TAILORABLE DIAMOND CAVITIES: A NOVEL APPROACH TO SELF-STANDING DIAMOND FILM FABRICATION

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Abstract

This study presents a novel approach for fabricating self-standing diamond films with tailorable cavities, eliminating the need for reactive ion etching (RIE). We employed selective area deposition on SiO_2/Si substrates in a microwave plasma CVD system at high temperatures (1000°C). The method exploits the thermal expansion mismatch between diamond and SiO_2/Si substrates to induce film delamination, resulting in free-standing structures. Diamond films with thicknesses of approximately 50 µm were produced, featuring cavities whose dimensions could be controlled by lithography mask dimensions and deposition time. Raman spectroscopy confirmed the high quality of the diamond films, showing a dominant peak centered at 1330 cm^{-1}. The presented technological approach offers a promising solution for microstructuring of diamond films with potential applications in high-tech applications.

Keywords: Diamond, chemical vapor deposition, SEM, self-standing, MEMS

1. INTRODUCTION

The diamond film exhibits a multitude of exceptional properties [1,2], including high mechanical hardness, Young's modulus, thermal conductivity, and a wide bandgap, which collectively afford it a vast array of applications in micro-electro-mechanical systems (MEMS), deep ultraviolet photoelectronics, and radiation detectors [3]. In addition, diamond's biocompatibility is highly advantageous as a functional layer in biosensors or artificial substrates for cell culture [4]. In such applications, the surface morphology significantly impacts cell differentiation and proliferation [5], and hermetically coated 3D substrates with diamond are preferred due to minimal toxicity. In particular, a self-standing diamond film with defined holes/cavities could be highly advantageous for these applications.

All these applications necessitate the microstructuring of diamond films. However, diamond's extremely high chemical inertness renders wet chemical etching impractical. An alternative method is dry reactive ion etching (RIE) [6,7], which using lithography masks can produce the desired patterns over large areas. The selective area deposition (SAD) [8] can circumvent the necessity for deep RIE. This technique, along with selective area nucleation (SAN), offers promising alternatives for creating self-standing diamond substrates, eliminating the need for deep RIE of thick diamond films.

In this paper, we discuss technological progress in SAN and SAD of self-standing diamond substrates, focusing on their potential to overcome the limitations of traditional microstructuring methods.

2. EXPERIMENTAL

The experiments employed 10x10 mm^2 Si substrates coated with a 1.2 µm thick SiO_2 layer. Prior to the deposition of the diamond, SAN was conducted using nanodiamond particles. In the SAN process [8], the

substrates are initially coated with a photosensitive resist (ma-P1215) and subsequently subjected to a soft baking at 100°C. Subsequently, the substrate is seeded with diamond nanoparticles through ultrasonic agitation in a diamond suspension, followed by a second photoresist layer deposition via spin coating. Optical lithography is employed to pattern the seeding layer. A periodic array of circles with diameters of 100, 200, or 300 μm was employed as a lithography mask (**Figure 1a**). As the final step, the development of the photoresist followed by oxygen-plasma RIE are employed to eliminate the diamond residuals, and the upper photoresist layer (**Figure 1b**). Subsequently, the SAN processed samples were loaded in the MWCVD ellipsoidal cavity reactor (Aixtron P6, [9]) to initialize the diamond growth on desired areas (**Figure 1c**).

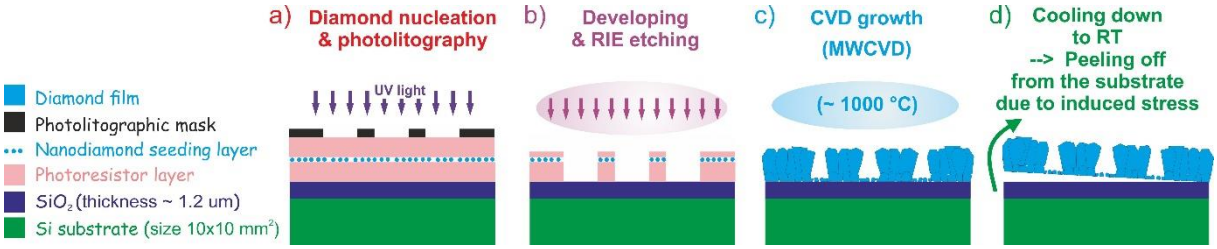

Figure 1 Technological procedure for fabricating self-standing diamond films using high-temperature deposition on SiO_2/Si substrates

The diamond growth conditions were as follows: microwave power 4200 W, pressure 90 mbar, gas mixture 5% CH_4 and 1.5% CO_2 in H_2, process time 40-60 h. The high microwave power and relatively high pressure resulted in a process temperature of 960-1000°C. The elevated deposition temperature and the discrepancy between the thermal expansion coefficients (TEC) of the diamond and SiO_2 layers and the Si substrate resulted in the peeling off of the diamond film from the substrate when the sample was cooled to room temperature (**Figure 1d**).

The morphology and chemical character of diamond films were characterized with scanning electron microscopy (MAIA3, Tescan Ltd., Czechia) and Raman microscopy (Renishaw InVia Reflex Raman spectrometer, UK) with an excitation wavelength of 442 nm.

3. RESULTS AND DISCUSSION

The surface morphology of the diamond film exhibited a replication of the area where diamond nanoparticles had selectively nucleated. **Figure 2a** depicts the final surface morphology of the sample to which a lithography mask with a periodic array of 100 μm circles was applied. Following the growth of the diamond film (with a thickness of approximately 50 μm), the initial 100 μm wide area devoid of diamond was reduced to a 22 μm wide cavity. This observation corroborates the hypothesis that the diamond film grows not only in the vertical direction but also in the lateral direction. It can be expected that increasing the deposition time will result in fully closed diamond cavities. So, the width of the diamond cavities can be controlled by the lithography mask (100, 200, or 300 μm wide circles) and the diamond deposition time.

Figure 2b depicts the peeling off/delamination of the diamond film from the substrate during the cooling process from deposition to room temperature. The high deposition temperature is a critical factor in the fabrication of self-standing diamond films. The disparate thermal expansion coefficients of diamond and SiO_2 (or Si) give rise to considerable internal stress at the interface between these dissimilar materials [10–14], ultimately resulting in the delamination of the diamond film from the substrate.

Figure 2c depicts optical photographs of the 10x10 mm^2 free-standing diamond films from the back and front sides. The optical photograph of the back side exhibits a markedly glossier appearance than the front side, reflecting the smooth surface roughness of the SiO_2/Si substrate. In contrast, the surface roughness of the

front (top) side of the sample is considerably higher, resulting in the scattering of light and a less reflective surface.

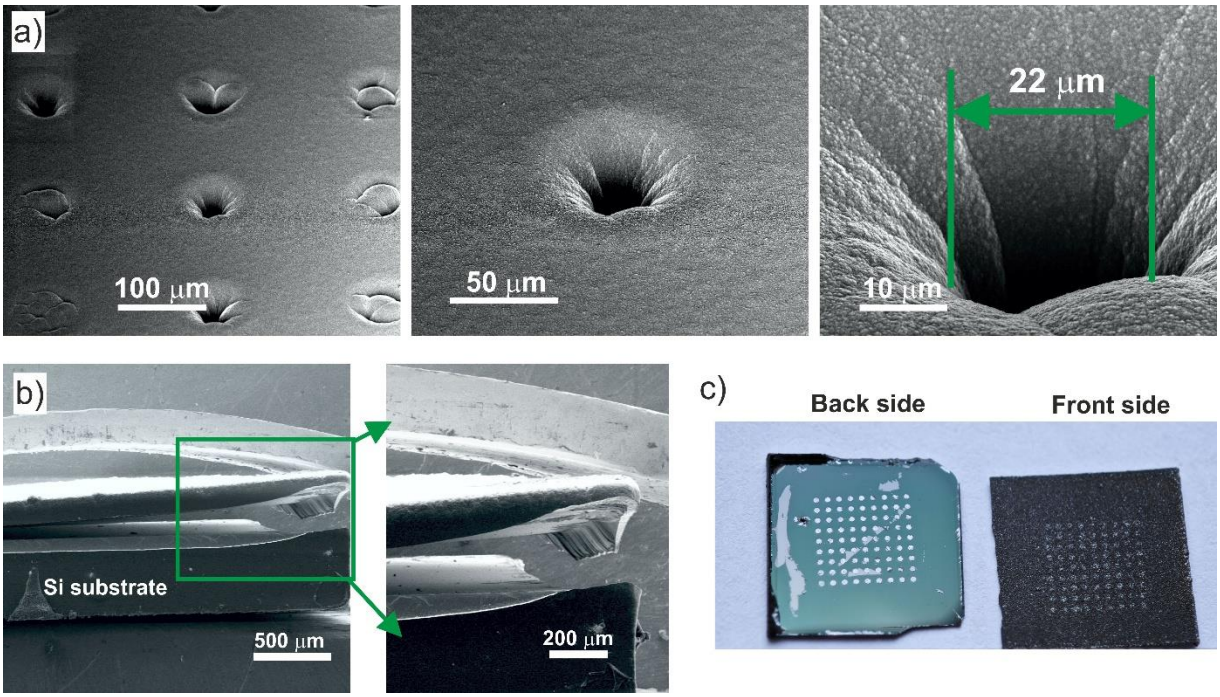

Figure 2 a) Top view SEM images of selective area-grown diamond film with periodically aligned cavities (the initial diameter of the circles in the SAN process was 100 μm). b) Illustration of peeling/delamination of the diamond film from the substrate taken by SEM. c) Optical images of 10x10 mm^2 free-standing diamond films taken from the back and front.

Raman spectroscopy also characterized the diamond film, utilizing an excitation wavelength of 442 nm. The Raman spectra exhibited high similarity across all samples, displaying a prominent diamond peak at 1330 cm^{-1} and a relatively weak G-band at 1532 cm^{-1} [15]. These findings substantiated the presence of a high-quality diamond film with minimal graphitic phases. Moreover, no Si peak was detected on the reverse side of the self-standing diamond film, suggesting that the diamond film is delaminated directly from the SiO_2 layer. In summary, these preliminary experiments have validated the potential of combining SiO_2/Si substrates with high-temperature diamond deposition to fabricate self-standing diamond films without etching. This approach offers a promising alternative to traditional microstructuring methods, potentially simplifying the production process of diamond-based devices for various applications. However, further experiments and simulations are necessary to provide a more comprehensive understanding of this research area. Future studies should focus on optimizing deposition parameters, investigating the effects of substrate properties on film quality, and exploring the scalability of this technique for larger-area diamond films.

4. CONCLUSION

Self-standing diamond films with tailorable cavities offer numerous potential applications, particularly in the fields of radiation detectors, (bio-) sensors, MEMS, and biotechnology. This study presented a straightforward approach for fabricating such films without the need for a RIE process. Tailorable diamond cavities were achieved using SAD in a microwave plasma chemical vapor deposition system.

The diamond growth process was conducted at a high temperature of approximately 1000°C, which was crucial in fabricating self-standing diamond films. Due to the differing thermal expansion coefficients of diamond and SiO_2 (and/or Si), high internal stress is induced at the interface of these dissimilar materials, resulting in the

delamination of the diamond film from the substrate. The diameter of the diamond cavities can be controlled by adjusting the lithography mask dimensions and deposition time. Finally, this allows for the customization of diamond film structures to meet specific application requirements.

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