

Synthesis of thick, uniform, smooth ultrananocrystalline diamond films by microwave plasma-assisted chemical vapor deposition

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Abstract

The deposition of uniform, low-stress, thick and thin films of ultrananocrystalline diamond (UNCD) is investigated. The process methods and apparatus that enable the uniform and smooth deposition of both thin and thick (>50 μm) UNCD across 3 in. diameters are described. UNCD films are synthesized by microwave plasma-assisted CVD using Ar/H₂/CH₄ input gas mixtures over a wide pressure range (60–240 Torr) and temperature range (400–850 °C). Films were grown on 3 in. diameter silicon substrates with thicknesses ranging from 58 nm to greater than 50 μm. Film surface roughness as low as 10 nm (AFM) was obtained. Film uniformities of 70 to over 95% were achieved on 3 in. diameter silicon substrates. The growth rate increased as pressure, percent hydrogen and percent methane in the gas mixture, and microwave power increased. The highest growth rate 1.12 μm/h was achieved at 180 Torr, H₂/Ar/CH₄=(4:100:2) sccm and 1.5 kW absorbed power. Overall, a robust, repeatable process has been demonstrated for the deposition of UNCD films.

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1. Introduction

Applications of ultrananocrystalline (UNCD) and nanocrystalline (NC) diamond films have been a common, recent topic of many investigations. The exceptional properties of these films, such as high hardness and chemical inertness combined with their small crystal size and smoothness and excellent mechanical properties such as high Young's modulus [1], fracture toughness [1] and low coefficient of friction, have suggested application as a protective, hard coating material, a material/substrate for micromechanical systems [2], a SAW device substrate [3], a robust conducting coating for electrochemical electrodes, and as a freestanding film for vacuum windows or ion beam stripping foils [4]. The commercial success of each of these applications requires the development of repeatable, CVD diamond thin film synthesis processes that are able to deposit these films on a variety of substrates. Additionally, uniform, stress free, thick and thin film deposition is desirable. In this paper we report on the development of process methods and

apparatus that enable the uniform, repeatable and smooth deposition of both thin and thick (>50 μm) UNCD.

2. Experimental description

UNDC films were synthesized on silicon substrates using Ar/H₂/CH₄ input gas mixtures [5] where H₂ and CH₄ were incrementally varied from 0–4% and 1–3%, respectively. Our experiments demonstrated that in order to routinely synthesize high quality, smooth and uniform UNDC films the deposition must be performed in a high purity environment [6]. Thus experiments were carried out using a high vacuum system and with (1) argon, (2) H₂, (3) CH₄ source gas purities of 99.999%, 99.9995%, and 99.99% respectively. The microwave plasma reactor system consisted of a variable power, 6 kW maximum, 2.45 GHz microwave power supply connected to a microwave cavity reactor [7]. A cross-sectional view of the plasma reactor and vacuum system is displayed in Fig. 1. As shown the microwave discharge is created by exciting the cavity applicator in the TM₀₁₃ mode and then the discharge is confined inside a 12.5 cm inside diameter cylindrical quartz dome which is located at the fixed end plate of the tunable

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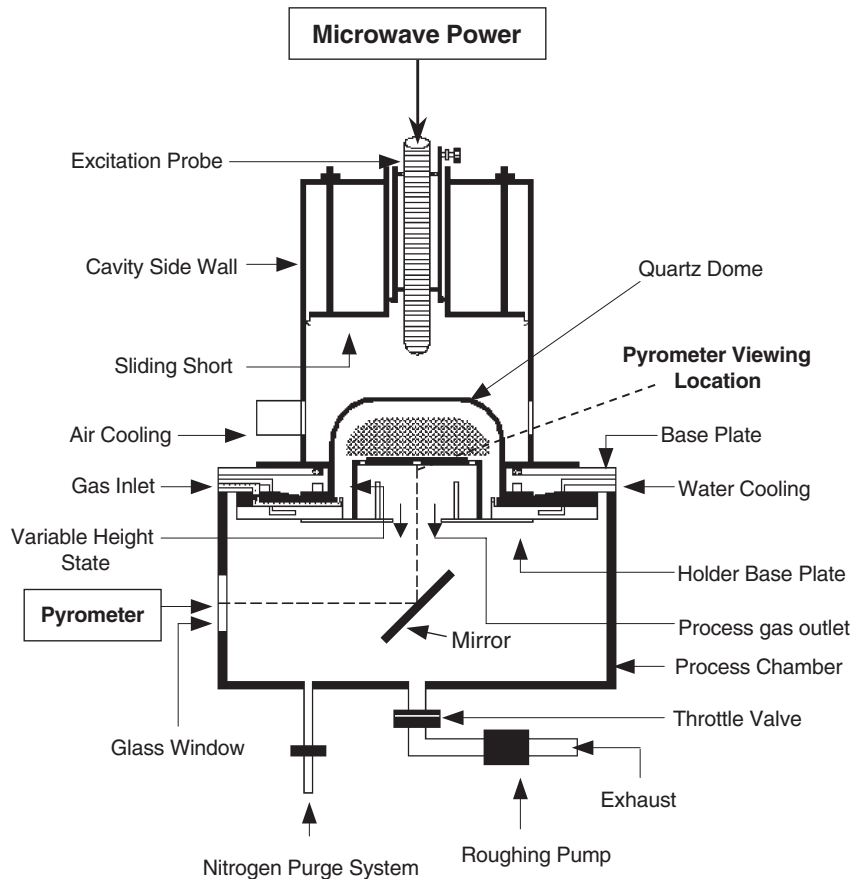


Fig. 1. Microwave plasma reactor with thermally floating substrate.

applicator. A wide range of experimental conditions, i.e. pressures from 50 to 240 Torr, absorbed powers between 400 and 1650 W, variable gas mixtures and total flow rates (100–630 sccm), substrate placement, etc., were explored to identify the optimal conditions that enable the repeatable deposition of uniform and smooth UNDC films over 3 in. silicon substrates.

As shown in Fig. 1 the silicon substrate was placed on a molybdenum holder which was placed on a stage connected to the holder base plate. At each pressure the stage height and the cavity tuning were adjusted to position the substrate in direct contact with the microwave discharge. The backside substrate temperature was measured by an optical pyrometer that viewed the backside of the substrate through several small, 3 mm diameter holes located across and in the molybdenum substrate holder. At each operating pressure discharge uniformity, substrate temperature uniformity and hence deposition uniformity were achieved over the substrate diameter by careful adjustment of (1) microwave input power, (2) the cavity tuning, and (3) stage height. As is also shown in Fig. 1 the reactor base plate is water cooled and the quartz dome is air cooled. Since deposition repeatability was desired, the air and water cooling temperatures were carefully measured and controlled so that process repeatability was insured. Additionally the reactor was operated in a warm/hot condition to efficiently produce a thermally uniform deposition environment inside the quartz chamber.

All the experiments were performed using, as is described in detail elsewhere [8,9], the thermally floating substrate config-

uration. In this deposition configuration the substrate holder and the substrate are not actively cooled or heated and thus all the energy supplied to the substrate is supplied by the microwave discharge. The balance of heat flow from the discharge and the loss of heat due to conduction, radiation or convection determine the steady-state substrate temperature. When operating in this configuration the substrate temperature is a function of both the pressure and the absorbed microwave

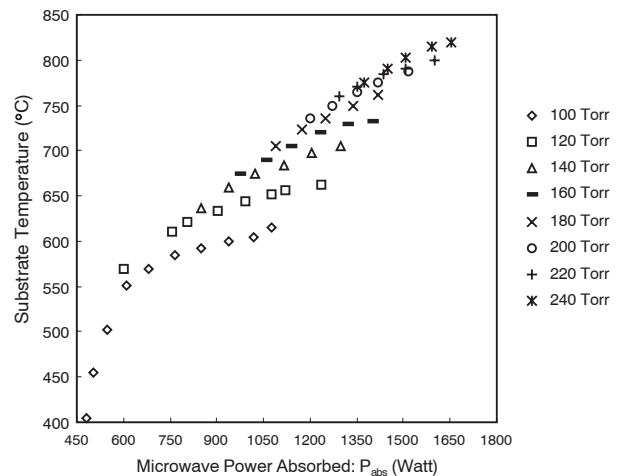


Fig. 2. Substrate temperature versus absorbed microwave power and pressure for the thermally floating configuration. The gas feed flow was argon at 100 sccm, methane at 1 sccm and hydrogen are at 4 sccm.

power. As is shown in Fig. 2, the experimentally measured substrate temperature varied from 400 to 850 °C as the pressure and power were varied from 100–240 Torr and 400–1650 W respectively. The pressure, power and substrate temperature variation shown in Fig. 2 served as the operating “road map” of the reactor system of Fig. 1 that enabled the deposition of uniform UNCD films.

Substrate pretreatment involved uniform mechanical scratch seeding with 0.1 μm diamond powder followed by an ultrasonic bath cleaning and acetone and de-ionized water rinse. The deposited films were characterized using high resolution TEM to determine crystal size distribution, atomic force microscope (AFM) to determine surface roughness, and SEM images of film cross section to determine film thickness and uniformity.

3. Deposition results and discussion

A large useful UNCD experimental uniform deposition window (60–240 Torr, 400–1650 W, total gas flow rate 100–110 sccm, H₂ 0–4%, CH₄ 1–3%) was identified. Across this entire parameter space uniform films (>70% uniformity as defined below) were synthesized. Using 0–1% H₂, i.e. hydrogen deficient conditions, discharges were sustained in contact with the 3 in. substrates over a 60–200 Torr pressure regime. High quality film deposition was extended to 240 Torr when H₂ concentrations were increased to 1–4%. The deposition rate as a function of pressure and hydrogen flow rate is shown in Fig. 3.

Film crystal sizes as measured by high resolution TEM ranged from 3 to 30 nm across the parameter space studied. A typical result included crystal size variations from 3 to 12 nm with the predominant size less than 7 nm for films deposited with 100 sccm Ar, 4 sccm hydrogen and 1 sccm methane. The film roughness as measured with AFM ranged from 11 to 50 nm. The film roughness as shown in Fig. 4 generally decreases as the hydrogen flow rate is decreased at the higher pressures above 100–120 Torr. An interesting observation is that the

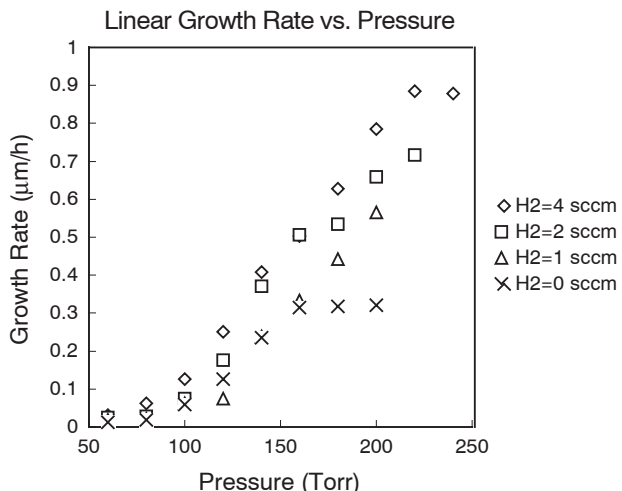


Fig. 3. Linear deposition rate versus pressure. The feed gas flow rates were 100 sccm of argon, 1 sccm of methane and either 0, 1, 2 or 4 sccm hydrogen.

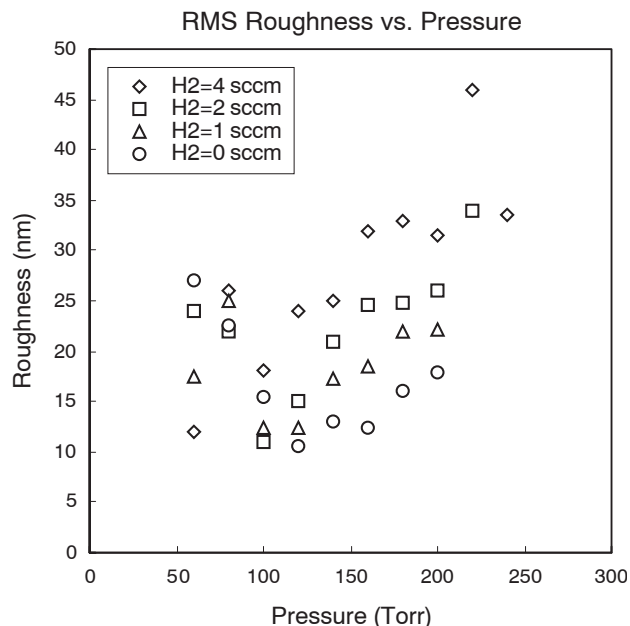


Fig. 4. Surface roughness as measured by AFM for varied deposition conditions. The feed gas flow rates were argon at 100 sccm, methane at 1 sccm and hydrogen at 0, 1, 2, or 4 sccm.

roughness of the surface has a minimum at 120 Torr for 0 sccm of H₂.

The uniformities of the UNCD films across a 3 in. diameter substrate are shown in Fig. 5. The uniformity is defined as

$$\text{Film Uniformity} = \frac{\text{(Minimum thickness)}}{\text{(Maximum thickness)}}$$

As seen in Fig. 5 the uniformity across 3 in. is greater than 95% at the lower pressure around 80 Torr. The uniformity decreases at the higher pressures to values that remain at 70% or greater. The film uniformity was optimized by adjustment of the pressure, input microwave power, substrate height position and microwave cavity tuning (especially the sliding short position). The growth rate data shown in Fig. 3 and the film uniformity data shown in Fig. 5 reveal that the highest growth

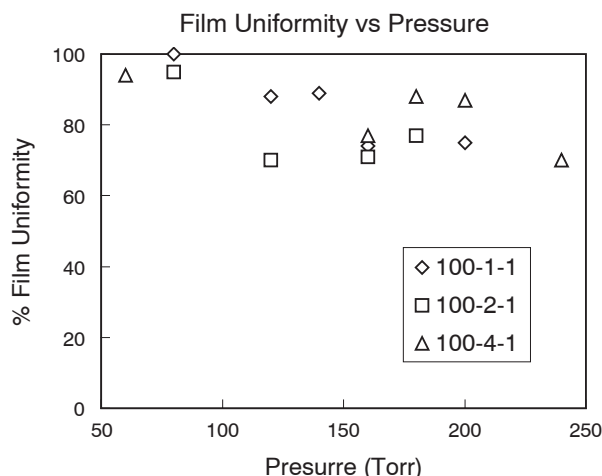


Fig. 5. Film uniformity across a 3 in. diameter versus deposition pressure. The argon–hydrogen–methane flow rates are indicated in the legend.

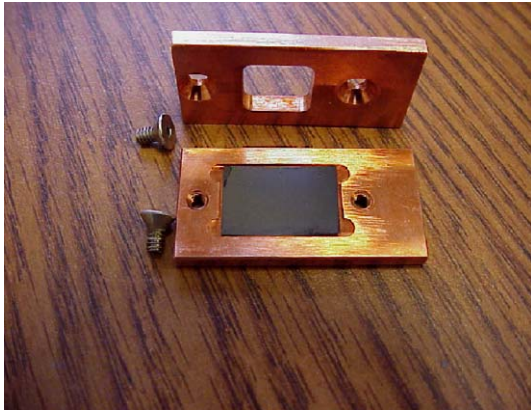


Fig. 6. UNCD film of 50 μm thickness being mounted in a copper holder. The film shown after the silicon substrate is etched away. The size of the film is 10×15 mm.

rates of more than 0.5 $\mu\text{m}/\text{h}$ result in uniformities across 3 in. diameter substrates of 75–90%, whereas the best uniformities occur at pressures that have lower growth rates.

The UNCD films have been grown to thicknesses of 50 μm for use as electron stripping foils for high energy ion beams. For this application the films were grown on 3 in. diameter silicon wafers to the desired thickness. Then the silicon wafer and deposited UNCD films are laser cut to the desired size (typically 10×15 mm). The UNCD film is then removed from the silicon by etching the silicon away with an acid mixture. One such UNCD film that is free standing (removed from silicon substrate) is shown in Fig. 6. The 50 μm thick UNCD is freestanding and relatively flat, and thus can be placed in the foil frame after wet etching the silicon away.

4. Conclusion

Uniform, low-stress, UNCD films have been deposited over a wide pressure range (60–240 Torr) and temperature

range (400–850 C). Films were grown on 3 in. diameter silicon substrates with thickness ranging from 58 nm to >50 μm . The film surface roughness as low as 10 nm (AFM) was obtained. Film roughness increased as pressure and hydrogen percentage in the gas mixture increased. The growth rate increased as pressure, gas mixture (% H_2 , % CH_4), and microwave power increased. A high growth rate of 1.12 $\mu\text{m}/\text{h}$ was achieved at 180 Torr, $\text{H}_2/\text{Ar}/\text{CH}_4=(4:100:2)$ sccm and 1.5 kW absorbed power. Overall, a robust, repeatable process has been demonstrated for the deposition of UNCD films. It appears that these process techniques and methodologies can readily be scaled to 4 in. diameter wafers in the current 2.45 GHz microwave plasma reactor system. Scaling to even larger diameter areas is possible using a 915 MHz reactor system.

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