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Effect of sputtered Mo interlayers on Si (100) substrates for the deposition of diamond film by hot filament chemical vapor deposition

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ABSTRACT

Dense, ultra-smooth and well-distributed nanocrystalline diamond films have been grown by hot filament chemical vapor deposition (HFCVD) on Si (100) substrates with a sputtered Mo interlayer in only 20 min. In order to investigate the effect of a Mo interlayer on the growth of CVD diamond films, each substrate was mounted over a range of HF-substrate separations, d_f. Spatially resolved scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy, X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS) and focused ion beam (FIB) milling of the deposited material provide a detailed relation of the evolution of film morphology, growth rate, surface roughness, grain size, sp^3/sp^2 content and phases with d_f in deposited samples. The deposited diamond film shows no internal stress. It is also found that the diamond nucleation density on sputtered Mo substrate after diamond powder pretreatment is more than $10^{14}/m^2$, which is a remarkable improvement compared with $10^{11}/m^2$ on bulk Mo substrate. The reason for the improvement is discussed in detail. This method can be a potential way to produce ultra-smooth nano-crystalline diamond for various applications. Also, the growth time of diamond can be greatly reduced.

1. Introduction

Studying the deposition of diamond films on various substrates, including ceramics, metals and semiconductors, is a beneficial way to understand the nucleation process of diamond. The favored substrates, such as W, Mo and Si, have a tendency to form an interfacial carbide layer under standard CVD conditions, which serves as a buffer layer, limiting carburization (the dissolution of carbon from the process gas mixture into the bulk of the substrate) and providing some stress relief at the interface [1–4]. The nucleation density of diamond on silicon substrate is very low in the absence of substrate pretreatments. The substrate pretreatment procedures include but are not limited to chemical erosion, mechanical scratching and powder ultrasonic bath. Erosion and scratching create defects on the surface of the substrate which serve as nucleation sites for diamond. Pretreatment in an ultrasonic bath containing diamond powder can create these defects. Also, diamond powder will be adsorbed on the surface. All these pretreatment methods faced the same problem: it is hard to deposit diamond film with a smooth surface because of the uneven distribution of defects and absorbed diamond powder.

Studies found that the growth dynamics of nanocrystalline diamond on silicon demonstrates two regimes [5,6]. Unlike Si substrates, it is possible to attain fair diamond nucleation on Mo substrates without any surface pretreatment [7]. The surface pretreatment for Mo is various. Ion sub-implantation was implemented to obtain very adherent diamond film on Mo substrate. The implantation process will effectively avoid phase transformation of Mo during the deposition process [8]. Another way to the enhance adhesion of diamond film is applying biased voltage during the deposition of diamond. In that study, it was also found that the large stress is originated from the disordered graphite phases and Mo_2C near the surface [9]. The diamond nucleation process is preceded by Mo_2C carbide formation, and the carbide will significantly affect the adherence of the diamond film [10]. The low nucleation density also leads to long growth times to obtain continuous diamond films. Moreover, the growth of diamond proceeds via a Volmer–Weber mechanism of 3D island formation. Therefore, it is hard to obtain ultra-smooth and well-distributed diamond film, which has various applications in many aspects.

For CVD diamond growth on many unfavored substrates, such as Fe and Ni, an interlayer is often used to enhance the nucleation density and diamond quality [11–13]. In many CVD diamond film applications, there is a need for very thin (several nanometers) or extremely smooth surfaces and interfaces [14–17]. The interlayers prepared by different kinds of physical vapor deposition (PVD) methods (such as magnetron sputtering) can control the grain size and roughness by changing PVD

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conditions to obtain nano-crystalline thin films. The nano-crystalline interlayers on substrates can enhance the nucleation density and uniformity, which makes the preparation of very thin dense diamond films possible by shortening the growth time.

The objective of this work is to investigate whether or not the nucleation rate will be effectively enhanced by a Mo interlayer at a large range of distances from the hot filament. A Mo interlayer was deposited by magnetron sputtering on polished single-crystal silicon (100) substrates (roughness < 4 nm) with the dimensions of 23 × 8 × 0.6 mm^3. Here we report more extensive investigations of HFCVD diamond films on large Si (100) substrates with a Mo interlayer. Each substrate is mounted over a range of distances (d_f) from the hot filament. In the present work, T_s is determined by a combination of radiative and conductive heat transfer from the HF and by the exothermicity of H atom recombination on the substrate surface. An additional objective is to study the effect of a Mo interlayer on CVD diamond nucleation over a large range of d_f for a very short growth period of 20 min.

2. Experimental details

Single-crystal silicon (100) pieces with dimensions of 23 × 8 × 0.6 mm^3 were used as substrates. Each specimen was initially subjected to the following pretreatments: (i) preparation of the molybdenum thin films by DC magnetron sputtering and (ii) ultrasonic abrasion in the suspension of diamond powder (particle size <500 nm) in acetone for 30 min.

The substrates were cleaned with a Kauffman ion gun in order to eliminate the potentially adverse effects caused by contamination and adsorbed gas molecules. The discharging voltage was 70 V, with a current of 1.25 A. A coil current of 6A was chosen, whereas the acceleration voltage and current was set as 500 V and 40 mA, respectively. The gas atmosphere was argon, with the pressure tuned to 0.2 Pa. The beam operation voltage was 1.5 kV, with a beam current of 78 mA. After the ion bombardment cleaning process, the molybdenum thin film was prepared by the DC magnetron sputtering technique in a high vacuum chamber with pressure $<10^{-4}$ Pa. The purity of the molybdenum target and the argon gas used was 99.99 wt% and 99.99 vol%, respectively. The pure molybdenum thin film was sputtered with a sputtering voltage of 350 V and current of 0.4 A. The sputtering pressure of the pure molybdenum thin film was 1.0 Pa with a sputtering time of 30 min. The target-substrate distance was 70 mm. In our experiments, it was determined that the sputtering process should take place at half the temperature range of the CVD diamond deposition (500–900 °C) to reduce residual compressive and tensile stresses and due to the fact that the sputtered samples must be returned to ambient temperature amid the processes of PVD and CVD, and the sputtering devices cannot perform at a temperature as high as that for the diamond deposition process. This temperature (400 °C) was chosen in a way that optimized adhesion and deposition was obtained without the appearance of film cracking.

The diamond films were synthesized by hot filament assisted CVD in a multifunctional vapor deposition system specifically designed for diamond deposition. The HFCVD reactor was designed and constructed in the Department of Physics at the Royal Institute of Technology, Stockholm, Sweden, and subsequently transferred to Central South University, Changsha, PR China [18–20]. The reactor is a stainless steel chamber with an inner diameter of 300 mm to which various electrical, gas and liquid feeds are fitted as well as a magnetron cathode for sputtering. A spiral coil tungsten filament suspended between two molybdenum rods mounted on water-cooled copper frames was used to activate the process gas for diamond film deposition. The substrate was positioned at an angle of ~30° to the vertical (z axis) as shown in Fig. 1(a) [21]. The filament temperature (T_f) was measured using an optical pyrometer. Substrate surface temperature (T_s) was controlled by T_f and the filament to substrate distance, d_f. T_s was measured with two K-type thermocouples attached to opposite edges of the substrate. A

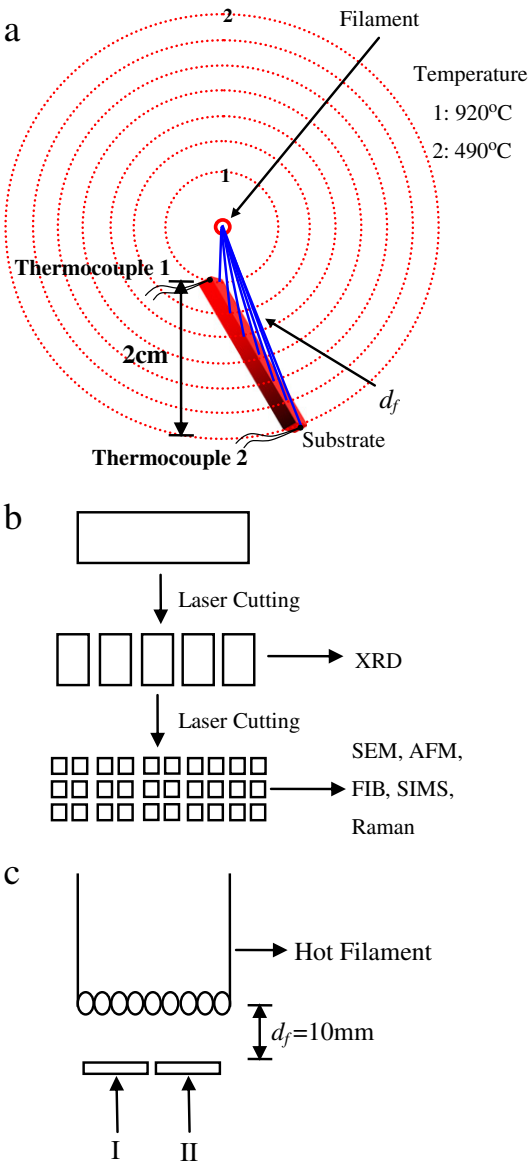

Fig. 1. (a) Schematic of the filament-substrate geometry during the HFCVD process. (b) Schematic of the characterization done on each specimen. (c) Growth experiment by sputtering Mo thin film on Si substrate: one sample was pretreated with diamond powder dispersion (I). The other one was only cleansed by acetone and alcohol (II).

vacuum ($<1 \times 10^{-6}$ Torr) was maintained by a turbomolecular pump while the deposition pressure, p, was monitored and controlled using a manometer. A pressure of 3.0 kPa was maintained during the diamond growth period, while CH_4 concentration was held at 2%. The gas mixture was hydrogen and methane. The flow rate of methane and hydrogen is 1 sccm and 50 sccm, respectively. The reaction time was limited to 20 min to study the nucleation process. The filament-substrate separation was varied within $6.0 \le d_f \le 25.9$ mm, while the substrate temperature varied with d_f. The temperatures at the top and bottom edge of the substrate, measured by two K-type thermocouples, were 490 and 920 °C, respectively. The temperature of the rest part of the substrate was simulated by solving partial differential equations. The simulated results at $d_f = 6.5$ mm, 10.3 mm, 14.1 mm, 17.9 mm and 21.7 mm are 890 °C, 770 °C, 680 °C, 620 °C and 580 °C, respectively. The simulated results are presented in Table 1.

As shown in Fig. 1(b), the sample was cut into five equal parts by laser cutting technology. After XRD analysis, each piece was cut into six equal parts for AFM, SIMS, FIB, Raman and SEM analyses. Samples were characterized with field-emission scanning electron microscopy