin films using the technique of microsphere lithography.

2. Experimental section

A schematic illustration of the main technological steps for diamond structuring is shown in Fig. 1:

(1.) **Diamond deposition.** Two types of diamond films were grown in a focused microwave chemical vapor deposition reactor (Aixtron P6) on a silicon substrate $1 \times 1\,cm^2$ in size (for the plasma parameters see rows 1 and 2 in Table 1).

(2.) **PS mask preparation.** Uniform periodic arrays of polystyrene (PS) microspheres were achieved by the standard Langmuir-Blodgett method, i.e. self-assembly of microspheres in a hexagonally close-packed monolayer at the water-air interface. The initial diameter of the PS microspheres was 1500 nm. Details abouth the preparation of the mask can be found in ref. [8].

(3.) **Mask modification – PS etching.** The preparation of the hexagonally close packed monolayer was followed by reactive ion etching. The PS microspheres were modified in a capacitively coupled plasma system (CCP-RIE, Phantom III, Trion Technology) in an oxygen atmosphere (for the etching parameters see Table 1, row 3).

(4.) **Diamond etching.** The samples were subsequently also treated by the CCP-RIE system. Two different gas mixtures were used: pure O_2 and 20 % of CF_4 in O_2 gas (see row 4 in Table 1).

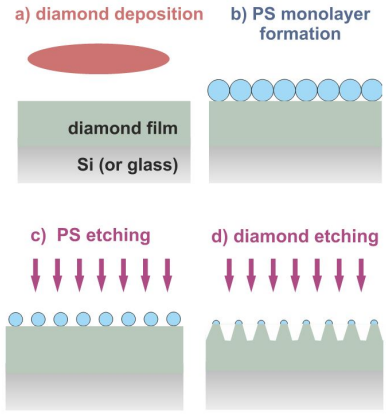

FIGURE 1. Schematic drawing of diamond film structuring using a PS microsphere array.

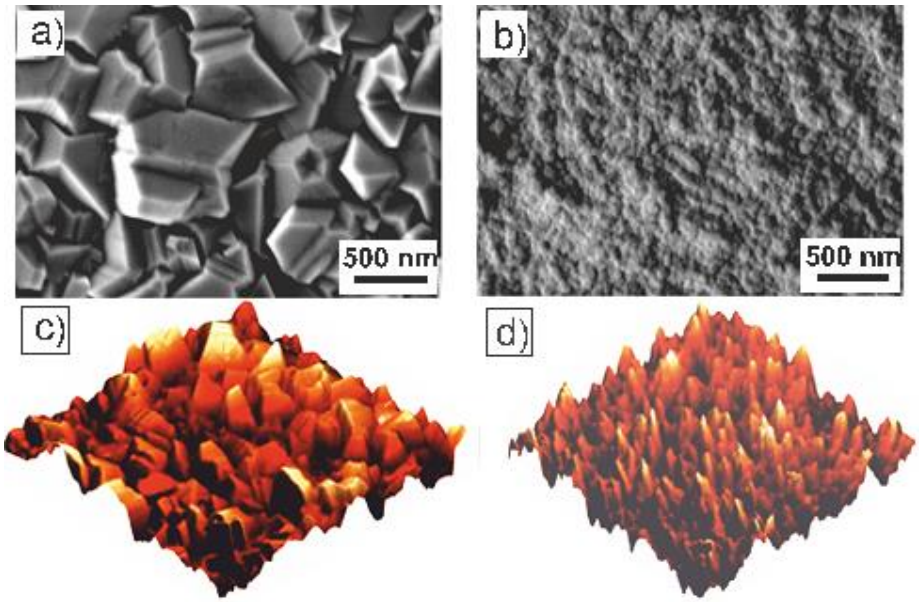

Figure 2. Top-view SEM and AFM ($2 \times 2\,\mu m$) images of a), c) MCD and b), d) NCD diamond thin films before the mask was prepared.

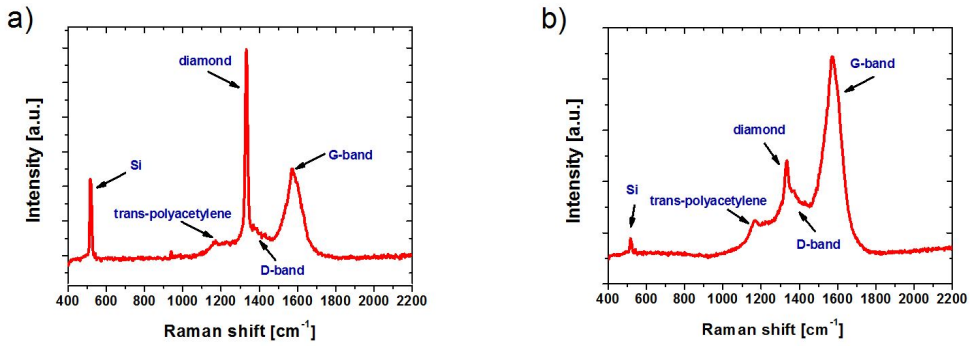

Figure 3. Raman spectra of a) MCD and b) NCD films measured by an excitation wavelength of 325 nm.

The plasma parameters were chosen on the basis of our previous study on PS and diamond etching [9, 10].

The samples were systematically characterized after each technological step. The morphology of the CVD grown and plasma etched samples was characterized by scanning electron microscopy (SEM, e_LiNE writer, Raith GmbH) and with the use of an atomic force microscope (Veeco Dimension 3100, NTMDT Ntegra). Raman spectroscopy (Renishaw inVia Reflex) with an excitation wavelength of 325 nm was employed to determine the chemical character (i.e. sp^3 versus sp^2 carbon bonds) of the diamond films.

3. Results and discussions

Figure 2 shows the surface morphology and the topography of the diamond films before the mask was prepared, taken by scanning electron microscopy. The diamond film with larger grain sizes ($\sim 1\,\mu m$) was labelled as MCD (microcrystalline, Fig. 2a), and the diamond film with smaller grain sizes (< 50 nm) was labelled as NCD (nanocrystalline, Fig. 2a). Both diamond films were about 3 µm in thickness. Figure 2c,d shows the 3D topography of the diamond films (before the mask was prepared), provided by an atomic force microscope (AFM).

The Raman spectra clearly confirmed the diamond character in both films (Fig. 4a,b). For the MCD film, the spectrum is dominated by a sharp peak located at 1332 cm^{-1}, which is the characteristic line for the phonon mode of the sp^3 crystalline diamond phase. Two broad bands located at frequencies $\sim 1374\,cm^{-1}$ and $\sim 1575\,cm^{-1}$ are attributed to the D-band (defects) and to the G-band (graphite), which represents the non-diamond carbon bonds (sp^2 phase). A weak band centered at $\sim 1154\,cm^{-1}$ corresponds to the trans-polyacetylene-like groups at the grain boundaries [11]. This band is more intensive for NCD films, where the crystals are much smaller, and more sp^2 carbon bonds are present at grain boundaries. Thus,

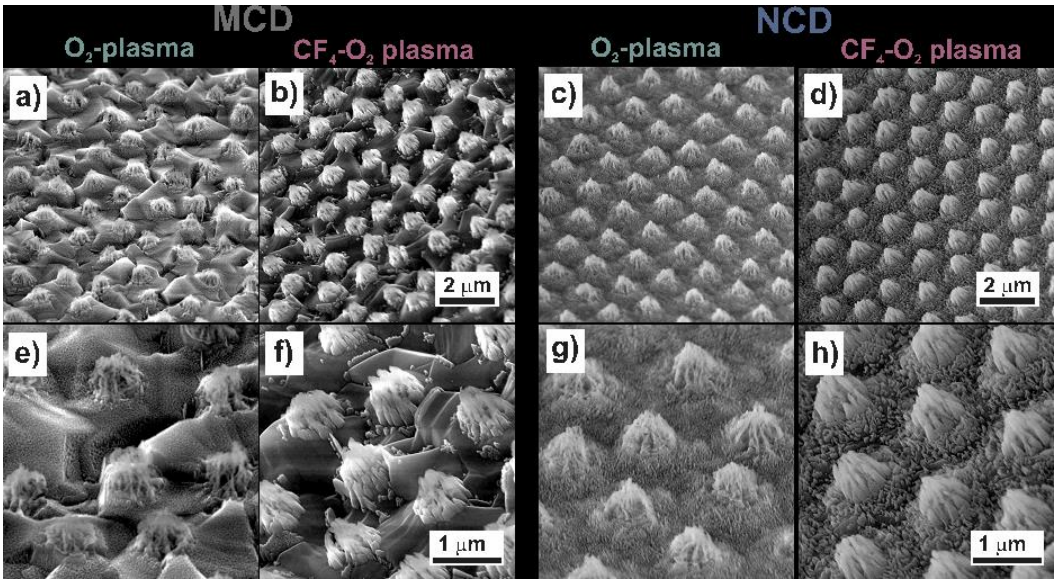

FIGURE 4. Tilted-angle view (45°) SEM images of etched MCD diamond films (columns 1, 2) and NCD diamond films (columns 3, 4) prepared using a PS microsphere mask (PS 1500 nm) by etching in oxygen plasma (a, c, e, g) and with the addition of CF_4 (b, d, f, h). (Note: the upper row and the bottom row differ only in magnification).

the intensity of the G-band increases and the intensity of the diamond-peak (at 1332 cm^{-1}) decreases, but it is still resolvable in the Raman spectrum.

Right at the beginning of the plasma treatment (step 2a in Table 1) we observed homogeneous etching of PS over the whole sample. The close-packed arrays of PS microspheres were converted into a non-close-packed template with the preserved period of the initial microsphere array (not shown here) [10].

The surface morphology of the diamond films after the CCP-RIE processes (step 2a and 2b, Table 1) is shown in figure 4. Periodic hillock-like structures with a period of $\sim$ 1500 nm were observed. Their height was estimated from the AFM image to be $\sim$ 600 nm for MCD and $\sim$ 800 nm for NCD. The fabricated hillock-like features were better recognized (i.e. their geometrical border was better defined) for the NCD films. This is attributed to the nanocrystalline character itself. In the case of MCD films, the fabricated structures reveal non sharp edges (borders), which we assign to the different etching rates for each crystal facet of the diamond. This means that the (111) facets were etched at different rates than the (100) oriented diamond crystals, etc. [12]. The MCD films consist of randomly and well faceted crystals and the surface roughness is higher for the thicker films. From this point of view, the NCD films do not reveal such dependences or nonhomogenities on the microscopic scale, i.e. the grain size and the surface roughness do not vary with the film thickness.

The surface of the etched MCD and NCD films in pure oxygen plasma (columns 1 and 3 of Fig. 4) corresponds well to our previous studies [9]. RIE etching in O_2 led to the formation of diamond needle-like structures (or so-called whiskers). The main reason for this effect is that the ions are vertically accelerated to the substrate and not only chemical etching but also physical sputtering takes place. Moreover, it is well-known that oxygen etches sp^3 diamond bonds much faster than sp^2 carbon bonds [13], resulting in the formation of needle-like structures. In NCD films, more sp^2 carbon bonds at the grain boundaries correspond to the formation of needle-like structures [14].However, the addition of CF_4 into O_2 resulted in flattening/smoothing of the diamond surface.

4. Conclusion

In summary, we have demonstrated that microsphere lithography is a promising technique for structuring diamond thin films in the so-called top-down strategy. Diamond films were grown using a focused microwave plasma CVD process, and their crystallographic character was controlled by the gas mixture that was used. The MCD films were grown from a $CO_2 + CH_4 + H_2$ gas mixture, and the NCD films were grown from a $N_2 + CF_4 + H_2$ gas mixture. Self-assembled, hexagonally close packed PS microsphere arrays obtained by the Langmuir-Blodgett method were used as the masking material. First, the PS layer was treated in plasma to predefine the final geometry of the diamond structures. During continued plasma etching, the primary PS were removed.

Using this cost-effective and time-efficient method, highly periodic and homogeneous hillock-like structures were achieved both for MCD films and for NCD films. It is believed that diamond structures fabricated over large areas will have a positive impact on their further applications as photonic crystals in optics or as active functional surfaces in sensorics, bioelectronics, biomedicine and electrochemistry.

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