

TECHNOLOGICAL ASPECTS IN FABRICATION OF MICRO– AND NANO–SIZED CARBON BASED FEATURES: NANORODS, PERIODICAL ARRAYS AND SELF–STANDING MEMBRANES

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Diamond and/or carbon thin films are in the center of interest due to their variability and extraordinary combination of intrinsic properties. However, some applications require fabrication of films with tailored properties. Especially, fabrication of periodic structures is highly attractive due to their increased surface area. In this contribution we point out the key technological aspects for fabrication of micro- and nano-sized carbon-based structures. Three representative structures are presented: diamond nanorods, self-assembled templates and self-standing diamond membranes. We found that the diameter of diamond nanorods can be controlled in a broad range from 10 to 200 nm by the masking material (Au vs Ni) and its initial thickness (from few to tens of nanometers). The assembly of polystyrene microspheres in mono- or multi-layer with square or hexagonal periodicities was controlled by the spin-coating parameters. The diamond porous membrane was selectively grown on Si substrate with an interdigital or mesh like geometry. Advantages of each structure as well as the fabrication limitations are discussed more in detail and finally their representative applications are pointed out.

Key words: diamond, carbon, nanorods, microsphere lithography, selective area deposition, SEM

1 INTRODUCTION

Diamond and carbon thin films due to their variability and superior mechanical, optical, electrical, and biocompatible properties, become widely used over the world in multi-disciplinary fields such as material engineering (composite materials), opto-electronics (electronic devices, sensors), bio-chemistry (catalysts), life science (implants, drug delivery, bio-labelling) or even microbiology (as anti-adhesive and antibacterial coatings) [1-5]. For each scientific or commercial field, intrinsic properties have to be often tailored to meet specific requirements on surface morphology, electrical conductivity, optical transparency, etc. Especially, for life science and (bio-) sensoric applications these requirements include tailorable material morphology/topology and surface area as large as possible [6]. Various pre- or post growth techniques have been developed to fabricate surfaces of wished features. Only briefly, these techniques include reactive ion etching [7,8] involving EBL [9], ink-jet printing of diamond seeds [10], selective area deposition [11,12] including selective etching of substrate [13]. However, only a limited number of above mentioned techniques allows the fabrication of geometrically ordered arrays or templates. Moreover, some of them are too complex and expensive for industrial applications.

In this contribution we review the fundamental technological aspects needed for the fabrication of diamond nanorods, self-assembled arrays (templates) and self-

standing diamond membranes. Some technological procedures represent a simple way to fabricate the geometrically ordered diamond arrays, or even hierarchically structured morphologies where micro- and nano-sized features are combined within one substrate. The fabricated surface features are characterized by SEM and Raman measurements.

2 EXPERIMENTAL

2.1. Fabrication of diamond nanorods

Polycrystalline diamond thin films with the thickness of $\sim 1.6 \mu\text{m}$ were grown by microwave plasma enhanced chemical vapor deposition system with an ellipsoidal cavity resonator on Si substrates [14]. After then, thin metal films (Au or Ni) with different thickness (2–15 nm) were thermally evaporated on diamond films and treated in hydrogen rich microwave plasma (at 500 °C for 10 min). This treatment resulted in the formation of nano-sized metal droplets on diamond surface [15]. The formed metal droplets were used as the masking material during the capacitively coupled plasma reactive ion etching (CCP-RIE) in 40% of CF_4 in O_2 for 10 min at 0.12 mbar and 100 W [27]. Raman measurements, not shown here, confirmed the diamond character for all samples used in this study.

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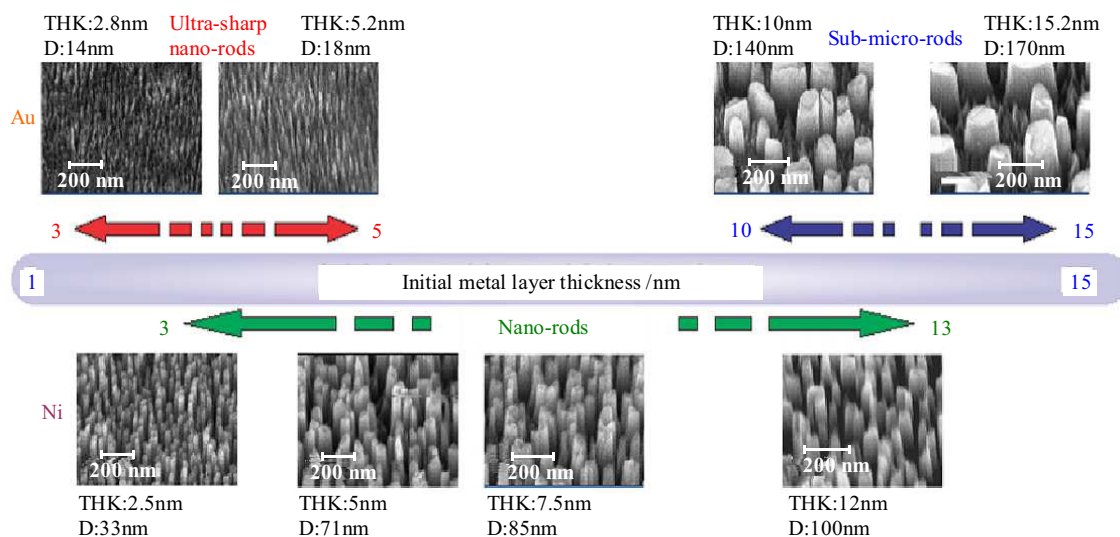


Fig. 1. Surface morphology of diamond films after reactive ion etching using different self-assembled metal droplets as the mask. Notes: (i) — SEM images are shown at angle 45° ; (ii) — abbreviations: THK — initial thickness of the metal layer, D — diameter of nano/micro-rods, scale bar represents 200 nm for all samples

2.2. Fabrication of periodical arrays

Self-assembled arrays of polystyrene microspheres (PSM) were obtained by using a spin-coating. Two types of monodispersed PSMs with the diameter of 500 nm diluted in deionized (DI) water were used: i) 1 wt% (from Phosphorex Inc., USA) and ii) 5 wt% (from microParticles GmbH, Germany). First, Si substrates ($10 \times 10 \text{ mm}^2$) were ultrasonically cleaned in isopropyl alcohol, then treated in oxygen plasma to make the surface hydrophilic. The aqueous dispersion of PSM (5 wt%) was further diluted in Triton X-100/methanol solution (1:400) at ratio of 1:2 and then $70 \mu\text{l}$ of the final dispersion was dropped onto the Si substrates. The spin-coating process was performed for 2 min at rotation speed of 8000 rpm with acceleration of 1000 rpm/s. A schematic overview of the spin-coating process is shown in Fig. 2a. In addition, PSM arrays were also spin-coated on diamond thin films and exposed to the etching in CCP-RIE [16].

2.3. Fabrication of self-standing diamond membranes

The self-standing membranes consisting of diamond bridges (beams) were fabricated by the selective area deposition. First, the Si substrate ($10 \times 10 \text{ mm}^2$) was spin-coated with a negative polymer (ma-N-1410) and dried at 100°C for 2 minutes. Then the polymer coated Si substrate was processed by a two-step optical lithography process which defined the diamond “frame” ($8 \times 8 \text{ mm}^2$) and interconnected with diamond bridges ($200 \mu\text{m}$ wide and $5 \mu\text{m}$ in length). After that, the ultrasonic treatment was done for 10 min in the water-based solution with diamond powder. Employing the *lift-off* technique, the diamond nano-seeds were selectively removed from unwished areas. The diamond growth was carried out in the focused microwave CVD system at following parameters: a) initial growth at MW power of 2 kW, total gas pressure of

5 kPa, gas mixture 2% CH_4 in H_2 and b) fast growth at 5 kW, 15 kPa, 3% CH_4 + 2% CO_2 in H_2 . To eliminate the spontaneous (or parasitic) diamond growth on the non-nucleated areas, the diamond growth was repeatedly combined with the wet etching of Si substrate to remove spontaneously formed diamonds grown on un-wished areas. Finally, the diamond membrane was formed by wet etching of Si substrate. Other technological details on the selective area deposition of mesh-like geometry are summarized in our previous works [17].

2.4. Characterization of diamond films

The grain size, surface morphology and cross-section views of diamond and carbon films were investigated by scanning electron microscopy — SEM, employing eLiNE writer (Raith GmbH) or MAIA 3 (Tescan). Surface topography measurements were performed in the tapping mode on ICON AFM (Bruker). The diamond character of the samples was studied by Renishaw InVia Reflex Raman spectrometer with the excitation wavelengths of 325 and 442 nm.

3 RESULTS AND DISCUSSION

3.1. Diamond nanorods

Figure 1 shows surface morphologies of diamond films after the reactive ion etching step. The morphology varies from ultra-sharp nano-rods to sub-micro rods depending on the used metal (Au or Ni) and its initial thickness. As found the thin gold layer (thickness $< 5 \text{ nm}$) is preferable masking material for formation of very dense and ultra-sharp diamond nano-rod arrays. The formation of perpendicular rods in diameter varied from 140 to 170 nm, also labeled as sub-micro-rods, was achieved by employing Au mask of initial thickness of $10 \div 15 \text{ nm}$. The plasma assisted thermal treatment of Au layers thicker

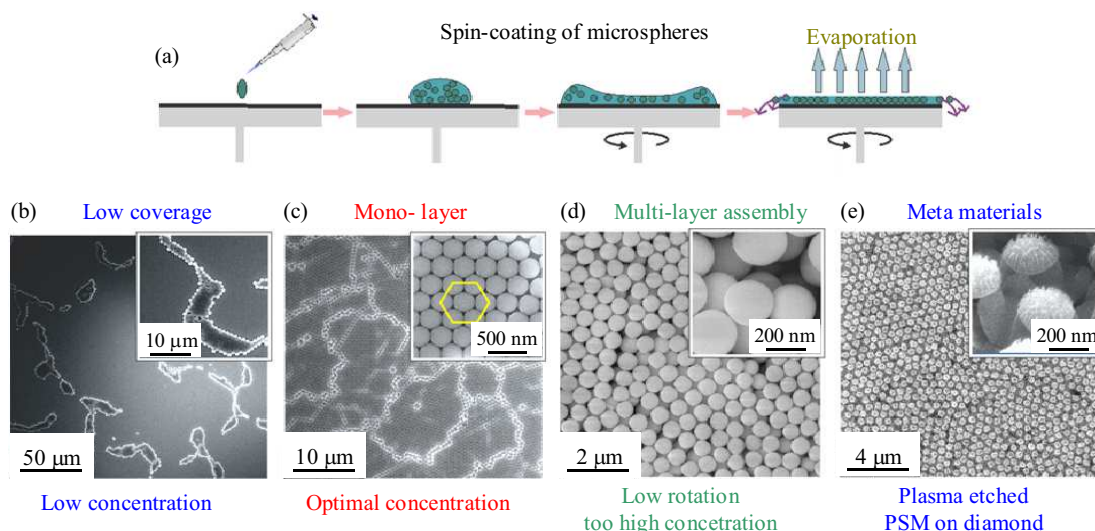


Fig. 2. Schematic view of spin coating of PS microspheres. High and low magnification SEM images of PS microsphere dispersed on silicon (b–d) and diamond thin film after reactive ion etching (e)

than 15 nm resulted in the formation of irregular clustered like Au structures which were not suitable for fabrication of diamond nanorod arrays. In contrast to Au, using a nickel thin layer ($3 \div 13$ nm) allows the fabrication of diamond nano-rods arrays with "medium" diameter varied from 33 to 100 nm. We were not able to fabricate sharper diamond nanorods due to limited de-wetting of Ni droplets [18]. Using thicker Ni layers (> 18 nm) did not result in periodically ordered droplets, as similarly observed for Au layer thicker than 15 nm. We found that the formation of Au or Ni droplets was negligibly influenced by the substrate material (silicon, diamond, silicon dioxide). However, treatment temperature higher than 350°C was needed to form metal droplets. Expect of the temperature effect, enough high dense hydrogen rich plasma was the additional key process parameter needed to form self-assembled droplets from metals initially thicker than 10 nm. Chang and coworkers have proposed that the dominant droplet formation mechanism in hydrogen rich microwave plasma is the plasma-enhanced coalescence, where the hydrogen plasma etching only acts at the "cracking" of the metal film [19].

3.2. Self-assembled templates

Even spin-coating technique has a number of advantages (such as simplicity, low cost, time efficiency, etc) the fabrication of microsphere monolayer is not a trivial task. Except the process parameters *ie* rotation speed, acceleration or time) the initial concentration of dispersion is found as key parameter to assemble microspheres into monolayer. It means that low concentration of dispersion (1 wt%) is not enough to achieve fully closed homogeneous PSM arrays regardless of the spin-coating process parameters (see Fig. 2b). However, increased concentration of dispersion (initially 5 wt%) and optimized process parameters resulted in the formation of the compact monolayer with hexagonal ordering and relatively low density of defects (see Fig. 2c). Too low rotation

speed (< 1000 rpm) leads to the formation of multi-layers (Fig. 2d). The same effect had too short process time. On the other hand, too high rotation speed or acceleration rate do not lead to formation of fully-closed monolayer. It was further observed that using multistep (*ie* first 20 s at 200 rpm, 1 min at 8000 rpm) spin-coating is better for a successful fabrication of monolayers. The self-assembled monolayer of PSM can be easily structured by reactive ion etching, which allows a control of PSM shape, diameter and gaps between them. The periodicity is controlled by the initial size of PSMs which are commercially available in a wide range from few nm up to $300 \mu\text{m}$. Such tailored arrays was used as the template for diamond thin film structuring.

3.3. Self-standing diamond membranes

Figure 3 shows surface morphology and Raman spectra of self-standing diamond membrane. Optical and SEM images (Fig. 3a–b) reveal the growth of long bridges ($200 \mu\text{m}$ in width) both-side fixed to the outside frame. The thickness of formed bridges was $8 \mu\text{m}$, as measured from the cross section view (Fig. 3c). For the SEM and Raman measurements, the membrane was fixed to carrier silicon substrate with polymer. Raman spectra of formed bridges are dominated by the diamond characteristic peak centered at 1332 cm^{-1} (Fig. 3d).

The area between the bridges is dominated by the Si carrier substrate with the peak at 520 cm^{-1} — the green line in Fig. 3d. The diamond bridge was measured from the back-side (blue and red lines). The Raman spectrum from the bridge back side reveals a weak signal from the silicon. In this case, the Si signal is attributed to the remaining silicon coming from the primary used substrate for the diamond growth. Surface morphology from the bridge back-side reveals diamond clusters in size up to 50 nm. SEM image from the top side shows well-faceted diamond crystals in size 58 nm. Based on this observation and cross-section view, the diamond growth follows the so

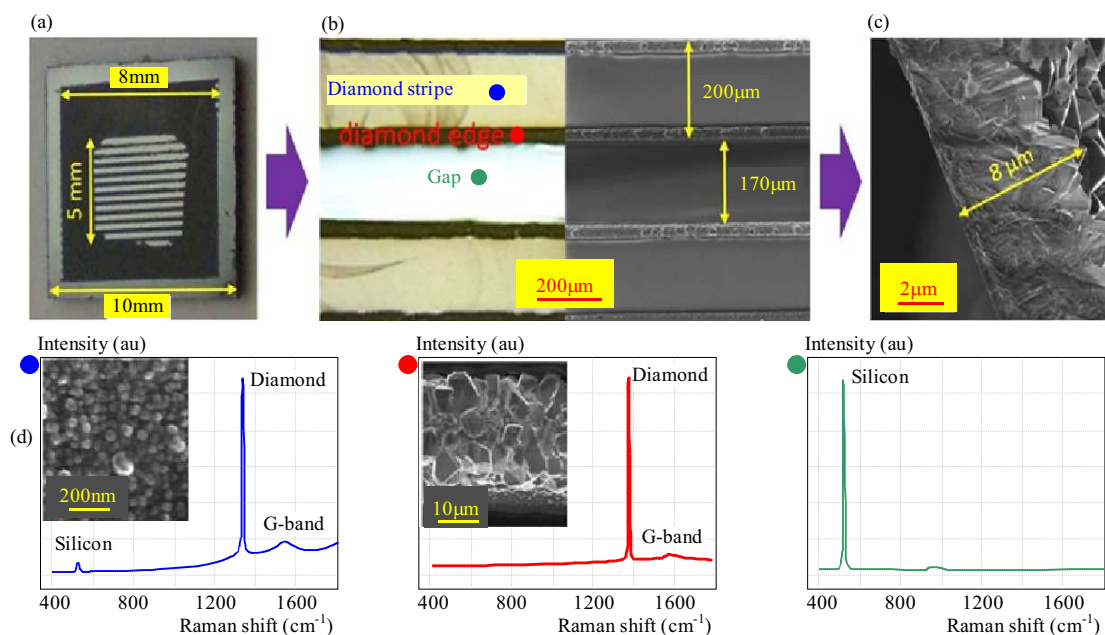


Fig. 3. Optical, SEM images and Raman spectra of self-standing diamond membrane with detailed view of individual diamond bridges (strips)

called evolutionary selection growth mode where crystals with the highest growth rate survive and continue the growth [20].

4 CONCLUSION

This work reviewed a technological progress in understanding and controllable fabrication a broad range of micro/nano-sized structures from allotrope carbon forms. The usability of such structures has been demonstrated by our previous works. For example, the diamond nanorods enhanced the detection sensitivity to gases [21] and biomolecules [22]. The spin-coated polystyrene microspheres confirmed their usability for structuring or growth of diamond periodical arrays [16]. The structured PS microspheres were used for Surface Enhanced Raman spectroscopy (SERS). Similarly, the SiO₂ microspheres were built in diamond layer and after their wet etching, spherical voids were formed in the diamond films which should be potentially attractive as meta materials with a periodically variable index of refraction. Moreover, the structured PS microspheres deposited on the diamond surface represent a hierarchical surface combining *nano*-sized soft material on micro-rough hard surface (diamond). We propose that such soft-hard/nano-micro surface is attractive as the artificial substrate for life science or as an anti-adhesive/antibacterial coating. The self-standing thin diamond membranes in bridge or mesh geometry offer not yet explored variability of experiments in which the diamond surface directly interacts with the flowing liquid medium allowing dynamic cultivation studies with bacteria, cells, or (bio) molecules. In such applications, the stress-free engineered management is the crucial issue for fabrication mechanically stable self-standing diamond bridges, beams or cantilevers. As challenging

technological part it is still remaining the fabrication of a broad range of structures with aspect ratio as high as possible. Presently, our research focuses on investigation of advanced properties of structured diamond or other carbon forms.

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