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EFFECT OF DIFFERENT SUBSTRATE TEMPERATURE ON GROWTH OF NANO CRYSTALLINE DIAMOND BY HFCVD TECHNINQUE

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ABSTRACT. In this paper, we investigated the effects of different substrate temperature and nitrogen etching gas on synthesis of Nano Crystalline Diamonds (NCDs). We prepared all samples by Hot Filament Chemical Vapor Deposition (HFCVD) system. Silicon wafers (100) were used as substrates for all experiments. All samples were coated by Au at 50 nm thickness, as catalyst layers, by sputtering system. To remove the native oxide on silicon, all the samples were cleaned in ultrasonic bath by acetone, ethanol and de-ionized water, respectively. Substrate temperature was controlled by thermocouple in contact with substrate holder, between 550°C and 650°C. The samples were examined by X-Ray diffraction spectroscopy at room temperature. The changes of surface morphology of the diamond Nano crystals were clearly viewed by the Scanning Electron Microscopy SEM. The results show nanocrystalline diamond films and diamond nano crystals grown on substrate under various temperatures with different crystalline structures.

Keywords: *Etching, Hot filament CVD, Nanocrystalline diamond films, SEM.*

INTRODUCTION

Due to the unique properties such as high thermal conductivity, chemical stability, and high field failure diamond nano crystals are used in various fields including mechanical, electrical, semiconductor parts, optical application, etc [1-11]. Since 1950, many researcher groups have investigated the growth of diamond by various Chemical Vapor Deposition CVD techniques in view of finding particular ways to obtain diamond for different applications by low pressure, low temperature methods instead of those methods using high

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pressure, high temperature [12 -25,38]. Compared to the other CVD technique, the Hot Filament Chemical Vapor Deposition HFCVD process presents several advantages, such as the possibility of deposition of thick layers on large areas (over 1000cm^2), the possibility of coating various types of substrate surface, high film uniformity, easy to operate, relatively cheap, etc [29,7].

Since 1990, studies were shifted from poly-crystal to nano-crystal diamond [34]. In these studies, different parameters have been varied: type of gas, gas pressure, gas concentration, substrate preparation, surface roughness, filament's temperature, on seed size and crystal growth rate, etc [7, 28-33]. Some studies reported measurements of the experimental parameters in the growth of Nano Crystalline Diamonds NCD [11, 25-26]. According to D.C. Barbosa's group [11], one of the most important parameters in growing NCD films is the substrate temperature (in the range 550˚C to 850˚C). In 2008, C. J. Tang et al. added N_2 and O_2 in the mixture of CH_4 and H_2 at MPCVD method; they could grow large-grained polycrystalline and nanocrystalline diamond [34]. They used N_2 as the main gas in the reaction chamber to promote the secondary nucleation rate. Similarly, Sobia Allah et al. have grown NCDs films by HFCVD in $Ar/N_2/CH_4$ gas mixtures; they found that N_2 concentration in the flow added to plasma has a great influence on the grain size of the nano diamonds, as measured by X-Ray Diffraction XRD. In this case the diamond peaks became narrower [32].

In this work, we investigate the growth of diamond nano-crystals on silicon substrate using HFCVD method and the effect of different temperatures on surface morphology and the formation of diamond crystals. The nitrogen was used in the pretreatment of the substrates for the first nucleation. Scanning electron microscopy SEM, X-ray diffraction XRD and Dektak profilometer were used for analyzing the samples.

RESULTS AND DISCUSSION

A. Methods for Substrate pre-treatment

Several methods for coating, including sputtering, evaporation, ion implantation and plasma-assisted chemical vapor deposition (CVD) can be used. Substrate coating adhesion can be enhanced by carrying out several pre-treatments of the substrate. Owing to growing diamond for better quality, we used some pretreatments before the main growing process.

In this study all samples were prepared by a sputtering system, previously described in ref [35]. Figure 2 shows the thickness of the gold catalyst layer, deposited on the substrates for 8 minutes (Dektak profilometer 3, version 2.13). The substrate temperature reached 550°C when the nitrogen was introduced into the system. This made gold islands on the surface; clearly, the nitrogen etching-treatment changed the morphology of the surface by creating nucleation sites thus increasing the diamond deposition.

B. Morphology Study

The surface morphology of the nanocrystalline diamond films was observed by SEM analysis (model XL30, Philips Company, Holland) as shown in Figure 3. In a first sample (Figure 3, a), the cauliflower nano crystalline diamond, grown at 550 °C substrate temperature, is evidenced. When the substrate temperature increased to 600 °C, the particle size decreased and a higher distribution of NCD could be observed (Figure 3, b). At 650°C, the grain size the particles became low and one can see a low density of NCD, which dispersed over the substrate surface (Figure 3,c). Thus, by increasing the temperature from 550°C to 650°C the crystal quality lowers. This indicates that nano crystalline diamond is suitably formed in a lower-temperature process.

C. X-Ray Diffraction XRD analysis

In XRD, the main peak is observed at 2θ=41.68°, 2θ=41.81° and 2θ=41.67°, which indicates the diffraction of (101) diamond for samples (a), (b) and (c), respectively. The results indicate a decrease in the quality of NCD by increasing the temperature up to 650°C and suggested that the film has a strong (101) preferential texture. The full-width-half-maximum (B) of these peaks was used to calculate the grain size from the well-known Sherrer's formula [7].

$$L(hkl) = \frac{K\lambda}{B\,\mathrm{Cos}\theta\ hkl}$$

Here K=0.9, λ=1.54A˚and θ is the Bragg angel.

The grain size decreases from 43.1nm to the 35.9nm with the substrate temperature increasing. Similar results have been reported by Barbosa‘s group. They suggested that the increase in defect density is induced by temperature raising [11]. Next, the patterns show the peaks with 2θ=42.72° and 42.90° which indicate the diffraction of (102) diamond structure. Figure 4 shows the XRD patterns for NCD grown on substrates at different temperatures.

CONCLUSION

In this paper, we investigated the effects of variation of the substrate temperature on the synthesis of nano crystalline diamond NCD. For enhancing the diamond nucleation, we used gold as a catalyst nano layer and nitrogen as an etching gas. We prepared all samples by a hot filament chemical vapor deposition system. The results show that the optimum conditions are placed at the minimum temperature (550 °C) in this experiment. The XRD, SEM and DEKTAK profilometer were the equipments used for analyzing the results in this experiment.

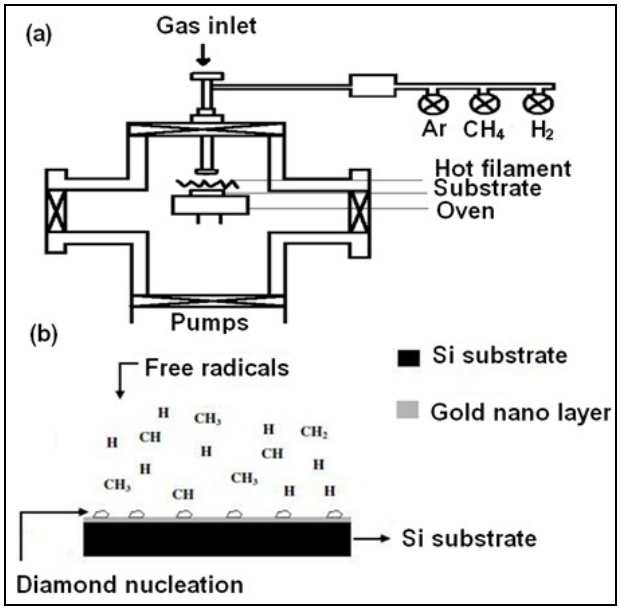

Figure 1. Generalized schematic HFCVD system (a) and the growth process in a diamond CVD reactor (b).

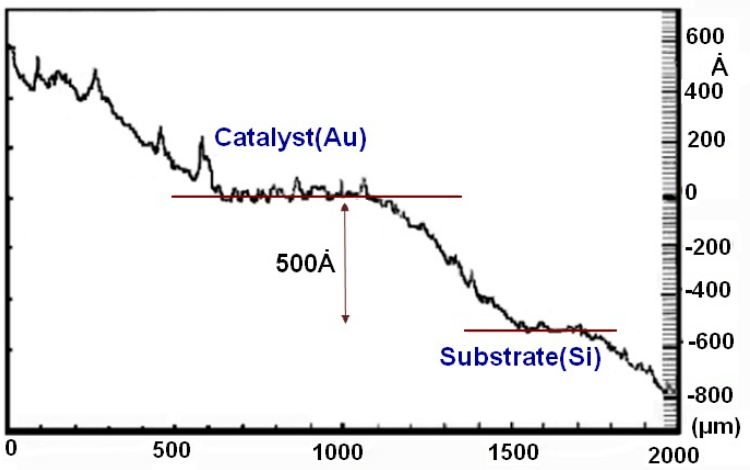

Figure 2. The gold layer thickness, on silicon substrates, equals 50nm.

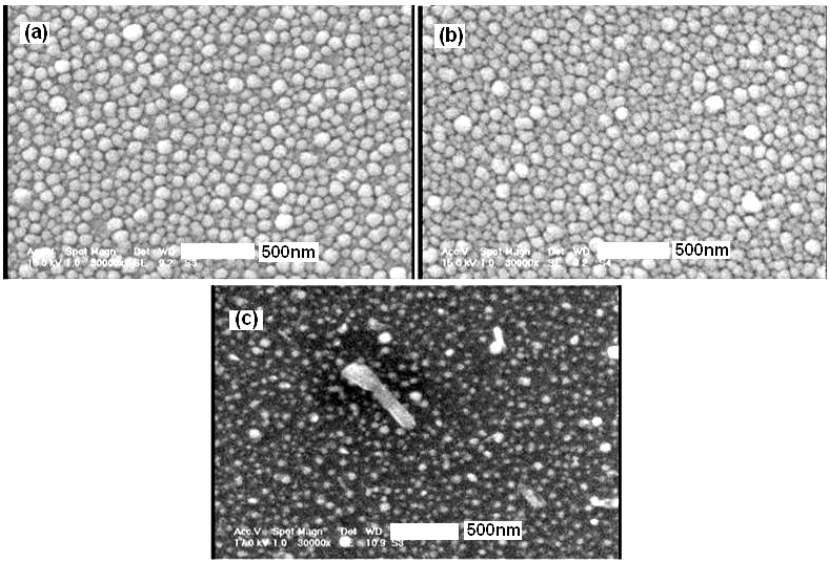

Fig. 3. SEM images of nanocrystalline diamond NCD grown at different substrate temperature (a): 550°C, (b):600°C, (c):650°C.

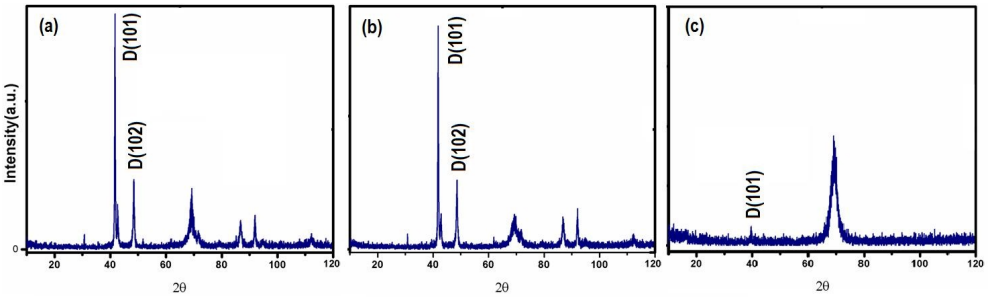

Fig. 4. X-Ray diffraction of nano crystalline diamond grown at different substrate temperature (a):550°C; (b):600°C; (c):650°C.

EXPERIMENTAL SECTION

A. HFCVD System

We prepared all samples in a Hot Filament Chemical Vapor Deposition HFCVD system. It consists of a reaction chamber, two rotary and diffusion pumps, an oven, water cooled vessel, a gas mixture, and a movable filament holder. The filament consists of a flat tungsten wire of 0.5mm in diameter for activating the source gas. The scheme of this system and therein reaction is shown in Figure 1.

B. Growth Process

Silicon wafers [p-typed Si (100)] was used as the substrates for all experiments. For pre-treating the samples and reducing the surface containments, we cleaned them, in an ultrasonic bath, by acetone, ethanol and de-ionized DI water for 15 min, respectively. The substrates were loaded to the CVD reaction chamber after pre-treatment. The distance between the substrate and filament was kept around 2cm. Before deposition process, to enhance diamond nucleation density and to improve the crystalline quality, argon Ar gas, was introduced into the system at a pressure of 8 Torr, and a flow ratio of 80 Sccm, for 45 minutes. Then N_2 gas was added to the reaction chamber. By using N_2 as etching gas, a suitable surface roughness was made [35]. In this step, the pressure, flow ratio, substrate temperature and etching time were: 15 Torr, 80 Sccm, 550 °C, and 45min respectively. For the deposition process, the chamber was evacuated down to 8.5×10^{-5} Torr. All the parameters were fixed during the deposition process except the substrate temperature, of which variation was controlled by a thermocouple in contact with the substrate holder, between 550°C and 650°C. The total flow rate of CH_4 /H_2 was fixed at 220 Sccm (concentrations Vol. 5.5% CH_4/ H_2). The overall pressure was 25 Torr while the deposition time was 80 min for each experiment.

Recall that the mechanism of deposition process was reported in many articles. In the growth process on silicon based materials by HFCVD, SiH_4 undergoes a catalytic decomposition into SiH_x or Si_2H_x (x = 1, 2, 3) radical species by the hot filament [36]. The radicals thus resulted can either deposit on substrates or further react with other gas phase species to produce precursor radicals for film deposition. These radicals were found to play an important role in producing high quality amorphous hydrogenated and polycrystalline silicon thin films [36]. Therefore, the nature of the precursor radicals has a great influence on the structure of the as-deposited films [36]. Recent studies performed by Matsumura et al. [37] on the radicals desorbed from a tungsten hotwire, by using threshold ionization mass spectrometry, evidenced various precursor radicals and their effect on the growth process. They shown that the H radical is one of the key radicals and it is used to determine the structure and characteristics of the as-grown diamond films. It was found that the crystalline fraction increased with the increasing dilution ratio (H_2/SiH_4), and amorphous and crystalline silicon were etched rapidly by the H radical [36, 37].

In this paper, the quality of diamond crystals was examined by X-Ray diffraction spectroscopy at room temperature. The surface morphology of the samples was investigated by the scanning electron microscopy SEM. The thickness of the catalyst layer was examined by Dektak profilometer.

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