



# Nano crystalline diamond MicroWave Chemical Vapor Deposition growth on three dimension structured silicon substrates at low temperature

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## ABSTRACT

Nano crystalline diamond (NCD) films grown at a temperature below 400 °C can open new applications on temperature sensitive substrates such as polymers or low-melting point alloys. One requirement for the applicative use of NCD is the ability of depositing on a structured substrate having high aspect ratio. This work presents a study on the three dimensional (3D) conformity of NCD deposition at low temperature (350 °C) and low pressure (30 Pa). Silicon wafers have been structured using a mask-less photolithography and (hardmask-less) Deep Reactive Ion Etching (DRIE) process and seeded with nano-diamond particles. The NCD films were grown on these 3D patterned Si substrates with various trench geometries to provide means of determining the limiting geometries of this technique. By measuring the step coverage with changing trench width, a threshold for conformal NCD growth can be determined. The NCD films at the bottom of the 100 µm deep trenches were continuous down to an aspect ratio of 1:7.

## 1. Introduction

The unparalleled hardness, low friction and heat conductivity properties of diamond make it attractive for many applications. The use of diamond as a coating has increased with the development of high growth-rate protocols using Hot Filament Chemical Vapor Deposition (HF-CVD), which usually operates at high substrate temperatures around 600 to 900 °C [1]. However, the high substrate temperatures (> 600 °C) of HF-CVD limits the possible substrate materials.

Developments over the past few years in the area of Micro-Wave Plasma Enhanced CVD (MW-PE-CVD) have made the deposition of CVD diamond possible at far lower substrate temperatures (< 400 °C) [2–4]. These developments have mainly focused on the deposition of Poly-Crystalline Diamond (PCD) and Nano-Crystalline diamond (NCD). In contrast to PCD, NCD has low surface roughness, while keeping similar mechanical properties [5]. Films with these properties have strong application interests [6] as protective layers for cutting tools, Micro-Electro-Mechanical System (MEMS) devices [7], thermal conductive layers for high power devices, and coatings for Atomic Force Microscope (AFM) tips [8–11].

Different approaches have been developed to achieve large area deposition of NCD at low temperatures. The linear array configuration

has been successful in depositing NCD at low temperatures on large substrate areas [2,3,12,13]. This process makes use of the surface-wave, i.e. propagation of the microwave at the interface between the plasma and a dielectric. A different approach using an array of coaxial plasma sources has been used to achieve NCD deposition at low temperatures and on large surface areas [14]. In both approaches, the possibility of producing large area treatment is somewhat compromised by the need for complex power distributors and impedance matching systems.

Application of the NCD deposition methods to industrial application requires deposition on structured substrates, with high aspect ratio features to determine the process's limitations. In addition, three-dimensional patterned substrates are a useful tool for the study and modelling of CVD growth [15–17], which is still not fully understood. Floter et al. [18] in 1995, reported a strong dependence of the nucleation density on the orientation of the surface when bias pre-treatment of structured Si substrate was employed. This led to a very low or absent diamond growth on the side-wall of trenches. However, the bottom of trenches were coated with diamond for aspect ratios reaching 7, with a maximum film thickness related to the width of the trench, rather than its depth or the length of the treatment. In this study, the MW-CVD deposition was performed at elevated temperatures (750 °C–900 °C) and a pressure of 4000 Pa. Monteiro and Liu [19]

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reported in 2003 on the effect of a diamond like carbon pre-treatment on diamond growth on structured surfaces. They achieved homogeneous growth on structures showing an aspect ratio below one. The exact deposition conditions were not reported in this work, but from the crystalline structure it can be concluded that the substrate temperature was above 500 °C. Ralchenko et al. reported in 2004 [20], again in the context of large diamond crystal growth, that seeding with diamond particles in an ultra-sonic bath treatment yielded best results in 3D conformity of the pre-treatment. Eaton et al. reported in 2001 [9] on modelling the effect of oxygen on the capability of conformal 3D diamond deposition. Due to the higher lifetime of OH radicals, compared to atomic hydrogen, they predict better step coverage when oxygen is added to the gas mixture. However, even if interesting information can be found in these publications, none of them explicitly addresses the low-temperature deposition of NCD on structured surfaces.

In this publication, we present work using a set of Hi-Wave sources in a Matrix Elementary Plasma Source configuration (MEPS) [21] for NCD deposition using low power density ( $< 7.6 \text{ W cm}^{-2}$ ), low deposition temperature (350 °C) and low pressure of 30 Pa. The structure of the deposited NCD film was evaluated on a structured three dimension (3D) silicon substrate with trenches up to 100  $\mu\text{m}$  deep with aspect ratios ranging from 1:1 to 1:7.

## 2. Experimental details

### 2.1. Substrate preparation

A 100 mm diameter single crystal silicon wafer with  $\langle 100 \rangle$  orientation and 525  $\mu\text{m}$  thickness was micro patterned in a cleanroom environment. The surface was first coated with the AZ 9221 photoresist from Microchemicals to a thickness of 2  $\mu\text{m}$  by spinning at 4200 RPM, then soft baking at 110 °C. This photoresist enables high resolution, straight sidewalls and good resistance to the subsequent deep reactive ion etch process, without the need for a post-development hard bake step. The resist layer was exposed by direct laser writing in a Heidelberg MLA150 with a beam diameter of 1  $\mu\text{m}$  and an exposure intensity of 130  $\text{mJ/cm}^2$ . The exposed photoresist is removed by immersion into Microchemicals AZ400K developer, then the substrate is rinsed with DI water. To transfer the pattern into the silicon substrate, an Alcatel AMS 200E inductively coupled Radio Frequency (RF) plasma etcher was used to run a Bosch process with the inductively coupled plasma (ICP) power set to 1800 W. In each cycle, the substrate was exposed to the silicon etchant ( $\text{SF}_6$ ) for 6 s, then to the sidewall passivation gas ( $\text{C}_4\text{F}_8$ ) for 2 s. This two-stage process was repeated until the target depth of 100  $\mu\text{m}$  was achieved. The average etch rate was 4.88  $\mu\text{m/s}$ . The remaining photoresist was removed using a barrel plasma etcher with 400  $\text{ml/min}$   $\text{O}_2$  flow and a 500 W RF plasma. The silicon wafer was diced into 10  $\times$  10 mm chips along the crystalline axes with a Disco DAD321 automated dicing saw.

All substrates were seeded by NeoCoat SA, CH, using a proprietary process by immersing in a bath containing diamond nanoparticles (around 10 nm in diameter) in suspension. This seeding process usually yields a high density of nuclei [14]. Prior to deposition, all samples were exposed to pure  $\text{H}_2$  plasma with increasing microwave power for approximately 1 h.

### 2.2. NCD deposition

The MEPS reactor used for the diamond deposition was home-built [21]. It employs seven microwaves antennas (Hi-Wave, SAIREM, FR) [22], arranged in a hexagonal configuration with a distance of 55 mm between sources. Each of the sources is individually connected via a coaxial cable to a 200 W solid-state microwave generator. Each of the seven microwave generators can independently frequency tuned to reduce the reflected power below 5 W. The reactor concept resembles in many points the Distributed Antenna Array (DAA) [4,14,23]. The major

differences are the use of solid-state generators and auto-matched microwave antennas, allowing for operation without power distributors and additional impedance matching. A more detailed description of the Hi-Wave antennas used in this work is given in [24]. The gas supply system consists of four mass flow controllers and an Edwards E2M40 rotary pump.

The CVD growth on silicon was conducted at a pressure of 30 Pa and a substrate temperature of 350 °C with a power density of  $6.8 \text{ W cm}^{-2}$  (180 W per microwave antenna). The plasma density, determined using Langmuir probe measurement, reaches  $2 \cdot 10^{11} \text{ cm}^{-3}$  corresponding to approximately twice the critical density for this excitation frequency (2.45 GHz). The distance between the substrate holder and the applicators was 50 mm. Since the substrate was heated directly by the plasma, no substrate heating was necessary. The dihydrogen and methane gas flows were 47 sccm and 3 sccm, respectively, diluted in argon. This gas mixture corresponds to a 97% $\text{H}_2$ -3% $\text{CH}_4$  concentration. It corresponds to the lower left corner in Bachmann diagram for CVD diamond growth and is typically used in the HF-CVD deposition technique. The average growth rate under these conditions was approximately 35 nm/h.

The emission of CVD system was monitored by an Ultima II, Horiba-Scientific, 1m Czerny-Turner spectrometer. The observed spectra included the CH A-X, -X, C-X molecular bands, the 429.902 nm line of atomic carbon and various atomic hydrogen lines indicating a high level of dissociation.

Raman spectroscopy characterization of the NCD films was performed using a MonoVista CRS+ with a ultra violet (UV) objective ( $\times 40$ ) @ (325 nm; 20 mW) laser and visible-light lens ( $\times 50$ ) @ (514 nm; 10 mW) laser. The detector is an InGaAs Andor Camera cooled to  $-70^\circ\text{C}$ .

Scanning Electron Microscope (SEM) cross sectional images of the structured Si samples were obtained by cleaving and imaging in a high resolution field emission SEM, model S4800 N from Hitachi, with a resolution around 2 nm at 1.5 kV.

## 3. Results

A silicon chip was cleaved to obtain a cross-section of the structure and to determine the trench geometries by high resolution scanning electron microscopy. Trenches with opening widths of 100, 50, 20, and 10  $\mu\text{m}$  were cross-sectioned. The attained trench depth reduces with decreasing feature width, which is a well-known side-effect [25] due to gas depletion during DRIE. For the Bosch process, this Aspect Ratio Dependent Etch (ARDE) effect becomes prominent as the aperture width decreases to a few microns.

The progress of the plasma etch was monitored on a large open area and was stopped when the top-to-bottom offset reached 100  $\mu\text{m}$ . The resulting trench depths were 100, 98, 80 and 70  $\mu\text{m}$ , respectively; and the achieved geometries correspond to aspect ratios of 1:1, 1:2, 1:4 and 1:7 (Fig. 1). The trench length in each case was 1 mm.

The sidewall scalloping is formed by the alternating etch and passivation steps of the Bosch process and slightly change with trench width due to the ARDE effect. The 10  $\mu\text{m}$  wide trench had a scallop height of 610 nm, and an edge to edge width of 190 nm. The values for the 100  $\mu\text{m}$  wide trenches were 680 nm and 230 nm, respectively (Fig. 2).

### 3.1. Seeding characterization

The surface coverage resulting from this seeding process was evaluated by treating HR-SEM top-view images (500K magnification) with the "Wand-Auto Measure" Tool of the ImageJ software package. It was found to be of approximately 66%, which then results in a distance between seed agglomerations of around 20 nm.

For features with an aspect ratio of 1, the seed density on the bottom is not significantly different to the top of a feature.

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