

## CVD Diamond Films Growth on Silicon Nitride Inserts ( $\text{Si}_3\text{N}_4$ ) with High Nucleation Density by Functionalization Seeding

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**Abstract.** Silicon Nitride is largely used as the base material to manufacture cutting tools. Due to its low thermal expansion coefficient it is ideal candidate for CVD diamond deposition. In this work, we functionalized the surface of silicon nitride inserts ( $\text{Si}_3\text{N}_4$ ) with a polymer (PDDA – Poly (diallyldimethylammonium chloride - Mw 40000)) to promote seeding with nanodiamond particles. The seeding was performed in water slurry containing 4 nm diamond particles dispersed by PSS – Poly (sodium4-styrenesulfonate) polymer. CVD diamond films, with high nucleation density, were deposited in a hot filament reactor. Film morphology was characterized by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Diamond film quality was determined by Raman Spectroscopy. CVD diamond film adherence was evaluated using Rockwell C indentation.

### Introduction

Since the dissemination of the HFCVD technique activated with atomic hydrogen, in the 80s by Matsumoto et al. [1], synthetic diamond has occupied a prominent place in the global diamond products [2]. The coating of cutting tools is one of the main applications of CVD diamond films. Several papers published in the literature have reported significant increases in tool life coated with CVD diamond films [3]. Many of the coated tools were manufactured from tungsten carbide (WC-Co), molybdenum (Mo) in addition to silicon nitride ( $\text{Si}_3\text{N}_4$ ). The silicon nitride is the material that has greater thermal shock resistance among the advanced ceramics. Due to this characteristic, the materials based on silicon nitride are widely used in automotive and aerospace. The use of silicon nitride as a cutting tool is due to the properties such as high hardness, excellent thermal conductivity, and mechanical strength. Another important feature of silicon nitride is its low thermal expansion coefficient ( $\sim 2.9 \times 10^{-6}\text{K}^{-1}$ ) [4], which makes it ideal for the deposition of CVD diamond films ( $\sim 1 \times 10^{-6}\text{K}^{-1}$ ). To assist the deposition of CVD diamond films on non-diamond substrates several mechanisms have been employed over the years to increase the density of nucleation during film growth [5, 6]. The nucleation mechanism based on BEN (Bias Enhanced nucleation) is the most efficient, with nucleation densities in the order of  $10^9\text{part}/\text{cm}^2$  [7, 8]. Despite the high density of nucleation in BEN process, there is a loss in quality of films grown by this technique due to the incorporation of diamond nuclei in a matrix of amorphous carbon [9]. Currently, one of the most efficient mechanisms of the nucleation process is based on ESA (Electrostatic Self-Assembly) [10, 11].

In this method, a monolayer of diamond nanoparticles is formed on the surface of the functionalized substrate. Functionalization is made with a polymer of opposite charge of the nanodiamond particles during the seeding. This work was uses a cationic polymer to functionalize the silicon

nitride substrate. This modifies the surface energy of the silicon nitride substrate, thus facilitating the interaction between diamond nanoparticles and substrate. After this pretreatment, CVD diamond films were grown at different times to evaluate the stages of nucleation on silicon nitride substrates.

### Experimental

In this study, we used silicon nitride inserts SX2 (NTK - Cutting Tools.Co LTD) ISO TNGA geometry for deposition of CVD diamond film. Before functionalization, the substrates were cleaned with acetone in an ultrasonic bath for a period of 5 minutes. The functionalization was performed with a cationic polymer PDDA {- Poly (diallyldimethylamonium chloride)} (Sigma-Aldrich.Co). The inserts were immersed for 30 minute in an aqueous solution with PDDA (10% in water) and then dried with nitrogen gas. The seeding was done in aqueous solution containing 4nm diamond powders dispersed and the anionic polymer PSS - (Poly (sodium 4 - styrenesulfonate), for a period of 30min. The deagglomeration of 4nm diamond particles in this solution was accomplished with the aid of zirconium spheres ( $ZrO_2$  - 250g) with 0.4 mm average diameter, assisted by a high-power ultrasound - 750W (Sonics VCX 750), in a cylindrical PTFE container for 120min. Afterwards, the silicon nitride inserts were cleaned in DI water (to remove any excess powder from the surface) and then dried with nitrogen gas.

A HFCVD (Hot Filament Chemical Vapor Deposition) reactor was used for deposition of microcrystalline diamond films (MCD) on pre-treated silicon nitride substrates. The activation region is composed of a set of eight straight tungsten filaments with a diameter of  $125\mu m$  and 3mm equidistant, heated at a temperature of  $2200^\circ C$ . The substrate was kept at controlled temperatures from 700 to  $900^\circ C$ , heated both by tungsten filaments and by a tungsten resistance placed under the substrate holder. The distance between filament and sample was set at 5mm. The gas concentrations was 2%  $CH_4$  in hydrogen at a total flow rate of 100sccm and constant pressure (50Torr.) [12, 13]. Morphological analysis of the substrate and films was supported by a scanning electron microscope (JEOL JSM-5310 SEM), and Atomic Force Microscope (Veeco Multimode - AFM). The Raman spectra in this work were obtained using a Renishaw microscope system 2000 (laser excitation at 514.5 nm). Indentation with diamond tip of  $120^\circ$  of durometer Reichert (Briviskop BVR 187.5) helped the evaluation of film adherence.

### Results and discussion

Figure 1 shows the X-ray diffractogram of the silicon nitride substrate with the characteristic peaks of the phase  $Si_3N_4$ . The radiation wavelength is  $1.5418740 \text{ \AA}$  (Cu-K $\alpha$ ). Figure 2 (Fig.2a, b, and c) shows the evolution of MCD films growth under the same conditions but at different times (40 min, 60 min and 15 h, respectively).

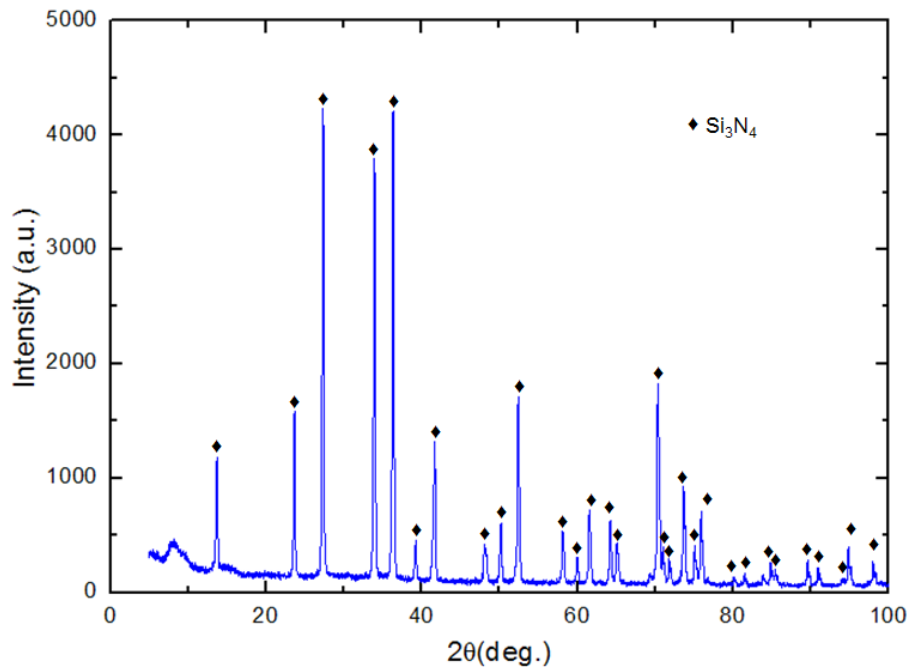


Fig. 1 – X-ray diffracting pattern of the silicon nitride substrate

Figure 2a shows SEM image of the MCD film grown for 40min. In this image, the film is still not continuous. After 80 min the films are continuous.

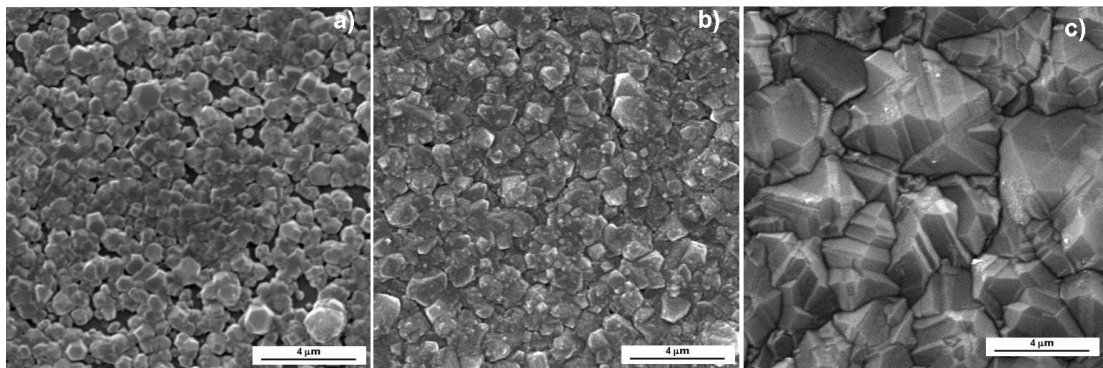


Fig. 2 – SEM top image view of MCD film with (a) 40min, (b) 80min and (c) 15h

Figure 3 shows the Raman spectra characteristic of the MCD film grown on the silicon nitride ( $\text{Si}_3\text{N}_4$ ) substrate [14] for 15h. Since silicon nitride has a thermal expansion coefficient very close to that of diamond [15], there is practically no Raman peak shift. The growth rate of MCD films under the conditions described above is approximately  $2\mu\text{m/h}$  [16].

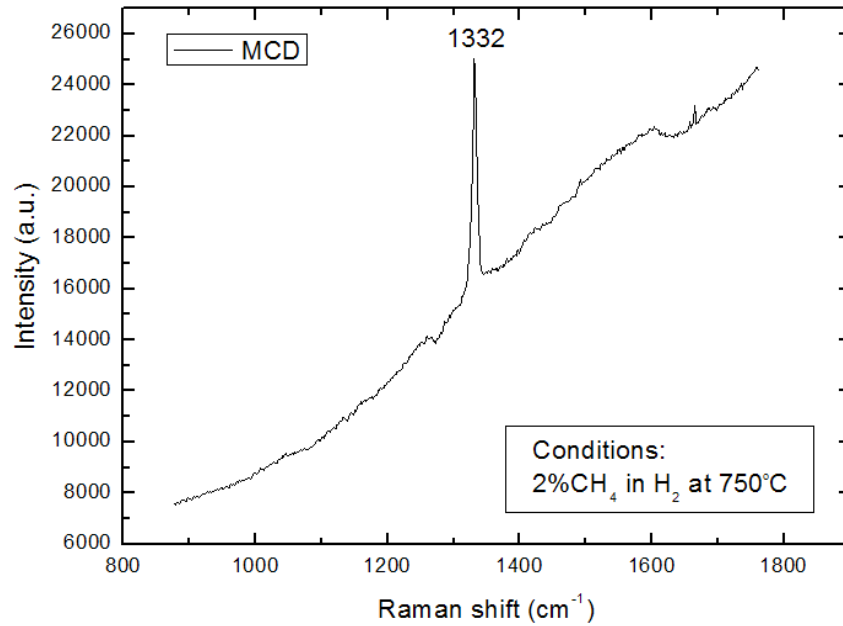


Fig. 3 - Raman characteristic of MCD film on  $\text{Si}_3\text{N}_4$  substrate.

Loads were gradually increased to determine the critical load to initiate the lateral crack [17-19]. Figure 4a show indentation with load of 45kgf applied on the substrate coated with diamond film grown for 15h. It is observed that the films follow the plastic deformation sustained by  $\text{Si}_3\text{N}_4$  substrate during the test. No delamination or rupture of the MCD films occurs, which indicates a good adhesion between film and substrate.

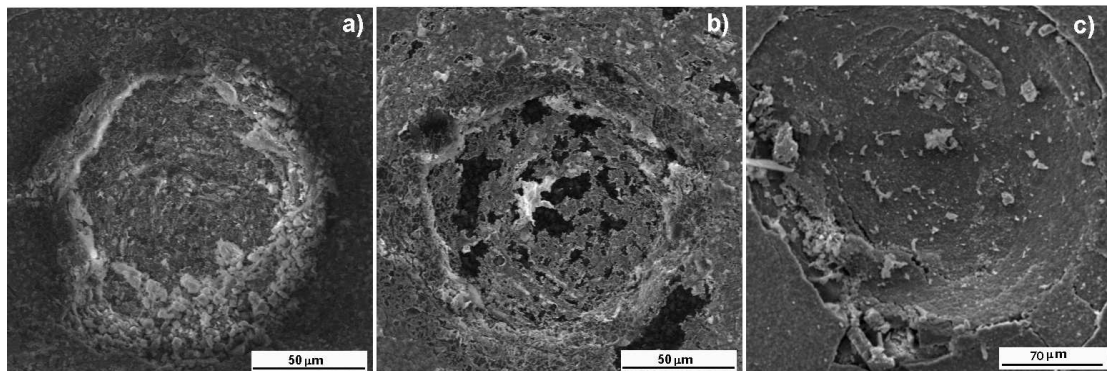


Fig. 4 - SEM image for different indentation loads

Figure 4b show result of indentation at 60kgf, on the same sample. The mechanical behavior is similar to load of 45kgf, namely, there is no film delamination. Figure 4c corresponds to a load of 100kgf for the same sample. Although there is little delamination, the film fails to follow the plastic deformation sustained by substrate. This is evident with the appearance of concentric and radial cracks around the indentation. In indentations tests with loads of 100 kgf made on uncoated silicon nitride the substrates (Figure .5) showed brittle behavior due to high load, which justified, for example, the delamination in Figure 4c.

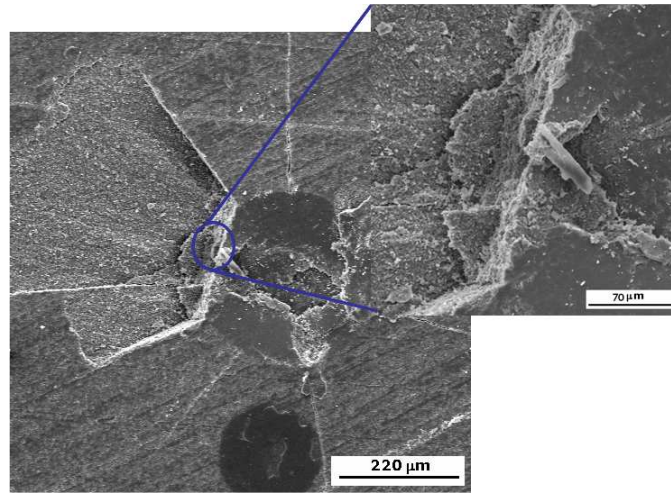


Fig. 5 - SEM image of the  $\text{Si}_3\text{N}_4$  substrate indented with load of 100 kgs.

### Conclusion

In this work, we have adapted the ESA (Electrostatic Self-Assembly) process to support the growth of CVD diamond films, from the functionalization of the silicon nitride substrate. With this functionalization process, the nucleation density was about 3 orders of magnitude higher than conventional seeding methods. Functionalization with polymer (PDDA) significantly increased the surface energy of the  $\text{Si}_3\text{N}_4$  substrate. This change of surface energy facilitated the interaction of 4 nm diamond particles with the substrate during the seeding. The mechanical tests showed an excellent adhesion between diamond film and  $\text{Si}_3\text{N}_4$  substrate.

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