



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

Qiuping Wei^{a,b,c}, Taimin Yang^a, K.C. Zhou^c, Li Ma^c, P. Zheng^a, Jie Li^b, D. Zhang^c, Zhou Li^a, Z.M. Yu^{a,b,*}

^a School of Materials Science and Engineering, Central South University, Changsha, 410083, PR China

^b School of Metallurgical Science and Engineering, Central South University, Changsha, 410083, PR China

^c State Key Laboratory of Powder Metallurgy, Central South University, Changsha, 410083, PR China

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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.

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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

* Corresponding author. Tel.: +86 731 8830335; fax: +86 731 8876692.

E-mail addresses: qiupwei@csu.edu.cn (Q. Wei), sufacecsu@csu.edu.cn, zhiming@csu.edu.cn (Z.M. Yu).

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 $23 \times 8 \times 0.6 \text{ mm}^3$. 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 $23 \times 8 \times 0.6 \text{ mm}^3$ 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 $\sim 30^\circ$ 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

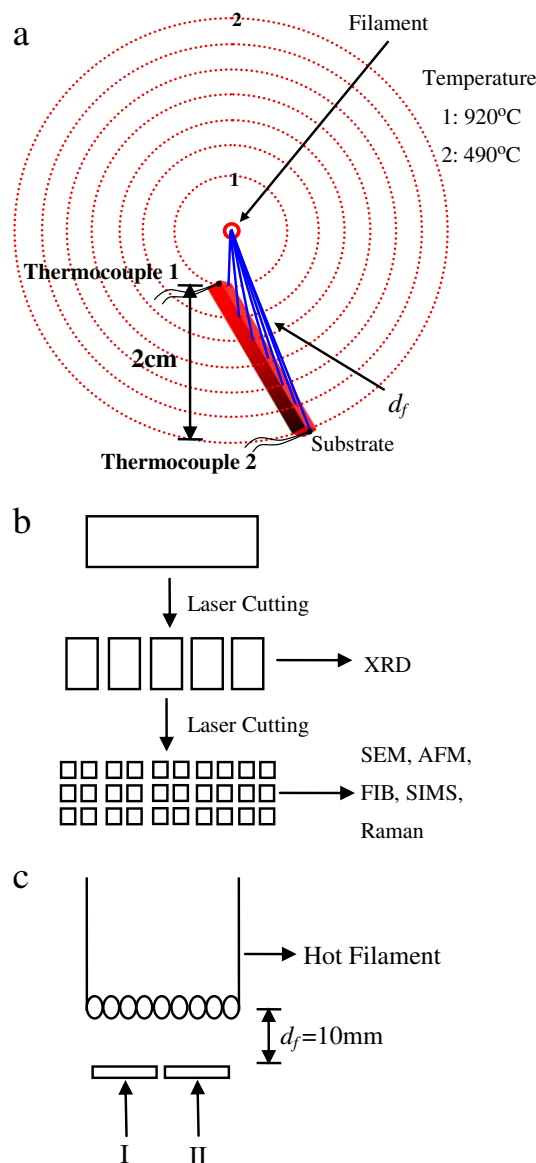


Fig. 1. (a) Schematic of the filament-substrate geometry during the HFCVD process. (b) Schematic of the characterization done on each specimen. (c) Growth experiment by sputtering Mo thin film on Si substrate: one sample was pretreated with diamond powder dispersion (I). The other one was only cleansed 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 $6.0 \leq d_f \leq 25.9 \text{ mm}$, 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 $d_f = 6.5 \text{ mm}$, 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

Table 1Data of diamond films grown at $d_f = 6.5$ mm, 10.3 mm, 14.1 mm, 17.9 mm and 21.7 mm.

d_f	6.5 mm	10.3 mm	14.1 mm	17.9 mm	21.7 mm
Simulated substrate temperature (°C)	890	770	680	620	580
Mean surface grain size (nm)	50	48	43	39	35.4
Diamond nucleation density (μm^{-2})	293	330	390	440	–
Surface roughness (nm)	3.9	2.9	2.7	2.4	4.5
Thickness of Mo-C layer (nm, estimated by FIB)	1030	–	1100	1080	1040
SIMS etching time of interlayer (s)	2000	1700	1100	1000	800
SIMS etching rate of interlayer (nm/s)	0.515	–	1	1.08	1.3
SIMS etching time of carbon layer (s)	1250	900	550	250	150
Thickness of carbon layer (nm, estimated by SIMS)	162	133	78	40	21

(FE-SEM FEI Sirion200), atomic force microscopy (School of Chemistry, University of Bristol), X-ray diffraction (XRD, Dmax-2500VBX with a Cu K α radiation source ($\lambda = 0.154$ nm), Raman spectroscopy (LabRAM HR800, Ar⁺ ion laser, $\lambda = 488$ nm, 5 mW), secondary ion mass spectroscopy (Magnetic sector SIMS with FEI gallium FIB source, Interface Analysis Centre, University of Bristol) and focused ion beam (FEI Helios X600, Interface Analysis Centre, University of Bristol). The cross-sectional images of the samples were obtained by FIB milling.

Fig. 1(c) depicts the growth experiment by which we investigated the effect of diamond powder pretreatment in diamond nucleation and growth. Two identical Si substrates, with sputtering Mo thin film on surface, were placed under the filament at the distance of 8 mm. Sample I was immersed in diamond powder dispersion and in ultrasonic bath for 30 min. Sample II was only cleansed by alcohol and acetone. The substrate temperature was 820 °C, while the pressure was maintained at 3 kPa. During the diamond growth period, CH₄ concentration was kept at 2% and the deposition time was extended to 120 min.

3. Results

3.1. Surface morphology

The surface SEM images of local areas on the diamond films are shown in Fig. 2, with d_f (in mm) displayed in the upper right of each panel. The left-hand panels in Fig. 2 show low magnification SEM images of diamond films. Fig. 2 shows that the diamond films are very smooth, homogeneous and dense over the range $6.0 \leq d_f \leq 20.7$ mm. The upper right-hand panels in Fig. 2 show the high magnification SEM images of the diamond films. As d_f increases from 6.0 to 20.7 mm, SEM images show the surface morphology evolve from dense, homogeneous, well-faceted, polycrystalline diamond film (at $6.0 \leq d_f \leq 12.9$ mm), through cauliflower-like morphology (at $d_f \sim 16.4$ mm), to agglomeration of quasi-spherical nanoparticles (at $d_f \sim 20.7$ mm). When $6.0 \leq d_f \leq 12.9$ mm, diamond grains connected to produce a dense and smooth film with no observable pores. The average diamond grain size was about 100–200 nm and some grains, with diameter smaller than 100 nm, can be found in the magnified images. A small number of uniformly distributed pores appeared on the surface of the diamond films when $d_f \geq 16.4$ mm. There are no large-size pores caused by heterogeneous nucleation. The emergence of pores mainly resulted from the grains having difficulty growing large enough to effectively connect with each other due to low substrate temperatures, a low concentration of reactive carbon radicals far from the hot-filament region and an insufficient deposition time (20 min).

When diamond growth time was extended to 120 min, as shown in Fig. 3(a, b), average diamond grain size is more than 1 μm . This result implies that the growth mode of diamond polycrystalline film is equiaxed dendritic growth rather than columnar growth. The growth of diamond grain is resulted from second nucleation during deposition process. Without diamond powder dispersion pretreatment, as shown in Fig. 3(c, d), the surface is not fully covered by diamond film and the average size of diamond is more than 3 μm . The nucleation density

was significantly lower than sample I, and some of diamond particles on the surface were stick by second diamond nucleation during the re-action. It can be speculated that diamond film will fully cover the whole surface when growth time is long enough because of second nucleation of diamond rather than the growth of diamond particles. For an equilibrium process, a subject with larger volume will grow faster and evaporate slower compared with a subject with larger surface volume rate. Therefore, deposition and growth of diamond by HFCVD is not an equilibrium process. Another interesting phenomenon is second nucleation site is choosy. Triangular surface, which represents {111} surface in diamond crystal, is a good site for second nucleation. However, rectangle surface, which represents {100} surface in diamond crystal, is clean and no second nucleation can be observed. We speculated that surface energy plays a leading role in determining whether smaller diamond particles nucleated on diamond surface or diamond epitaxy on diamond surface.

AFM was employed to further determine the grain size of diamond film at different distance between hot filament and substrate. Fig. 4(a) shows an AFM image of the surface morphology of a silicon substrate with sputtered Mo thin film. The roughness of Mo thin film Ra was about 4.593 nm. Considering the roughness of Si substrate is about 4 nm, the sputtered Mo thin film is rather smooth. Fig. 4(b–f) shows the surface AFM images of local areas of the diamond films deposited at $d_f = 6.5$ mm, 10.3 mm, 14.1 mm, 17.9 mm and 21.7 mm. It can be seen that the AFM results match very well with that of SEM, i.e. when $6.0 \leq d_f \leq 20.7$ mm, diamond films are characterized not only as dense and continuous, but also as reasonably smooth, with roughness Ra < 200 nm. The mean surface grain size decreases accordingly with increasing d_f . The surface roughness and mean surface grain size data are listed in Table 1.

3.2. Raman spectroscopy analysis

Raman spectroscopy is widely used within the CVD diamond community, given its ability to reveal important information on the chemical and physical properties of diamond films. Specifically, Raman spectroscopy is capable of differentiating between different carbon phases (most notably diamond and graphite) present in a film and can reveal information concerning average grain sizes and film crystallinity[22]. The films were characterized by Raman spectroscopy at several locations with varying values of d_f , as shown in Fig. 5, the values of d_f are shown in the bottom middle of each panel in Fig. 5. Fig. 5 shows that when $6.0 \leq d_f \leq 17.9$ mm, the diamond Raman peak can be observed at approximately 1332 cm^{-1} , which down-shifts with increasing d_f . When $d_f \geq 21.7$ mm, the diamond peak disappears. When $14.1 \leq d_f \leq 17.9$ mm, two Raman peaks appear in the region of 1140 and 1470 cm^{-1} whose intensity is synchronously enhanced with increasing d_f , besides the diamond (1332 cm^{-1}), the “D” disordered (1355 cm^{-1}) and the “G” graphite (1575 cm^{-1}) peaks. However, when $d_f \geq 21.7$ mm, the diamond peak and the peaks located at 1140 and 1470 cm^{-1} disappear, with only the D and G peaks remaining. The result shows that low temperature and large

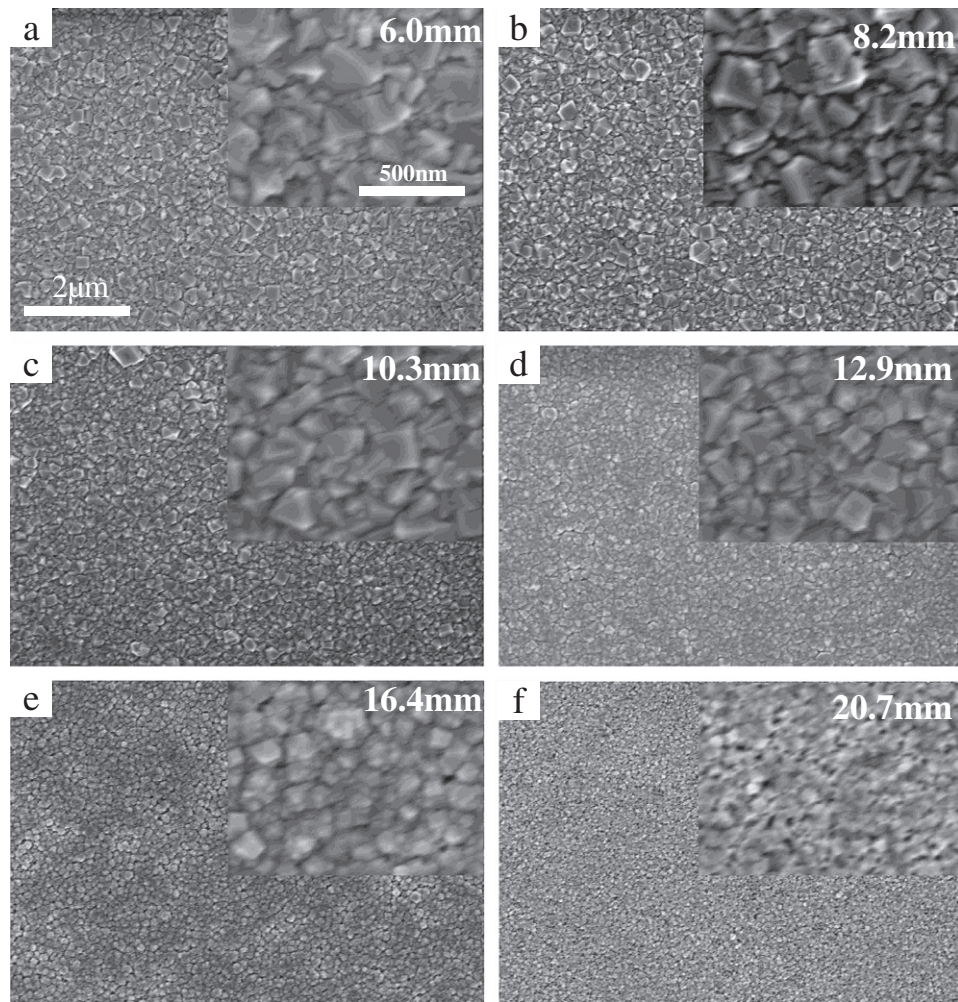


Fig. 2. Representative surface SEM images of diamond films with increasing of d_f (in mm, indicated in the top right panels in each picture) (a) $d_f = 6.5$ mm, (b) $d_f = 8.2$ mm, (c) $d_f = 10.3$ mm, (d) $d_f = 12.9$ mm, (e) $d_f = 16.4$ mm and (f) $d_f = 20.7$ mm.

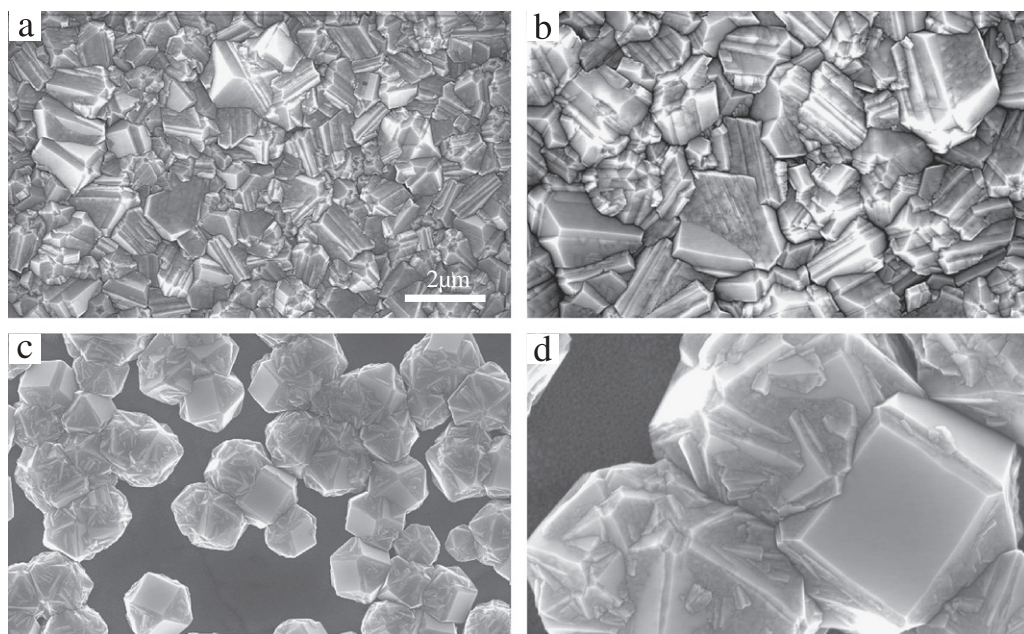


Fig. 3. (a, b) SEM images of diamond film growth on PVD Mo thin film on Si substrate with diamond powder pretreatment. (c, d) SEM images of diamond film growth on PVD Mo thin film on Si substrate without diamond dispersion ultrasonic pretreatment.

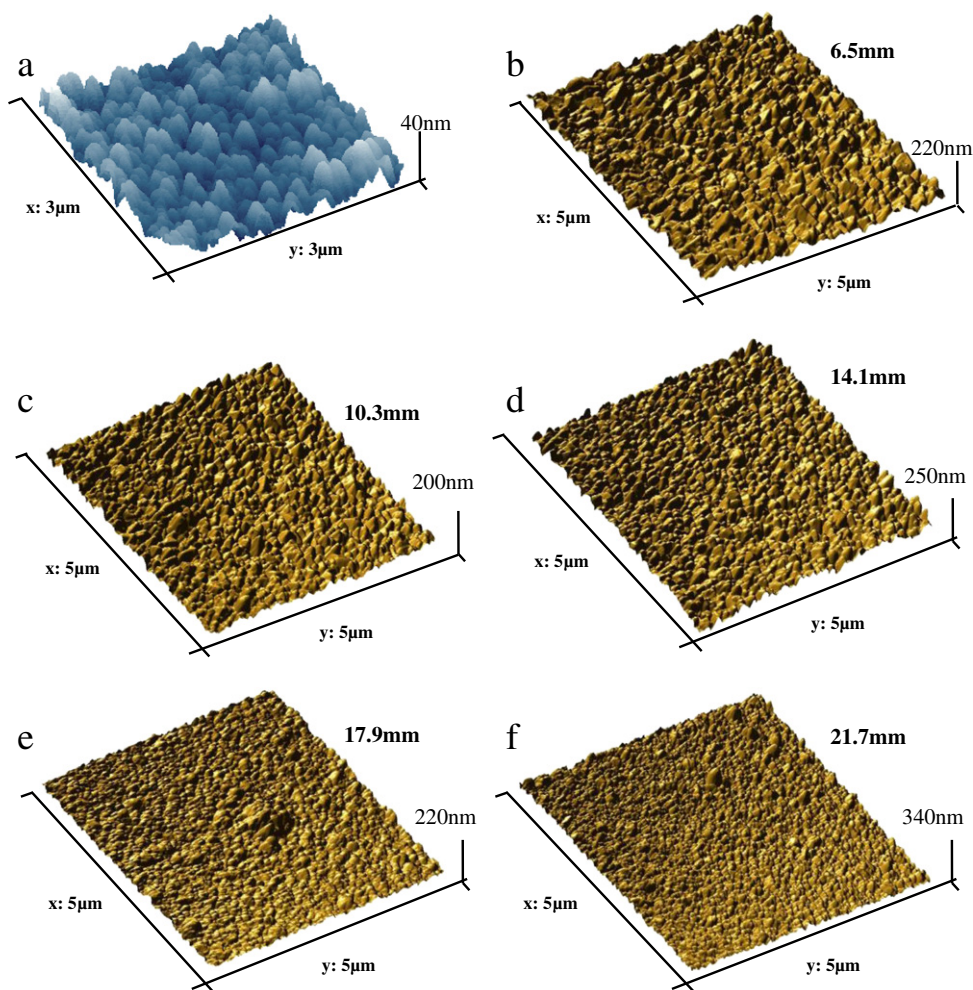


Fig. 4. (a) Surface AFM image of sputtered Mo layer on Si substrate. (b–f) Surface AFM images of diamond films with increasing of d_f (in mm, indicated in the top right panels in each picture) (b) $d_f = 6.5$ mm, (c) $d_f = 10.3$ mm, (d) $d_f = 14.1$ mm, (e) $d_f = 17.9$ mm and (f) $d_f = 21.7$ mm.

distance is unfavorable for diamond nucleation because activated carbon clusters cannot reach the critical level for diamond nucleation. Instead, amorphous (graphitic) carbon layers are deposited.

Another interesting feature that is worth noticing is the diamond peaks deviated little from 1331 cm^{-1} , as shown in Fig. 5(a–d). As is generally known, diamond deposited on heterogeneous substrates will display stress because of the difference in thermal expansion or phase transformation of substrates during deposition. The stress in the film will lead to a shift of the diamond peak in Raman spectroscopy. Therefore, the nano-crystalline diamond film deposited on the sputtered Mo film displayed little or no internal stress.

3.3. X-ray diffraction studies

One sample was cut into five equal parts ($4.6 \times 6 \times 0.6\text{ mm}^3$) by laser cutting technology, which were labeled from (a) to (e). To investigate the diffusion of carbon atoms into the Mo interlayer, XRD analysis was performed. Fig. 6(a–c) depicts the XRD peaks of local areas on the as-deposited diamond films at different distance. The right-hand panels in Fig. 6 show a very strong diffraction peak from Si (100), and the presence of Mo_2C phase following the deposition of diamond films, but no sharp Mo_2C diffraction peaks are detected. Because the thickness of Mo interlayer is less than $2\text{ }\mu\text{m}$ (about $1.6\text{ }\mu\text{m}$), it is very easy for the X-rays to penetrate through the interlayer to detect the Si (100) substrate. After magnifying the XRD patterns, it is observed that after

diamond deposition the diffraction peaks approximately match with Mo_2C at $6.0 \leq d_f \leq 25.5$ mm, but the diffraction peaks decrease significantly with increasing d_f . The XRD intensity of the Mo_2C phase is very strong, indicating that during HFCVD processing at high substrate temperature for 20 min, the partial Mo phase is transformed mainly into Mo_2C phase due to the diffusion of active carbon atoms. Furthermore, the diffraction peaks are narrower than those of local areas at large d_f , which may be attributed to differences in the crystallization of the nano-structure under different substrate temperatures. In Fig. 6(a), an MoC peak can be observed. This result indicates that high deposition temperature and high activated carbon source favors MoC formation. During the deposition, Mo_2C phase was formed at first, even though Mo_2C is not a thermodynamically stable phase, as can be deduced from the Mo–C phase diagram. When Mo layer was completely transformed into Mo_2C , the MoC phase started to grow. In Fig. 6(c), a comparatively strong carbon peak and Si peak can be observed and no diamond peak has been found, which confirms the existence of non-diamond carbon growth.

3.4. Cross-sectional morphology

The cross-sectional morphology of samples (a) to (e) was revealed by cross-sectioning the samples by FIB milling. Images of the cross-sections from the local areas on the diamond films are presented in Fig. 7. It shows that the diamond layer thickness of samples (a), (b) and (c) is fairly close

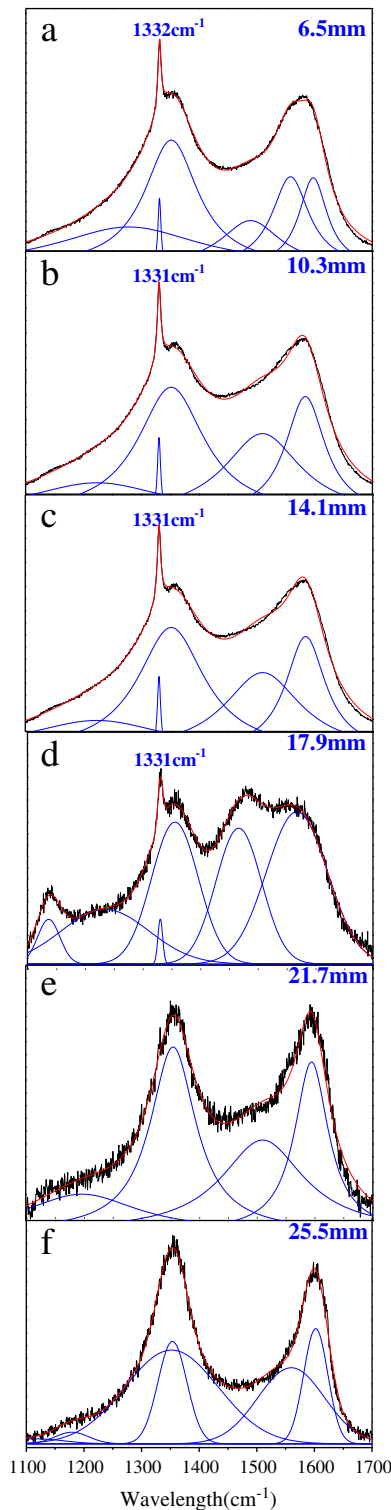


Fig. 5. Raman spectra of diamond films grown at different d_f (a) $d_f = 6.5$ mm, (b) $d_f = 10.3$ mm, (c) $d_f = 14.1$ mm, (d) $d_f = 17.9$ mm, (e) $d_f = 21.7$ mm and (f) $d_f = 25.5$ mm. Deconvolution into the different carbon bonding signals is shown.

to those values estimated from the SIMS data. However, the extreme thinness of samples (d) and (e) constrains the estimation by FIB imaging. Additionally, significant variation of diamond layer thickness between different regions of the same sample still exists due to a distance of 2 mm each sample extends horizontally. In Fig. 7(a), the thickness of the sputtered Mo thin film was about 1.6 μm . After HFCVD processing,

the average thickness of the interlayer was extended to approximately 2 μm . The detailed thickness data of Mo-C interlayer at different d_f are listed in Table 1.

3.5. SIMS depth profile analysis

As previously described, one sample was cut into thirty equal parts ($2 \times 2 \times 0.6$ mm³) by laser cutting technology. The middle ten squares were labeled from No. 1 to No. 10. Samples No. 1, No. 3, No. 5, No. 7 and No. 9 were analyzed by SIMS and FIB and subsequently relabeled as (a), (b), (c), (d) and (e), with (a) nearest to, and (e) farthest from the hot filament.

The SIMS depth profile analysis curve obtained from samples at different d_f is presented in Fig. 8. SIMS applies positive accelerating voltage to obtain positive ion mass spectrometry with C^+ , Si^+ , Mo^+ and Mo^{2+} as the featured ions in each layer. Sputtering time and ionic strength have been used to obtain the SIMS depth profiles in Fig. 8. The SIMS profiles of sample (a) show that when etching time is less than 1200 s, C^+ is the most abundant detected ion, which indicates that this is the diamond film. After 1200 s of etching, Mo^+ and other related ions rapidly increase in abundance, indicating that the diamond film has been breached, revealing the Mo interlayer. After 3000 s, a rapid decrease of Mo^+ and other related ions indicates that the interlayer has been consumed and etching of the silicon substrate has begun. Under known conditions, the rate of diamond etching is 0.14 nm/s, and we assume that the etching rate of sp^2 carbon layer is similar to that of diamond. Therefore, the thickness of carbon layer can be estimated at (a) ~ 162 nm, (b) ~ 133 nm, (c) ~ 78 nm, (d) ~ 40 nm and (e) ~ 21 nm based on the SIMS data. As shown in Table 1, the etching rate of interlayer increased from 0.515 nm/s to 1.3 nm/s as d_f increases because carbon concentration in Mo layer will greatly affect the etching rate. The result indicates that the etching of highly carbonized Mo layer is much less efficient than lowly carbonized Mo layer.

4. Discussion

From the surface morphology characterized by SEM and AFM, it is clear that thin Mo interlayers significantly increase the nucleation density of diamond after seeding with nanodiamond powder. The nucleation rate is $10^{14}/\text{m}^2$ compared with $10^{11}/\text{m}^2$ on bulk Mo substrate [23]. Also, diamond film growth on sputtered Mo interlayer is well distributed and smooth. Two factors mainly contribute to these improvements.

The first one is that the sputtered Mo interlayer adsorbed more nanodiamond powder and the nanodiamond seeding is evenly spread over the substrate. Ultrasonic abrasion in a suspension of nanodiamond powder (< 500 nm) in acetone for 30 min treatment, often described as “seeding” [23–25], promotes the subsequent inhomogeneous nucleation of diamond during CVD, either by implanting ultrafine diamond fragments into the substrate surface or by creating suitable surface defects. Because the sputtered Mo film is composed of nanoparticles, an abundance of grain boundaries and defects is produced by sputtering. Also, the surface energy of nanoparticles is extremely high and diamond nanoparticles have more tendencies to adsorb to the film. The sputtering generates films with high surface energy, making the surface highly active. This high surface energy greatly increases the amount of nanodiamond powder adsorbed onto the films. Also, ultrasonic treatment significantly increased the defect density on Mo surface, which serves as active site for diamond nucleation.

The second reason is that the sputtered Mo film is apt to form carbonized Mo layer. Before diamond nucleation, Mo layer will be transformed to Mo-C layer. The carbonization and phases formed during transformation are determined by the temperature of the substrate and the density of activated carbon species. As temperature arises, carbon diffused quicker in the interlayer and more activation

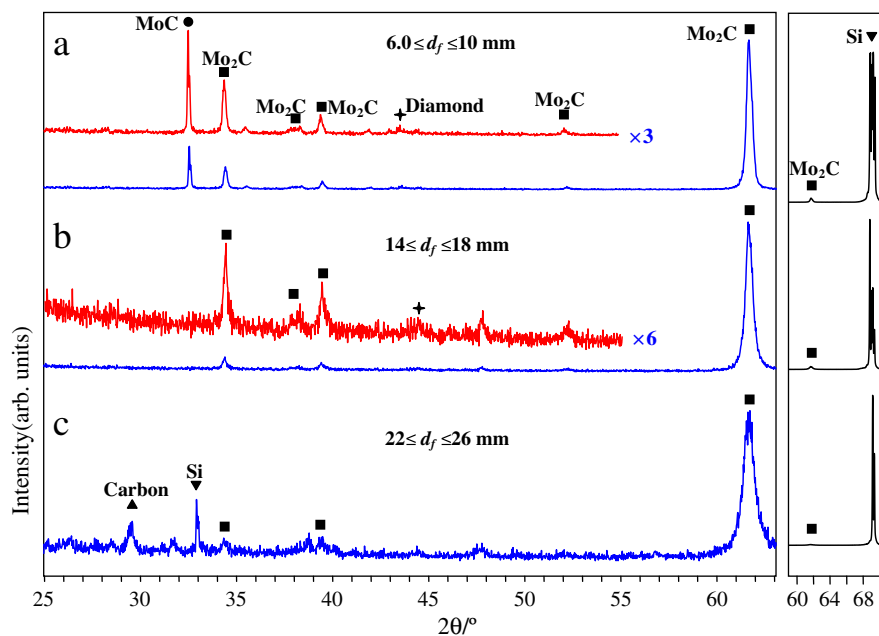


Fig. 6. X-ray diffraction patterns of diamond films at increasing d_f (a) $6.0 \leq d_f \leq 10$ mm and 3 times magnification pattern (b) $14 \leq d_f \leq 18$ mm and 6 times magnification pattern (c) $22 \leq d_f \leq 26$ mm.

energy will be provided so that more carbide, like MoC and Mo₂C, will form during the deposition process. As the density goes up, more carbon source will be provided on the surface of substrate, which

accelerates the process of carbonization. When the activated carbon density reached a critical value, diamond nucleated on the surface of the substrate.

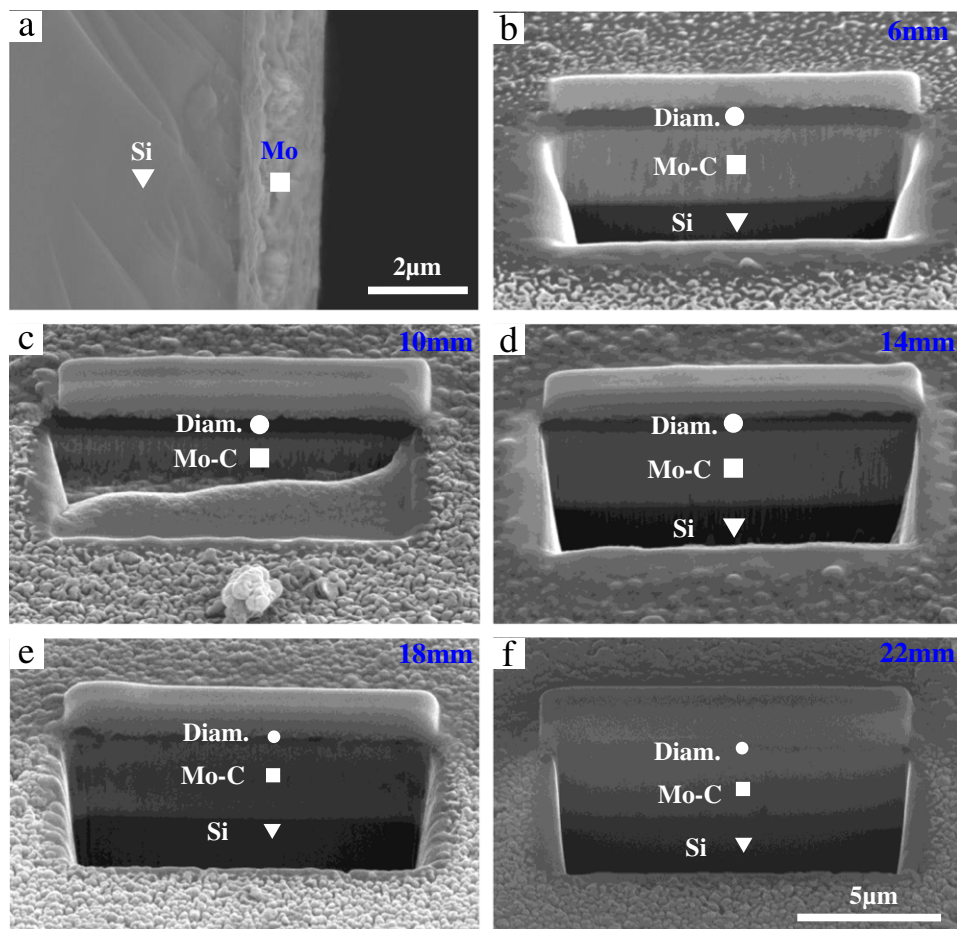


Fig. 7. (a) Cross-sectional SEM images of sputtered Mo film on Si substrate (b–f) FIB cross-sectional SEM images of diamond films with increasing of d_f (b) $d_f = 6$ mm, (c) $d_f = 10$ mm, (d) $d_f = 14$ mm, (e) $d_f = 18$ mm and (f) $d_f = 22$ mm.

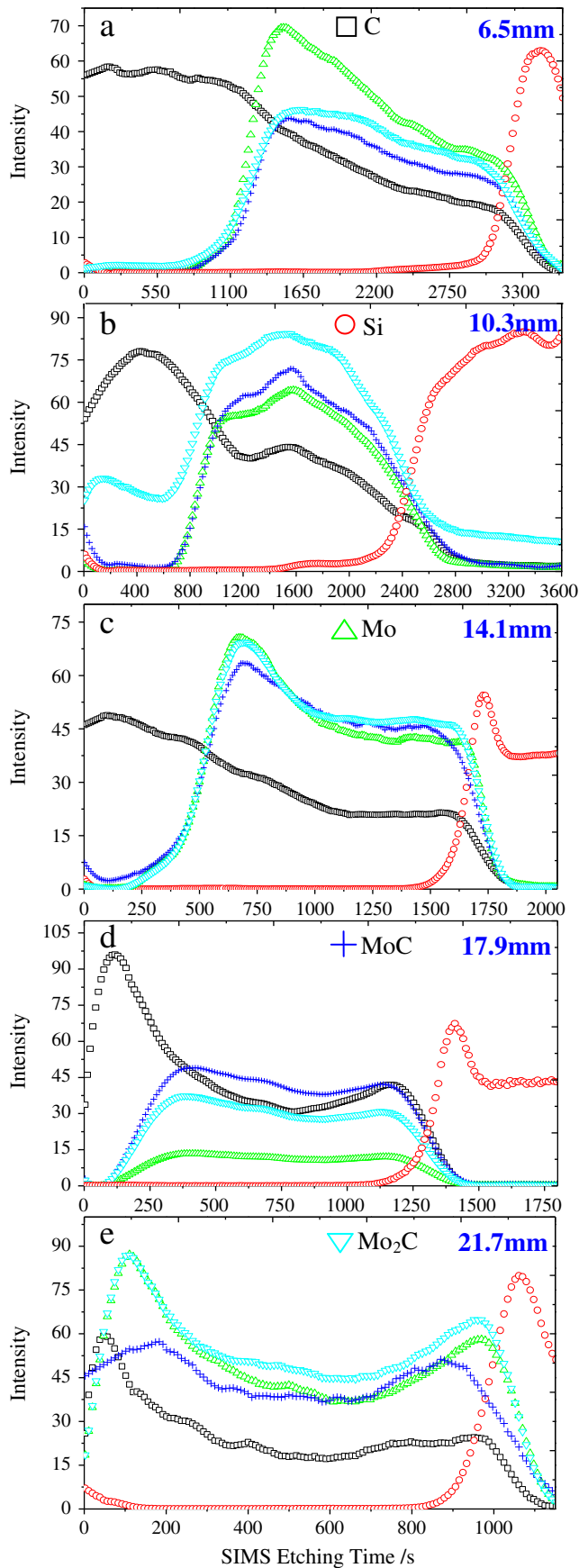


Fig. 8. SIMS elemental depth profiles of diamond films grown at different d_f (a) $d_f = 6.5$ mm, (b) $d_f = 10.3$ mm, (c) $d_f = 14.1$ mm, (d) $d_f = 17.9$ mm and (e) $d_f = 21.7$ mm.

5. Conclusions

Sputtered Mo on heterogeneous silicon substrates was found to increase the efficiency of carbide formation and lead to huge increases in nucleation density at a large range of distances from the hot filament (d_f) after seeding with nanodiamond. Homogeneous, continuous, dense diamond films can be formed in a short growth period (20 min) at $6.0 \leq d_f \leq 20.7$ mm. Mo films deposited by magnetron sputtering can be transformed during the HFCVD process into MoC and Mo₂C phases and by changing the substrate temperature and gas chemistry, the content of MoC and Mo₂C can be altered. The Raman peaks centered at ~ 1140 , ~ 1220 , ~ 1332 , ~ 1355 , ~ 1470 and ~ 1575 cm^{-1} are found at different d_f . The diamond film displays no internal stress and the quality of diamond deteriorated rapidly as the distance increases. When the distance was larger than 20 mm, the deposited layer consisted only non-diamond phases. The surface modification greatly improved the nucleation density and the distribution of absorbed diamond powder during pretreatment. The method shows great potential to produce ultra-smooth and well-distributed nanocrystalline diamond films.

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