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Synergetic surface modification effect of argon and oxygen for diamond films by MPCVD

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Abstract: Diamond films were synthesized in a $\text{CH}_4\text{-H}_2$ system with good surface quality by adjusting the additive amount of argon and oxygen gas. The diamond phase content and surface roughness of samples are 86.1% and 81.5 nm, respectively. The results indicate that only Ar addition will decrease the purity of diamond films, whereas Ar- O_2 mixed gas can further increase the diamond phase content. It is worth noting that the content of diamond phase has no significant increase when O_2 flow exceed 1 sccm. The surface roughness reduced from 199.8 to 81.5 nm by the addition of 14 sccm Ar and 1 sccm O_2 , and the surface quality will be deteriorated in case of further increasing O_2 or decreasing Ar concentration. Meanwhile, the growth rate under different conditions and the synergetic surface modification effect of Ar- O_2 mixed gas for diamond films growth process were discussed.

Keywords: diamond films; MPCVD; synergetic effect; surface roughness.

1 Introduction

Diamond films have exhibit many outstanding properties such as high hardness, low friction, electrical insulation, chemical inertness, biological compatibility, high optical transparency, and high thermal conductivity [1–4], which make these attractive for application in a variety of current and future systems. In particular, high optical transparency in a broad wavelength range of diamond films makes them an ideal optical window for optical devices [5, 6]. There are several methods for preparing diamond films, such as DC plasma jet chemical vapor deposition (CVD) [7], hot filament CVD [8], and oxyacetylene combustion flame [9]. However, the microwave plasma chemical vapor deposition (MPCVD) is the most widely used technique to synthesize diamond films because it exhibits some advantages in diamond quality, thin film area and uniformity, etc. [10, 11].

Normally, microcrystalline diamond films are perceived as an ideal optical candidate because of accepted growth rate and high diamond phase content [12], but the unsatisfactory surface roughness always deteriorates its optical performance [13, 14]. Therefore, the surface quality is an important factor of diamond films as an optical coating [15]. The nanocrystalline diamond film is

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also considered as a promising optical material because of its smooth surface due to small grain size [16, 17]. Unfortunately, the massive practical application is restricted to the andante growth rate. Meanwhile, the existence of the nondiamond component in grain boundary will also be adverse to the optical performance. It is reported that the introduction of auxiliary gas, such as Ar, N₂, or O₂ in the CH₄/H₂ system, can efficaciously improve the surface quality of microcrystalline diamond films because the ionized auxiliary gas is beneficial in refining grain size, etching lattice plane, and adjusting growth rate [18]. For example, Ar as an inert gas can promote the dissociation of methane and increase the concentration ratio of C₂ than CH₃. Moreover, the CH₃ specie is an important precursor [19] for the growth of nanodiamond films, and the C₂ specie can decrease surface roughness, grain size, and growth rate [20]. The ability of plasma etching to diamond and nondiamond phase can be improved by adding oxygen to the mixed gas of methane and hydrogen because of the O and OH free radicals [21]. If a small amount of Ar-O₂ mixture gas is introduced to the CH₄/H₂ system because of the decrease in grain size, on the one hand, and improvement in etching, on the other hand, synthesizing diamond film with high surface quality and maintaining high sp³ content by the synergetic effect of Ar and O₂ are possible.

To obtain the smooth surface of diamond films with high crystal growth rate, we conducted a tactful design. In the growth stage, the microcrystalline diamond films were deposited in substrate using the CH₄/H₂ system for 6 h to maintain high growth rate. After that, Ar-O₂ mixed gas was inducted to decorate the surface of the diamond for 2 h. To our knowledge, the collaborative influence of Ar-O₂ and its related mechanism using MPVCD have not been reported.

In this work, the diamond film was synthesized with a high diamond phase content and a good surface quality. The collaborative effect of Ar-O₂ on the diamond phase content and surface morphology of films has been investigated. The structure, the morphology, the surface roughness, and the quality of the prepared diamond films were evaluated by X-ray diffractometer (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and TR200 roughness meter, respectively. The etching mechanism of Ar-O₂ was discussed.

2 Materials and methods

2.1 Seeding

All chemicals used were analytical grade without further purification. Before growth process, polished commercial *p*-type (100

silicon wafer (2 inch in diameter, 200±10 μm) was scratched uniformly with 0.25 μm diamond powders for 45 min to disperse nucleation seeds and then ultrasonically cleaned in acetone, alcohol, and deionizer water for 10 min, respectively. The substrates were then dried in nitrogen gas before placing on the removable substrate holder. The nucleation density of the diamond on the substrate surface was approximately 10⁹–10¹⁰ cm⁻² under the condition of seeding.

2.2 Experimental plan

Diamond film samples were synthesized in an 8-kW, 2.45-GHz homemade MPCVD system, as shown in Figure 1. The system is capable of operating at a reactor pressure up to 30 kPa and featured with a patented tunable cavity design to ensure optimum mode control for plasma generation and coupling efficiency. In general, the fabrication process was divided into the nucleation and growth stages. All the experiments were conducted strictly according to the following steps. After the evacuation of the chamber to the base vacuum (approximately 0.1 Pa), H₂ gas (99.999%) with 200 sccm was first introduced into the reactor. The samples were first cleaned for 20 min in the hydrogen plasma ball ignited at 1000 W and 2 kPa [22]. After the substrate temperature was approximately 650°C (infrared thermometer sensor with high precision [error range ±1%] used for temperature measurement and the temperature correction by control the cooling water flow rate of sample stage or adjust the “three stub tuner”), CH₄ (99.99%) with 4 sccm was introduced. The flow rate of each gas was regulated by a mass flow controller, and the mixture gas was well mixed before input to the chamber. The nucleation process was accomplished at 700°C for 60 min by adjusting the microwave power at 2.6 kW and the chamber pressure at 4 kPa. The growth process was accomplished at 836°C for 8 h by adjusting the microwave power at 2.8 kW and the chamber pressure at 6.95 kPa. Details of adding argon and oxygen mixed gas to the reaction chamber at the last 2 h of the growth stage are described in Table 1.

2.3 Characterization

XRD (Bruker D8 XRD with Cu-Kα radiation source, λ=1.5406 Å, Bruker, Karlsruhe, Baden-Württemberg, Germany) was used to investigate the crystal structure of the obtained samples. A SEM (JSM-6701F with an accelerating voltage of 15 kV, JEOL, Akishima-shi, Tokyo, Japan) was applied to explore the microstructures of the samples. The surface morphology and the thickness of the obtained diamond films were observed from the top and cross-sectional view of the SEM images, respectively. The growth rate was calculated as the ratio between the thickness and the growth time. Raman spectra (Raman spectrometer, LabRAM HR Evolution with ~1 μm spot size using a 514-nm Ar source, HORIBA Jobin Yvon, Paris, France) were adopted to confirm the content of diamond phase in obtained samples. The XPS (AXIS-ULTRA DLD-600W photoelectron spectrometer with Al K1 radiation, Kratos, Manchester, England) was used to further analyze the relative content of the diamond to other impurities phase. TR200 (Beijing Times Reida Technology Co. Ltd, Beijing, China) roughness meter was used to investigate the surface roughness of diamond film samples (R_a from the average of 10 measuring position).

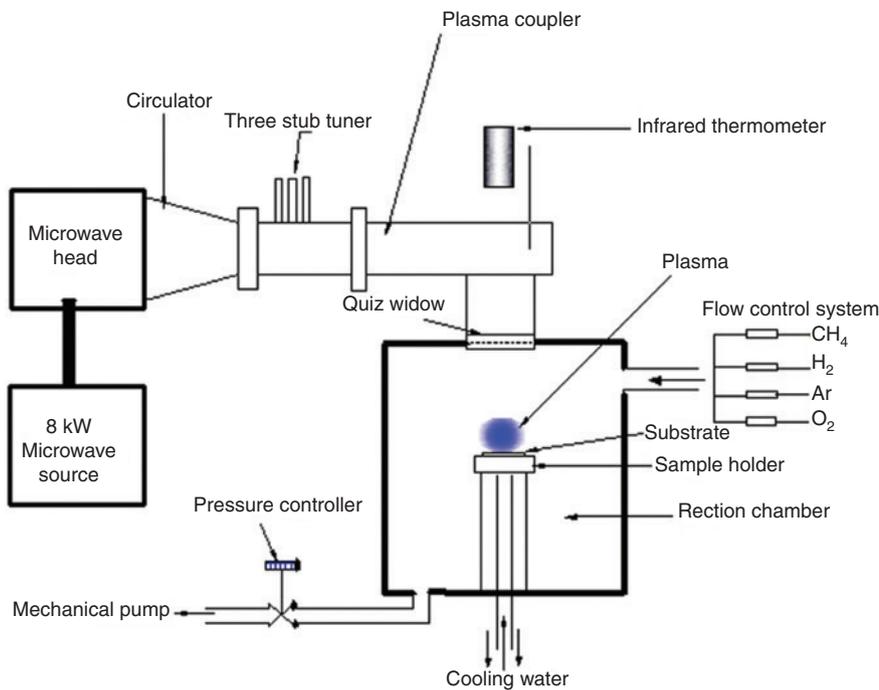


Figure 1: Schematic diagram of MPCVD system.

Table 1: The flows of Ar and O₂ in the diamond growth stage.

Samples label	a	b	c	d	e	f	g
Ar (sccm)	0	15	14	13	12	11	0
O ₂ (sccm)	0	0	1	2	3	4	2

3 Results and discussion

3.1 Films thickness and growth rate

To obtain the information of diamond growth films, we investigated all samples using cross-sectional SEM. Figure 2A–F shows the cross-sectional SEM image for samples with a columnar growth structure, which is a trait from mixtures of CH₄/H₂ plasma [23]. Figure 2A shows the growth phase of the diamond with a large “pyramid shape,” which is reduced in size because of the addition of argon gas, as shown in Figure 2B. The pyramid shape almost disappeared when O₂ (1 sccm) and Ar (14 sccm) are added into the CH₄/H₂ mixture gases, as shown in Figure 2C, because of O₂ etch. By increasing the flow of O₂, the large “pyramid shape” appeared and the sharp disappeared because of the excessive etching effect from O₂, as shown in Figure 2D–F.

Commonly, a thickness of diamond films was found based on the measurement of the cross section. The growth rate can be calculated by the thickness, and the results are

listed in Figure 3. Thus, if the deposition time is constant, growth rate increases with thickness. Figure 3 shows that the growth rates of the sample B decrease because the addition of argon gas greatly improved the secondary nucleation rate and inhibited the growth of diamond films. It is well known that a small amount of O₂ to join the CH₄-H₂ mixture gases not only improves the ability of plasma etching but also promotes the growth rate of diamond films. When the promotion effect is dominant, the thickness of diamond films tends to increase; when these two effects are equal, the thickness of diamond films tend to keep constant; and when the etching effect is dominant, the thickness of diamond films tend to decrease. In our experiment, the growth rate and the thickness of diamond films are 0.603 μm/h and 4.427 μm under the condition of O₂ flow keep at 1 sccm.

3.2 Morphology and structure

For a morphology overview, Figure 4 shows the SEM micrographs of the growth surfaces for the five diamond samples grown at low microwave power (2.8 kW) with the same total flow (15 sccm) in addition to argon and oxygen and one diamond sample using only CH₄/H₂ plasma. It can be seen that the addition of Ar and O₂ into the plasma significantly changed the surface microstructure of the diamond. Well-faceted diamond films with a dominant larger particle (approximately 3 μm) were synthesized

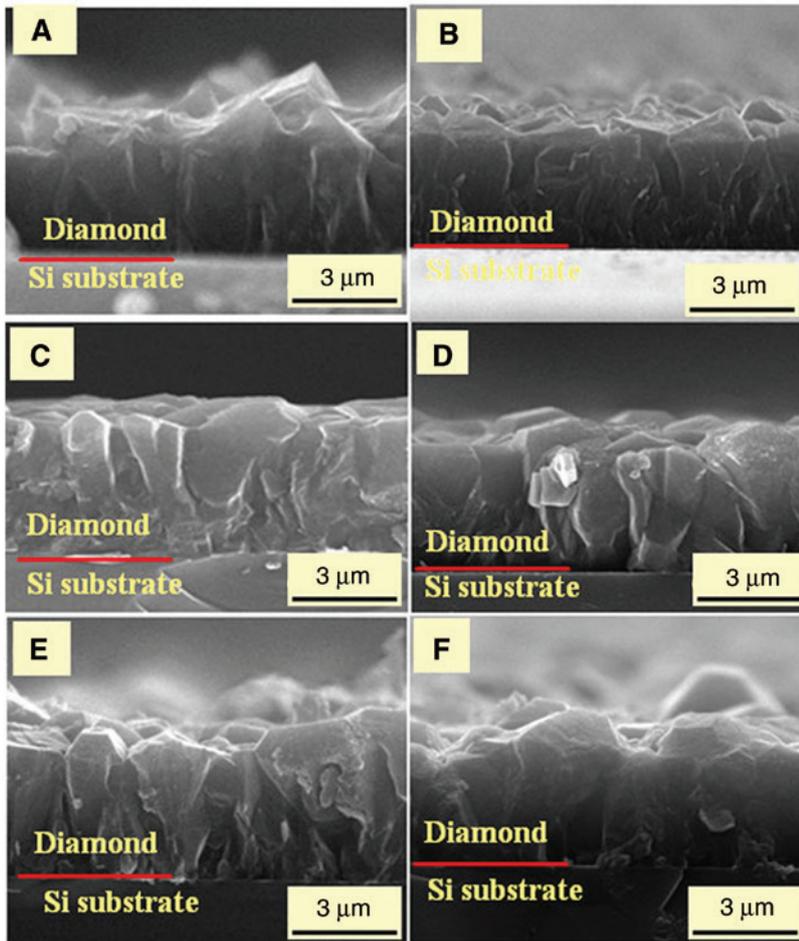


Figure 2: SEM image for the cross section of diamond film samples obtained at various gas flow rates (sccm). (A) O₂-0, Ar-0; (B) O₂-0, Ar-15; (C) O₂-1, Ar-14; (D) O₂-2, Ar-13; (E) O₂-3, Ar-12; (F) O₂-4, Ar-11.

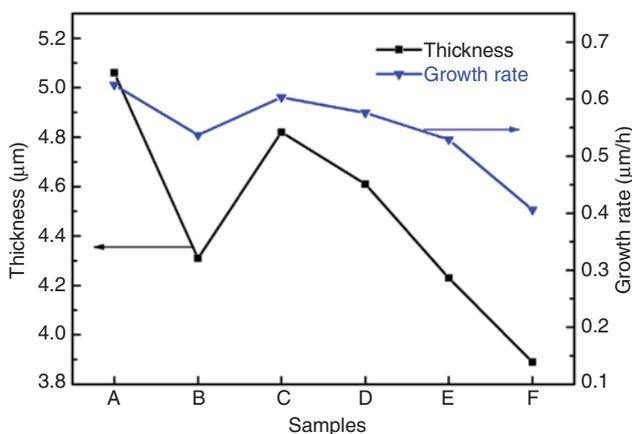


Figure 3: Thickness and growth rate for different samples.

using the CH₄/H₂ mixture gas, as shown in Figure 4A. However, a lot of small particles (approximately 0.5–1 μm) were obtained, as shown in Figure 4B, when Ar (15 sccm)

was presented. It can be clearly seen in the Figure 4C that the particles were etched when the mixed gas composed of 14 sccm Ar and 1 sccm O₂ were added into the plasma. The diamond particle size increased with the concentration variation of Ar and O₂ in the plasma under the condition that total flows were invariant, as shown in Figure 4D–F. For example, the large particle size approximately 2 μm is shown in Figure 4F.

The crystal structure of diamond films deposited under different Ar and O₂ flows was investigated using XRD. As shown in Figure 5, there are four primary peaks at the diffraction angle 2θ of 43.94°, 75.22°, 91.42°, and 119.58° for all samples, which correspond to (111), (220), (311), and (400) reflections of the diamond films [24], respectively. It indicates that all diamond films show not only the polycrystalline nature but also the preferential [111] texture, and similar conclusions were reached by Cong et al. [25]. The diffraction spectrum of samples A and B from Figure 5 is very similar because the Ar can reduce

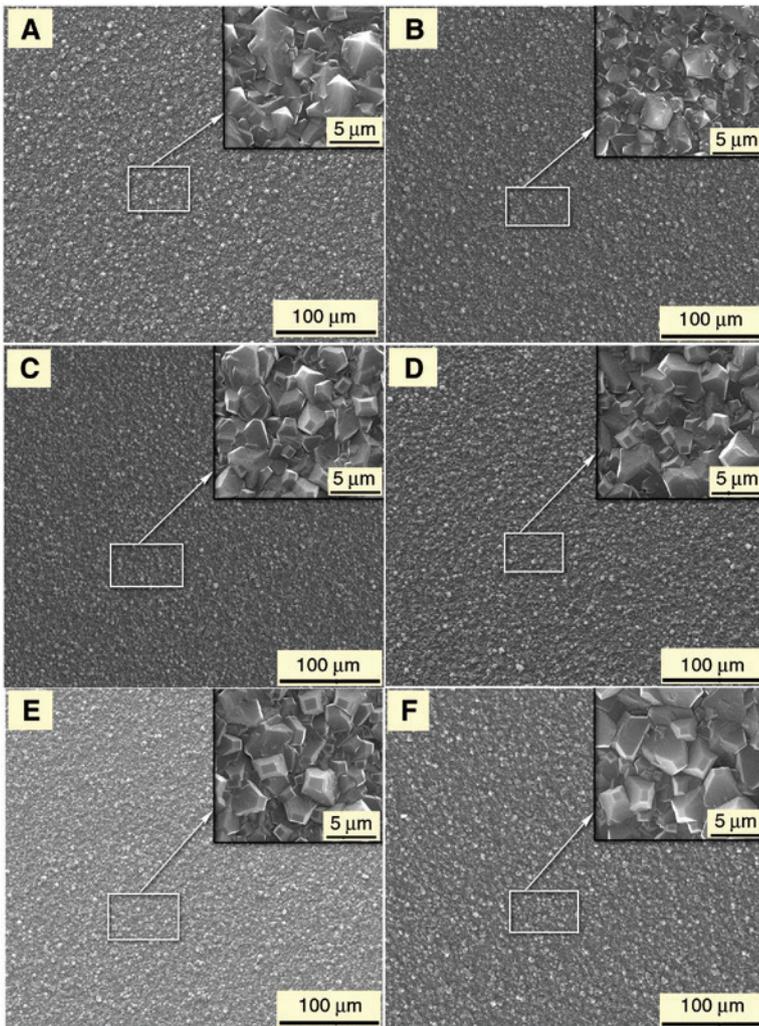


Figure 4: SEM image for surface microstructure of diamond film samples obtained at various gas flow rates (sccm). (A) O₂-0, Ar-0; (B) O₂-0, Ar-15; (C) O₂-1, Ar-14; (D) O₂-2, Ar-13; (E) O₂-3, Ar-12; (F) O₂-4, Ar-11.

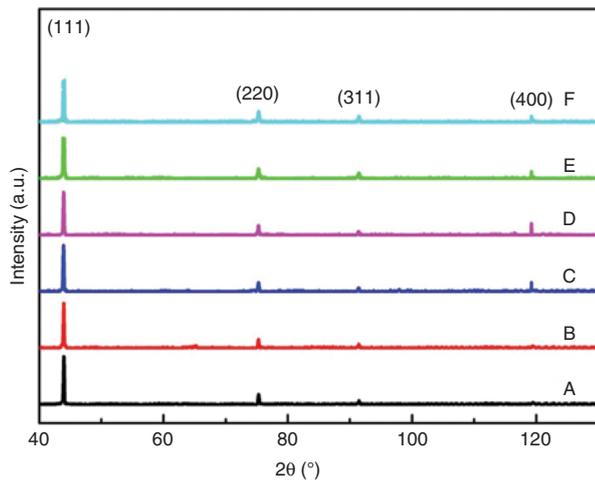


Figure 5: X-ray diffraction patterns of diamond film samples obtained at various gas flow rates (sccm). (A) O₂-0, Ar-0; (B) O₂-0, Ar-15; (C) O₂-1, Ar-14; (D) O₂-2, Ar-13; (E) O₂-3, Ar-12; (F) O₂-4, Ar-11.

only the grain size of diamond and has no effect on structure. It is worth noting that the diffraction peak of (400) at 119.58° appeared when O₂ was added into the plasma, indicating that the (100) orientation of diamond was achieved because of oxygen etch. This result is consistent with the study of Tang et al. [26]. The average grain size was approximately 49.6 nm for sample B, calculated using the well-known Sherrer's equation when Ar (15 sccm) was added into the plasma, which suggests that Ar can promote the dissociation of methane and increase the concentration of C₂ species [27]. However, it increased from 49.6 to 72.5 nm as O₂ flow increased, indicating that the ability of Ar to reduce the grain size is more effective than O₂. The interplanar crystal spacing values of the (111) phase are 2.0563, 2.0569, 2.0604, 2.0568, 2.0605, and 2.0533 for samples A–F, respectively (while nature diamond is 2.0600), indicating all samples have high quality.

3.3 Quality evaluation of diamond films

Normally, the quality of diamond films is evaluated by some features in the Raman spectra, such as a sharp peak of sp³ phase approximately 1332 cm⁻¹ and other non-diamond peaks. The high-resolution Raman spectra from samples A and B–F deposited under different Ar and O₂ flows are shown in Figure 6. There are two primary peaks at the Raman shift of 1332 and 1500 cm⁻¹ for all samples, which correspond to sp³-bonded and sp²-bonded, respectively. The peak 1332 cm⁻¹ is strong and sharp in the spectra of diamond films, implying the high content of diamond phase [28] for all samples. However, the peak 1500 cm⁻¹ was attributed to nondiamond, which was enhanced by Ar. The reason may lie in the crystal boundary (usually made up of sp²) that increased because of the decrease in grain size [29]. However, it was diluted when the O₂ (1 sccm) was added into the plasma, as shown in Figure 6C, because the O atomic in the plasma enhanced the etching effect on the nondiamond phase. Furthermore, in the case of diamond films that were etched by O₂/Ar plasma, as shown in Figure 6C–F, no remarkable change in the Raman structure can be observed, indicating the isotropic etching feature of the O₂/Ar plasma for nondiamond and diamond [30]. It is worth noting that the relative intensity of the Raman peak at 1332 cm⁻¹ is an effective means to characterize the sp³ content. The Raman peak intensities of 1332 cm⁻¹ are 10876.079, 10051.543, and 11184.637 for samples C–F, respectively, indicating the almost same sp³ content. Thus, the sp³ content of sample

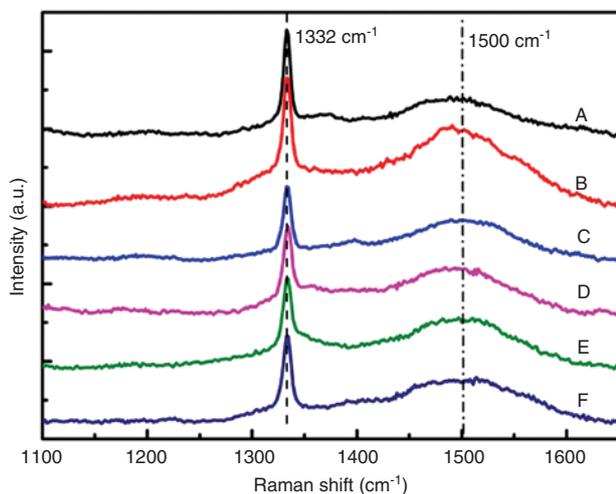


Figure 6: Raman spectra of diamond film samples obtained at various gas flow rates (sccm). (A) O₂-0, Ar-0; (B) O₂-0, Ar-15; (C) O₂-1, Ar-14; (D) O₂-2, Ar-13; (E) O₂-3, Ar-12; (F) O₂-4, Ar-11.

C can be represented by samples D–F by using the XPS analysis result.

It is known that the full width at half maximum (FWHM) is a very important parameter for the crystallinity status of diamond. In this work, FWHM was calculated using the Raman peak of 1332 cm⁻¹, and the results are shown in Figure 7. For sample A, the FWHM is only 8.71 cm⁻¹, indicating that the crystallinity is excellent [31], and the second smaller value is 9.12 cm⁻¹ for sample c. Meanwhile, the FWHM increases with the increasing O₂ concentration, indicating that the quality and crystallinity of the films decreased because of the O₂ etch effect [32].

The XPS is an important technique to estimate the relative content of various sp hybridization [33] components of carbon in materials, and it is used to assist the result of Raman from the electronic level frequently. The high-resolution XPS C1s spectra of diamond film samples (A–C) are shown in Figure 8. From this figure, all of the spectra were partitioned into three components, two of which (approximately 285.25 and 284.45 eV) correspond to the sp³ and sp² hybridization of carbon, respectively, whereas the remaining component (286.28 eV) is assigned to C-O chemical bonds [33]. The relative content of sp³ hybridization of carbon was calculated using the Multipak V9.3 software under different grown conditions, that is, 89.5%, 59.6%, and 86.1% for samples A, B, and C, respectively. The results are nicely consistent with the micro-Raman analysis.

In many cases, surface roughness is a functional requirement, and hence, it is necessary to control it [34]. In our work, the surface roughness of diamond films was evaluated by TR200 roughness meter (measuring range:

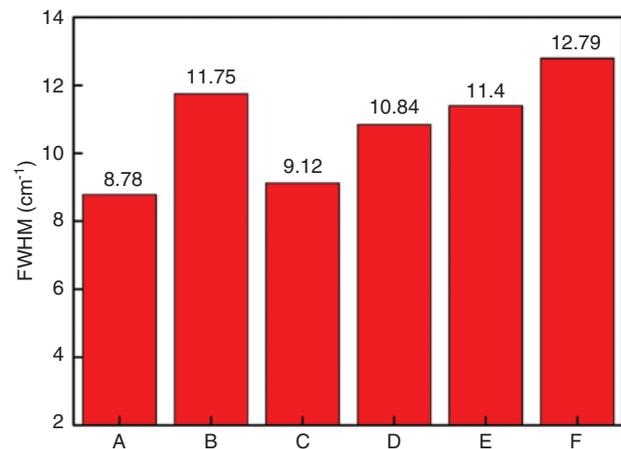


Figure 7: FWHM of diamond film samples at various gas flow rates (sccm). (A) O₂-0, Ar-0; (B) O₂-0, Ar-15; (C) O₂-1, Ar-14; (D) O₂-2, Ar-13; (E) O₂-3, Ar-12; (F) O₂-4, Ar-11.

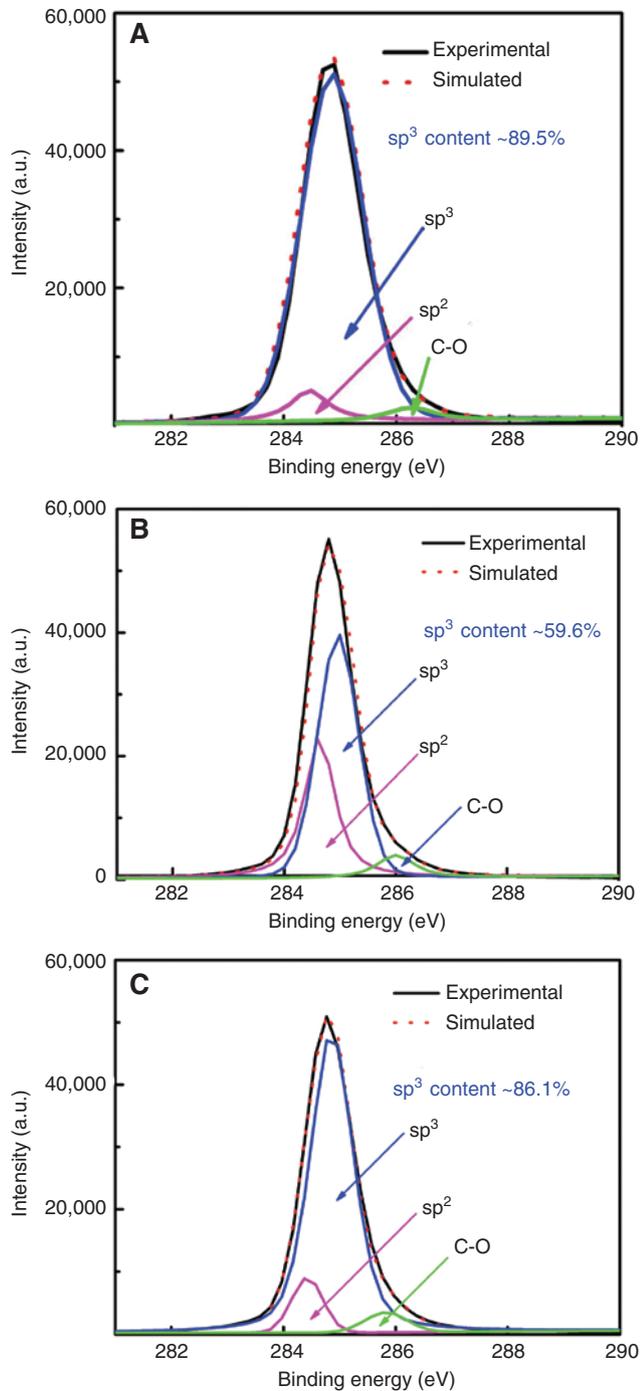


Figure 8: High-resolution XPS spectra diamond film samples at various gas flow rates (sccm). (A) O₂-0, Ar-0; (B) O₂-0, Ar-15; (C) O₂-1, Ar-14.

0.025–12.5 μm), as shown in Figure 9. The diamond film with 199.8 nm of surface roughness was synthesized at the conventional mixture gas of CH₄/H₂. However, roughness is 81.5 nm when 14 sccm Ar and 1 sccm O₂ were added into the plasma, indicating that Ar and O₂ can reduce the

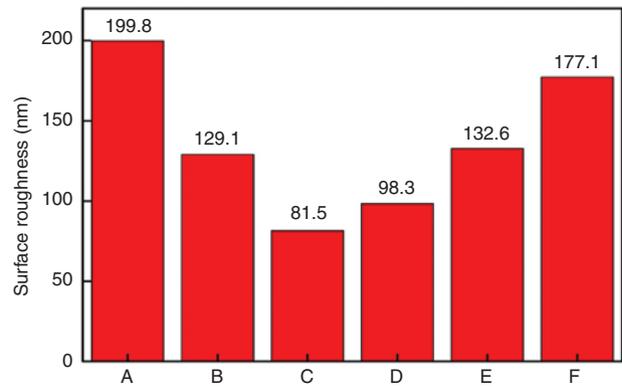


Figure 9: Surface roughness of diamond film samples obtained at various gas flow rates (sccm). (A) O₂-0, Ar-0; (B) O₂-0, Ar-15; (C) O₂-1, Ar-14; (D) O₂-2, Ar-13; (E) O₂-3, Ar-12; (F) O₂-4, Ar-11.

surface roughness significantly. Furthermore, the surface roughness increased by improved O₂ and reduced Ar flow under the total concentration was constant.

3.4 Effect of pure O₂ and O₂/Ar plasma on diamond

As we know, pure oxygen plasma can selectively etch sp²-bonded carbon. Thus, adding a few of pure O₂ can improve the quality of diamond films in CH₄/H₂ plasma. However, the oxygen plasma can also etch sp³-bonded carbon when sp²-bonded carbon content is very low in the surface of diamond films. Figure 10A shows an image of diamond films under the condition of pure O₂ (2 sccm) and no Ar. From this figure, the crystal edges and corners of diamond disappeared, and a lot of etch pits appeared on the surface, indicating that the diamond phase was etched by oxygen plasma. Meanwhile, the crystal edges and corners are worse because of the electronic level gathered [35].

Diamond films etched using O₂/Ar plasma is shown in Figure 10A, which is very different from Figure 10B. In this figure, the top of the diamond gain was etched into the plane. However, the crystal edges and corners are remarkable so the etch pits were not found. A possible mechanism lies in two aspects. On the one hand, pure oxygen plasma has a low electron density that leads to fewer particles available for plasma self-preservation [36]. The plasma can increase its density and directionality by added Ar because of the increasing number of reactive O-species [37]. Thus, the etching ability of the O atom especially improved on the top of the crystal. On the other hand, oxygen can accelerate the growth of [100] orientation effectively [26].

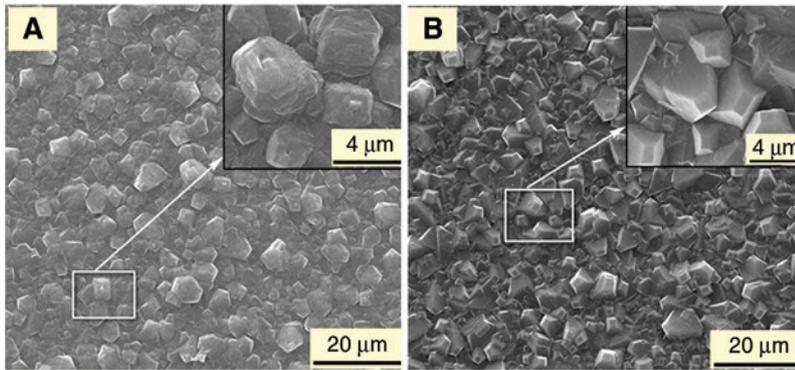


Figure 10: SEM of oxygen plasma etched diamond obtained at various gas flow rates (sccm). (A) O₂-2, Ar-0; (B) O₂-2, Ar-13.

4 Conclusions

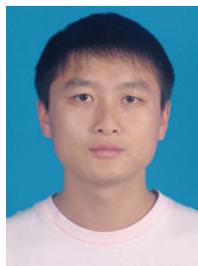
We have developed a novel approach to improve the surface quality of microcrystalline diamond films by the addition of Ar-O₂ as the auxiliary gas. The results indicate that Ar-O₂ mixed gas can further improve surface quality, and the obtained samples showed high diamond phase content and good surface quality. The diamond phase content reach up to 86.1%, whereas the surface roughness is only 81.5 nm by the addition of 14 sccm Ar and 1 sccm O₂. It found that the maximum addition of O₂ is 1 sccm within the scope of investigation in this paper. The synergetic effect origin from Ar and O₂ is beneficial to improve the surface quality of microcrystalline diamond films. The added Ar and O₂ can contribute to the grain refining of diamond, but the refining efficiency of Ar is more significant than O₂. Overall, this work provides a useful technique to improve the surface quality of microcrystalline diamond films, and the novel design will facilitate the optical application process. In terms of future work, there is room for the deposition of samples with higher diamond phase content and lower surface roughness by adding other auxiliary gases.

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