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LOW-TEMPERATURE GROWTH OF ULTRA-THIN NANO-CRYSTALLINE DIAMOND FILMS BY HFCVD IN A CH_4/H_2 MIXTURE

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Abstract: The diamond nucleation and growth on Si substrate by hot filament chemical vapor deposition (HFCVD) at the low temperature (~550℃) and low pressure (~7 Torr) were studied. Nucleation density (ND) as high as 1.5×10^{11} cm^{-2} was obtained on well ultrasonically pretreated substrate at the nucleation conditions of 2.5% CH_4/H_2. Diamond grain sizes change form sub-micron to nano-meter scales with the increase of CH_4 concentration. Smooth ultra-thin (thickness < 500 nm) nano-crystalline diamond (NCD) films with grain sizes less than 50 nm and surface roughness as low as 4nm have been synthesized. The adhesion between the film and substrate is good. The optical absorption coefficient in visible (VIS) to infrared (IR) wavelength range is less than $2\times10^4 cm^{-1}$. Smooth ultra-thin NCD films can be synthesized at low temperature and low pressure by our conventional HFCVD technique.

Key words: HFVCD; *nano-crystalline diamond film*; *ultrasonic pretreatment*; *low temperature growth*; *absorption coefficient*

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热丝化学气相沉积法在 CH_4/H_2 混合气体中低温生长超薄纳米金刚石膜

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摘要:用热丝化学气相沉积方法研究了低温(~550℃)和低反应气压(~7 Torr)下硅片上金刚石膜的成核和生长.成核过程中采用2.5%的CH_4浓度,在经充分超声波预处理的硅片上获得了高达$1.5\times10^{11}cm^{-2}$的成核密度.随CH_4浓度的增加所成膜中的金刚石晶粒尺寸由亚微米转变到纳米级.成功合成了表面粗糙度小于4nm、超薄(厚度小于500nm)和晶粒尺寸小于50nm的纳米金刚石膜.膜与衬底结合牢固.膜从可见光至红外的光吸收系数小于$2\times10^4cm^{-1}$.用我们常规的HFCVD技术,在低温度和低压下可以生长出表面光滑超薄的纳米金刚石膜.

关 键 词:热丝化学气相沉积;纳米金刚石膜;超声波预处理;低温生长;光吸收系数

Introduction

In recent years, NCD films, which have smooty surface, low friction coefficient and most of the outstanding bulk diamond properties, have been synthesized and recognized to use for optical protective coatings and wear resistant coatings[1~2]. NCD films are mainly grown by microwave CVD in a CH_4/Ar or argon-rich $CH_4/Ar/H_2$ mixture on various substrates (Si, SiO_2, SiC and various metals) seeded with dia-

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mond nano-powder.

The HFCVD is one of the most common techniques for poly-crystalline diamond films growth. It is an attractive technique for industrial applications due to its simple equipment, easy growth of large area films and low operating costs. It is important to successfully grow NCD films at low temperatures on a variety of substrates using the HFCVD technique, since the transition temperature of most optical materials, such as optical glass, is below 600℃, and the high growth temperature induces the high stress in the film. But, up to now, only a few papers reported on the synthesis of NCD films by HFCVD in hydrogen-poor, argon-rich $CH_4/Ar/H_2$ mixture at the substrate temperature of 800 ~950℃[3]. To the best of our knowledge, there is no report on the synthesis of NCD films by conventional HFCVD method without Ar at the substrate temperature below 600℃.

In this work, we investigated the effects of the ultrasonic pretreatment, substrate temperature and pressure on the growth of smooth NCD films, which are made by using conventional HFCVD technique at the relatively low CH_4 concentration, low pressure (~7 Torr) and temperature (~550℃).

1 Experiment

Si wafers (dimensions: $12 \times 12 \times 0.56 mm^3$) were first ultrasonically cleaned in acetone and subsequently etched in 20% HF acid to remove the oxide layer on the surfaces, then ultrasonically pretreated in slurry of diamond powder (grain size 20 ~30μm) and acetone for 1 h, followed by ultrasonically cleaning in acetone for 3 times.

Our improved HFCVD system has been described elsewhere[4,5]. The conditions of the three-step process are presented in Table 1.

The substrate surfaces after nucleating and the morphologies of as-grown film were observed by a field emission scaning electron microscope (FE-SEM) and an atomic force microscope (AFM). The ND was estimated by counting the grains on the FE-SEM photographs. A high-resolution laser Raman spectroscope ($\lambda = 514.5$ nm) was used to characterize the films. X-ray diffraction (XRD) measurment was performed

Table 1 The nucleation, growth and annealing parameters of the three-step synthesis process

表1 三步合成过程的成核、生长和退出参数

	CH_4/H_2 (Vol.%)	Tf (℃)	Ts (℃)	Pressure (Torr)	Total gas flow rate (SCCM)	Time (hour)
Nucleation	2.5	~2000	550	7	150	1
Growth	0.5~2.5*	~2000	550	7	150	4
Annealing**	0	~2000	≤550	40~50	150	5.5

* The best CH_4/H_2 for NCD film growth was 1 ~1.5%.

** in situ annealing from 550℃ to room temperature at 100℃ intervals (1h in duration).

using CuKα radiation. The selected-area electron diffraction (SAED) patterns were obtained by a transmission electron microscope (TEM). An UV-VIS spectrophotometer and an IR spectrophotometer were used to measure the transmittance spectra of the films. In order to obtain the correct transmittance of the film, a diamond film window on Si was made by chemical etching. The surface roughness and thickness of the films were measured with a surface profiler. The adhesion between the films and the substrates was examined by pulling with adhesive tape.

2 Results and discussion

In our previous papers[5], we have reported the results of our study on the nucleation enhancement by the ultrasonic pretreatment. The order of $10^{10} cm^{-2}$ ND and smooth diamond films on the fused silica have been obtained under optimal conditions. We have also observed that lower nucleation temperature and higher CH_4 concentration promote the nucleation.

A well ultrasonically pretreated Si wafer was cut into two pieces as the substrates to study the diamond nucleation under different CVD conditions. The substrate temperature and pressure were: (a) 800℃, 30 Torr and (b) 550℃, 7 Torr. The nucleation time was 15 min in (a) and 1h in (b), respectively.

Fig. 1 shows the FE SEM photographs of the two samples. From Fig. 1, it can be seen that the diamond grain at 800℃ and 30 Torr are bigger and the ND is lower than that at 550℃ and 7 Torr. The ND shown in Fig. 1 (b) is one order of magnitude higher than that in Fig. 1 (a), i.e. 3×10^{10} and $1.5 \times 10^{11} cm^{-2}$ in (a) and (b), respectively. In our knowledge, such high ND on Si is reported for the first time in the literatures.

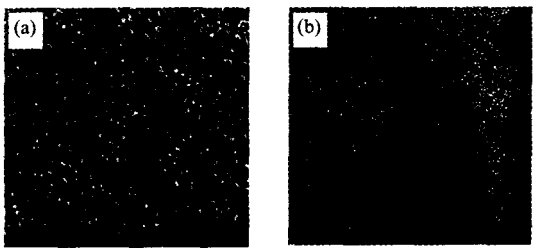

Fig. 1　FE-SEM photographs of diamond nucleation on the pretreated Si　(a) 800℃ and 30 Torr for 15 min　(b) 550℃ and 7 Torr for 1h. The other CVD conditions are all the same. The NDs in (a) and (b) are 3×10^{10} and $1.5 \times 10^{11}\,cm^{-2}$, respectively

图 1　经预处理的硅衬底上金刚石成核的 FE－SEM 照片　(a) 800℃、30 Torr 成核 15 min　(b) 550℃、7 Torr 成核 1 h. 其它 CVD 条件全相同(a)和(b)中的成核密度分别为 3×10^{10} 和 $1.5 \times 10^{11}\,cm^{-2}$

The morphologies of the diamond films grown at 0.5, 1.5 and 2.5% CH_4/H_2 (noted as sample A, B and C, respectively), 550℃ and 7 Torr are shown in Fig. 2. From Fig. 2, it can be seen that the film morphologies and the sizes of diamond grains are strongly related to the CH_4 concentration. In sample A, the diamond nuclei grow to 100 ~ 200 nm grains with well facets and some <111> texture, due to the relatively low concentration of active hydrocarbon radicals for secondary nucleation, no secondary nuclei appear in the nucleation step. For the samples grown at higher CH_4 concentration (B and C), the secondary nucleation appears, resulting in the final grain sizes smaller than 50nm and smooth films (see Fig. 2 (b) and (c)). In our work, no micro-crystalline diamond grains coexist in the films, it is better than that reported by Zhang *et al*[3].

Fig. 3 (a) and (b) show the AFM images of the morphologies of sample A and B, respectively. The AFM image of the sample C is almost the same as that of sample B; hence, it is not shown here. It can be seen clearly that the grain sizes are in the range of 50 ~200nm in (a) and 30 ~ 50min in (b). The grain sizes are more uniform and the surface is much smooth in (b) than that in (a), same as observed by FE-SEM in Fig. 2. In Fig. 3 (b), larger grains are composed of small diamond particles (~30nm), while in Fig. 3 (a),

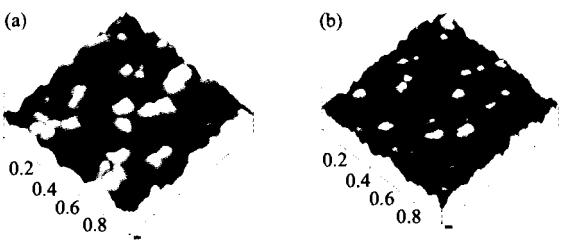

Fig. 3　The AFM images of the films grown at CH_4 concentration　(a) 0.5% and (b) 1.5%

图 3　两种 CH_4 浓度下生长的膜表面 AFM 形貌照片　(a) 0.5%　(b) 1.5%

Table 2　The thickness, growth rate, surface roughness, grain size and light transmittance at 700nm wavelength of the films grown at different CH_4 concentration

表 2　不同 CH_4 浓度下生长的同类的厚度、生长速率、表面粗糙度、晶粒大小及 700nm 波长的光透射率

Samples (CH_4/H_2)	Thickness (nm)	Growth rate (nm/h)	Surface roughness (nm)	Grain size (nm)	Transmittance at 700nm (%)
A(0.5%)	450	112.5	7.5	50 ~ 200	55
B(1.5%)	390	97.5	4	30 ~ 50	71
C(2.5%)	240	60	3.5	30 ~ 50	(fail to obtain unbroken film)

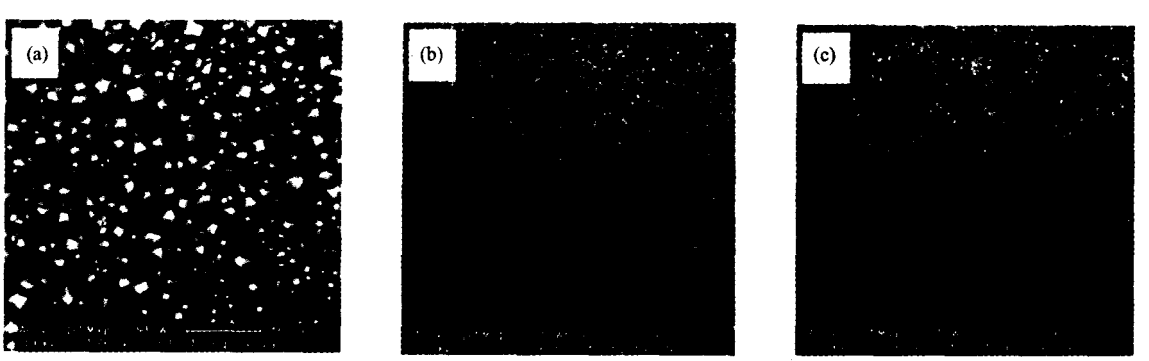

Fig. 2　The FE-SEM photographs of the surface morphologies of the films grown at different CH_4 concentration　(a) 0.5% (b) 1.5 and (c) 2.5%

图 2　不同 CH_4 浓度下生长的膜表面形貌的 FE-SEM 照片　(a) 0.5%　(b) 1.5%　(c) 2.5%

large grains (~200nm) are single-crystal particles.

Fig. 4 is the XRD spectra (a) and one of the SAED patterns (b). From Fig. 4(a), the peaks at $2\theta = 43.90°$ of the sample A, B and C (spectrum 1, 2 and 3, respectively) can be seen, which corresponds to the (111) peak of cubic diamond. The large full width at half maximum (FWHM) of the (111) peaks is well correlated with small grain sizes of the films, and the FWHM increases with the increase of CH_4 concentration. Fig. 4(b) is the SAED pattern of the sample B; the SAED patterns of the other two samples are similar to the pattern shown in Fig. 4(b), therefore, they are not shown here. In Fig. 4(b), the SAED pattern with three circles indicates that the diamond grains have a random orientation. The circles correspond to the cubic diamond (111), (220) and (311) reflections.

Fig. 5(a) is the measured Raman spectra of the samples. The fitting spectra of the sample A and B are shown in Fig. 5(b) and (c), respectively. The fitting spectra of the sample C is similar to that of the sample B and not shown here. As shown in Fig. 5(b) and (c), the measured Raman spectra were resolved by computer. The computed spectra were generated as a superposition of six (Fig. 5(b)) and five components (Fig. 5(c)), respectively. The two strong peaks at 1350 and 1580 cm^{-1} are due to the "D" and "G" band of graphite, respectively. The Raman intensity of sp^2 bond is nearly 50 times higher than that of sp^3 bond [6] with the 514.5 nm laser excitation, therefore, the amount of sp^2-bonded carbon in the films is small. In Fig. 5(b), a relatively small and sharp peak at 1333cm^{-1}, which is the characteristic Raman peak of the diamond, indicates the existece of sub-micron grains in the film, as shown in FE-SEM (Fig. 2(2)) and AFM (Fig. 3(a)) images.

The two peaks at 1140 and 1480cm^{-1} are commonly assigned to NCD, and the peak near 1200cm^{-1} is also found in diamond nanocrystals[7]. From the computer-resolved spectra in Fig. 5(b) and (c), the Raman peaks near 1140, 1200 and 1480 cm^{-1} are

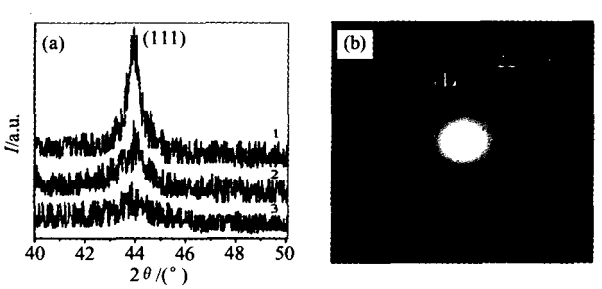

Fig. 4 (a) The XRD spectra of the films grown at 0.5, 1.5 and 2.5% CH_4/H_2, corresponding to spectrum 1, 2 and 3, respectively (b) SAED pateern of the film grown at 1.5% CH_4/H_2

图4 (a) 0.5, 1.5 和 2.5% CH_4/H_2 浓度下生长的膜的X-射线衍射谱, 分别对应图中谱 1, 2 和 3 (b) 1.5% CH_4/H_2 浓度下生长的膜的选区电子衍射图

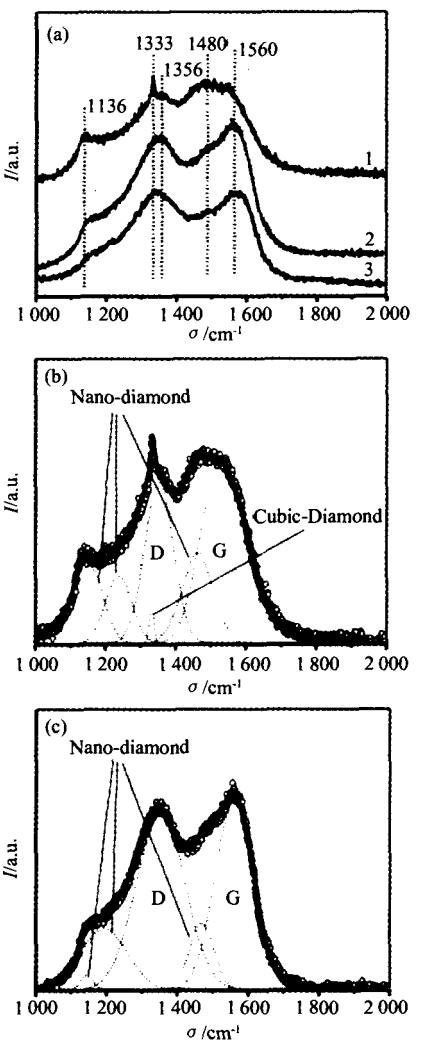

Fig. 5 The Raman spectra (a) the films grown at 0.5%, 1.5% and 2.5% CH_4/H_2, corresponding to spectrum 1, 2 and 3, respectively (b) and (c) the computer-resolved spectra of the spectrum 1 and 2 in (a), respectively
° experimental points — computer-fitted spectra ··· computer-resolved components

图5 Raman 谱 (a) 0.5, 1.5 和 2.5% CH_4 浓度下生长的膜, 分别对应图中谱 1, 2 和 3; (b) 和 (c) 是 (a) 中谱 1 和 2 的计算机解谱
° 测量谱 — 计算机拟合谱 ··· 计算机解谱

clearly seen.

The transmittance at 700 nm wavelength of two samples is listed in Table 2. The sample C is too thin to obtain an unbroken film; hence, the transmittance data of this sample were not obtained. The transmittance of NCD films is affected mainly by the absorption of the films and the light scattering at the films' surfaces. The transmittance ranges in 40 ~ 80% in VIS-NIR wavelength and rapidly decreases to almost zero from the wavelength less than 300 ~ 200nm, this proves again that the quality of NCD films is quite good.

Since the thicknesses of the samples are different, absorption coefficients of the films were calculated from the transmittance data and plotted in Fig. 6. The absorption coefficient curves of the two samples alternate from UV to NIR range, there is no obvious difference between them in this experiment. The surface roughness of the sample A is still small, compared with micro-crystalline films. In order to obtain high transmittance of NCD films, a compromise should be reached between the surface roughness and the quality of NCD films. The absorption coefficient spectra in Fig. 6 are deduced from transmittance spectra supposing zero reflectance, which may result in: (1) higher absorption coefficient than the real value; (2) existence of Fresnel interference effect in these spectra, due to multiple reflections at the diamond-air interfaces.

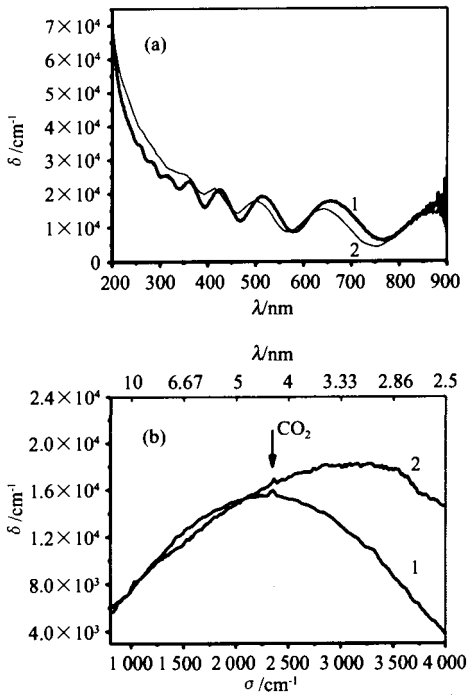

Fig. 6 The absorption coefficient spectra of the films grown at 0.5% (spectrum 1) and 1.5% CH_4/H_2 (spectrum 2) in (a) UV-VIS-NIR range and (b) IR range
图 6 0.5 和 1.5% CH_4 浓度下生长的膜光吸收系数谱 (分别对应图中谱 1 和谱 2) (a) UV-VIS-NIR 谱 (b) IR 谱

3 Summary

The ND and CH_4 concentration strongly influence the morphology and micro-structure of the diamond film. With the increase of CH_4 concentration, the diamond grain sizes change from sub-micron to nano-meter scales. ND as high as $1.5 \times 10^{11} cm^{-2}$ was obtained on ultrasonically pretreated Si substrate at 2.5% CH_4 at nucleation step. Ultra-thin NCD films with grain sizes less than 50nm, surface roughness lower than 4nm and thickness less than 500nm have been synthesized at 550℃, 7Torr and 1.5% CH_4/H_2 at growth step by our conventional HFCVD technique. NCD films have 40 ~ 80% optical transmittance and absorption coefficient $< 2 \times 10^4 cm^{-1}$ in VIS to IR wavelength range. The good adhesion of NCD films has been achieved. NCD films obtained can be used as optical protective coatings on optical materials such as optical glass.

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