Compact and Efficient HFCVD for Electronic Grade Diamond and Related Materials.

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Compact and Efficient HFCVD for Electronic Grade Diamonds and Related Materials


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ABSTRACT

A compact and efficient hot filament chemical vapor deposition system has been designed for growing electronic-grade diamond and related materials. We report here the effect of substrate rotation on quality and uniformity of HFCVD diamond films on 2” wafers, using two to three filaments with power ranging from 500 to 600 Watt. Diamond films have been characterized using x-ray diffraction, Raman Spectroscopy, scanning electron microscopy and atomic force microscopy. Our results indicate that substrate rotation not only yields uniform films across the wafer, but crystallites grow larger than without sample rotation. Well-faceted microcrystals are observed for wafers rotated at 10 rpm. We also find that the Raman spectrum taken from various locations indicate no compositional variation in the diamond film and no significant Raman shift associated with intrinsic stresses. Results are discussed in the context of growth uniformity of diamond film to improve deposition efficiency for wafer-based electronic applications.

INTRODUCTION

Diamond films are attractive for electronic, optical, and mechanical applications because of their excellent hardness, strength, chemical and thermal stability, thermal conductivity, breakdown voltage, hole and electron mobility, radiation hardness, and optical transmission [1-3]. Enormous efforts have been made in studying diamond thin film growth by several chemical vapor deposition techniques including plasma assisted CVD (microwave, RF, DC), hot filament, electron and laser assisted, and ion beam assisted [4-13]. Large area and uniform diamond films are required for wafer-based semiconductor device applications including Microelectromechanical (MEMS) devices. Among many chemical vapor deposition techniques, HFCVD is the simplest and most versatile technique for growing diamond films on various substrates over a large area. Owing to its low capital cost and the ease of scalability, HFCVD has been considered as a very useful technique for producing low cost diamond films for industrial applications. In order to exploit HFCVD diamond for wafer-based electronics applications such as cold cathode field emitters, high thermal conductivity substrate materials for white LEDs, and high power Schottky diodes, diamond deposited substrate areas need to be scaled up without loss of uniformity or film quality.

The main motivation of the present study is to identify the effects of various processing parameters on growth of diamond films on a rotating substrate or wafer to achieve uniform diamond films over large area substrates while minimizing thermal and power requirements for efficient reactor operation. In this context, we have developed a commercial HFCVD reactor in which the substrate or wafer can be rotated at 10 rpm while keeping the number of filaments to be as low as two or three. Our research efforts allowed us to develop a low cost, highly efficient, and high throughput commercial HFCVD system for production of high quality diamond films. Here, we discuss optimization of process parameters on the growth of diamond films with emphasis on quality, morphology, and uniformity of diamond films. Results are discussed in the context of enhancing crystallite size, which is useful for various applications of diamond films in electronics.

EXPERIMENTAL

The stainless steel, double-wall, water cooled vacuum chamber was design to accept a 2” dia wafer (capable up to 4” dia wafer) through a load lock chamber (Fig. 1). A load lock transfer chamber is attached to the gate wall and it allows for easy and quick access to the substrate without breaking vacuum in the main HFCVD chamber. A multi-axis positioner is connected to the load lock and allows the transfer arm to be tilted in the desired position. The load lock chamber is also beneficial for carburization of filaments before loading wafer for deposition. The bottom port holds a flange with a rotating substrate heater capable of reaching 850 °C with linear z directional travel of 2 inches that allows variable distance between substrate and filaments. The components of the filament assembly are presented in Fig. 1. It shows a filament assembly capable of having a number of filaments (0.5 mm dia and 8 cm
long) from 2 to 8 with spring loaded moly holders to adjust tension in the filaments associated with change in length due to thermal expansion and sagging of the filaments. Tungsten filaments were placed 15 mm apart with one position originating near the center of a 2” substrate. The substrate heater, measuring 2.2” in diameter suitable for a 2” substrate, is mounted on a vertical z stage with susceptor capable of rotating at 10 rpm during diamond deposition. The purpose of substrate rotation is to introduce uniform diamond deposition throughout wafers with diameter equal or larger than 2”. For optimization studies, we mainly focused on 2” single side polished silicon wafers. Prior to diamond growth, wafers were first cleaned in an ultrasonic bath of acetone for 5 min. and then blown dry by compressed air. The substrates are then seeded with either 0-0.2 micron or 3 micron diamond pastes by applying the paste mechanically onto the substrate surface followed by ultrasonic bath treatment in diamond slurry for 15 min. and then finally rinsed and then cleaned in ultrasonic bath of acetone and methanol.

To avoid poisoning of tungsten impurities and enhance chemical purity in the deposited thin films, tungsten filaments were pretreated and carburized for 30 min. to 1hr. New tungsten filaments were installed every experiment to ensure reproducibility of deposition process. The filaments were exposed to higher methane concentration (10%-50%) at approximately 1500°C for 10min, then at 1800–1900°C for 5min and finally for a brief moment at 2100°C to form a thin tungsten carbide layer, which prevents tungsten evaporation during subsequent growth. This filament pretreatment is similar to that of reported by Yap et.al. [14] which confirms no sign of W contamination in their samples as verified by X-ray photoemission spectroscopy. Once the carburization of the filaments is completed, the pretreated wafer is transferred to growth chamber without breaking vacuum and the process parameters for diamond growth are set. Filament temperature was monitored using an infrared pyrometer to 2000°C. Typical power for the filaments was found to be about 500 watt to reach deposition of good quality diamond films. The distance between filament and substrate was kept constant at about 10 mm. HFCVD diamond samples were characterized by scanning electron microscopy, Raman spectroscopy, and x-ray diffraction, and electrical resistivity measurements. Raman spectroscopy was performed using confocal Raman Imaging mode (alpha 300 R) made by WITech. Raman spectra are collected with a high sensitivity confocal microscope connected to a high-throughput spectrometer equipped with a CCD camera. Excitation laser wavelength used for the Raman spectroscopy was 532nm.

RESULTS AND DISCUSSION

Initially, we optimized the diamond deposition process using conventional approaches to deduce the effect of wafer rotation on diamond quality. For optimization, we systematically varied methane to hydrogen ratio for growth of diamond films without substrate rotation. Fig. 2 shows scanning electron micrographs of the HFCVD diamond films grown at various CH₄/H₂ ratios.
Fig. 2(a) corresponds to diamond film grown at higher methane flow rate of 7 sccm (H₂ of 93 sccm). From the SEM image it is clear that the growth of the film is supersaturated with carbon (typically observed sp² bonded material in sp³ matrix). As the methane content was reduced to 5 sccm (H₂ of 95 sccm), diamond crystallites began to show facets. Upon further decrease in methane flow to 1.5 to 2 sccm (H₂ 98sccm) highly faceted diamond crystals are visible in the microscope. Scanning electron micrograph of this sample is shown in Fig. 2(c). Diamond crystals of about size 4-5 micron are clearly visible in this micrograph. Thus, this study provided optimum growth conditions for the formation of polycrystalline diamond films irrespective of substrate rotation. This means that CH₄/H₂ ratio, and the filament temperature are adequate for diamond growth. Importantly, note that the film grown at lower methane conditions has poor surface coverage indicating poor lateral growth of crystallites or significantly less multiple nucleation of diamond crystallites.

Fig. 2 SEM micrographs of the HFCVD diamond films grown at (a) 7sccm of (b) 5sccm and (c) 2 sccm of CH₄ in H₂ of about 93-98 sccm of H₂.

Fig. 3 SEM micrographs of the HFCVD diamond films grown at substrate rotation of 10 rpm for (a) 6 hrs and 25 hrs respectively. Fig 3 (c) is the magnified image of 3 (b).

Fig. 3 SEM micrographs of the HFCVD diamond films grown at substrate rotation of 10 rpm for (a) 6 hrs and 25 hrs respectively. Fig 3 (c) is the magnified image of 3 (b).
Upon optimization and establishing diamond growth parameters for the given reactor, substrate rotation was introduced to study its effect on diamond film morphology, crystallite size of microcrystalline diamonds film, and its uniformity and quality. Figs 3 (a) and 3(b) show SEM micrographs of the diamond films grown at 2 sccm (H₂ 98sccm) for the duration of about 6 hrs and 20 hrs while the wafer was rotated at 10 rpm, respectively. Clearly, diamond growth with high nucleation density and complete coverage is observed for the rotated substrate. We noted that diamond film coverage was within 5-7% of the film thickness over the 2” wafers. We also noted that the diamond crystals grow larger with time as observed from the SEM micrograph of the thicker film (Fig. 3c). This means the substrate rotation uniformly exposes the wafer to atomic hydrogen and carbon radical species and improves uniform growth of diamond crystallites. The growth rate under substrate rotation is found to be 0.3 micron/hr for the given power.

In order to further study the effect of sample rotation on diamond quality (Sp³ bonded carbon versus sp² bonded graphitic material), compositional homogeneity, and intrinsic stresses, we conducted Raman spectroscopy in confocal imaging mode. Fig. 4 shows the video image (on the left) and Raman spectrum (on the right) for the deposited diamond sample under optimum conditions (i.e. CH₄ of 2 sccm and H₂ of 98 sccm) with sample rotation. The data was recorded with the integrated white light stitching function of the microscope. The cross indicates the positions where the single spectrum shown on the right side was recorded. The yellow box indicates the area where the scan was performed and the resulting Raman spectrum is shown on the right side. The results indicate a peak at 1332 cm⁻¹ for diamond and it is much narrower (<13cm⁻¹) than any other samples discussed above. Such a sharp peak is typical for microcrystalline diamond or large crystallites in diamond film. Interestingly there is no significant increase of the peak near 1500 cm⁻¹ that is associated with graphitic or sp² bonded material. Thus substrate rotation does not adversely affect the quality of the diamond film.

We have also performed Raman scans at various locations on the diamond deposited wafer with substrate rotation as shown in Fig. 5. After performing a scan with the high resolution grating, the diamond line of each of the 22500 spectra (corresponding to each pixel of the 150x150 image) was fitted using a Lorenzian fit. The images below show the results of two of the fit parameters: the line width (FWHM) and the exact peak position of the line. The spectra beneath the images show the extreme cases color coded according to the images taken for diamond film near the center and near the edge of the wafer. The results indicate that the line width broadening of the Raman peak near the center of the wafer is within 5-8 cm⁻¹ and peak position is within 2-3 cm⁻¹. Similar Raman results are found near edge of the wafer as shown in Fig. 5(b). From these results we conclude that the substrate rotation introduces uniform diamond deposition process without significant increase in sp³ or graphite phase material or any significant stresses associated with compositional changes throughout the wafer.
We have also conducted x-ray diffraction studies on the optimally grown diamond films. The films are found to be polycrystalline as expected from SEM results. However, major orientation of the diamond microcrystals is found to be \{111\} normal to the substrate plane. This is consistent with the surface morphology obtained during HFCVD that depends critically upon the gas mixing ratio and the substrate temperature [3]. The electrical resistivities of these

Fig. 5 Confocal Raman images and corresponding Raman scans near (a) the center and (b) the edge of the diamond deposited wafer. Left side images and spectra indicate variation in line width of characteristic 1332 cm\(^{-1}\) peak while right side images and spectra indicate variation in peak position over the wafer’s various locations.
Polycrystalline diamond films were found to be greater than $10^{10}$ ohm-cm at room temperature. We are studying additional controllable methods of enhancing nucleation such as bias induced ion bombardment. Our reactor design is capable of biasing substrates up to -250V. Simply adding a negative bias of a few hundred volts to the substrate will allow the ions to damage the surface and implant into the lattice which are known to favorably affect diamond growth. One can envisage (at least) two routes to this objective: one has to either identify growth conditions which naturally result in the formation of smooth films, or optimize heteroepitaxy with bias enhanced nucleation (BEN). In the negative bias enhanced nucleation step, a high nucleation density and a high degree of orientation alignment can be achieved by bombarding the Si substrates with positive ions of hydrogen and hydrocarbon [4-13].

In conclusion, we demonstrated uniform diamond film deposition using an introduction of substrate rotation mechanism. The results indicate that wafer rotation and dynamics of crystal growth support enhancement of the growth uniformities of diamond films. Due to this we anticipate reduction of non homogeneities in HFCVD polycrystalline diamond film. This is an important consideration when it comes to the potential applications of diamond films made using high throughput HFCVD. Our reactor design also allowed system integration of diamond for other physical and chemical deposition system for fabrication of metal-semiconductor interfaces for device fabrication, and other common applications of diamond films in optical and power devices (Schottky diodes and field emitters).

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