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Study of the moderate-temperature growth process of optical quality synthetic diamond films on quartz substrates

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Abstract

Growth of undoped and boron-doped diamond films on quartz substrates at moderate temperature of 500 °C by microwave plasma chemical vapor deposition method was studied in terms of growth rate, surface roughness and optical transmittance. Similar density of diamond seed particles on quartz surfaces seeded mechanically before the deposition process and diamond grains within diamond films grown on those substrates is observed. The growth rate is found similar to that reported for diamond deposited on silicon substrates in the same plasma deposition system, although with substantially higher activation energy. Furthermore, increased level of dopant concentration in the gas mixture resulted in a decrease of the growth rate, while a gradual reduction of the surface roughness occurred at high dopant levels. Overall, the highest measured regular optical transmittance of the undoped diamond film on quartz was 45% at 1100 nm (including quartz absorption), whereas that of boron-doped diamond peaked 5% at 700 nm (tail absorption of boron centers).

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1. Introduction

A large variety of oxides such as: MgO, LaAlO₃, Al₂O₃ (sapphire), SrTiO₃, SiO₂ (quartz, fused silica), have been used for deposition of thin diamond films by chemical vapor deposition (CVD) method, most of which, however, exhibiting some disadvantageous structural properties. For example, MgO, although stable, is unavailable in the form of large single crystals and presents substantial surface roughness, while SrTiO₃ exhibits surface instability in ultra high vacuum (UHV) at high temperatures. Among these oxides, quartz substrate seems to be appropriate for advanced technological applications, including for instance: surface acoustic wave (SAW) devices [1], and optical coatings [2,3], particularly because no carbide interfacial layer is formed during the growth process leaving unaffected both high optical transmittance and low electrical conductivity of the diamond/quartz structure.

Unfortunately, there are several factors that still limit the use of diamond films on quartz substrates in industrial applications, such as: poor film adhesion, thermal expansion coefficient mismatch, substantial roughness of the coating, and its low growth rate. In order to grow smooth diamond films on foreign substrates, high density of diamond nuclei distributed homogenously across the substrate is necessary. To this end, the growth process on quartz usually follows various pre-treatment procedures including, for instance, mechanical seeding with diamond powder or a slurry [2,4], as well as titanium implantation [5]. The inevitable consequence of the latter process is, however, that a very thin titanium carbide interfacial layer forms during diamond deposition, which is opaque, and hence useless for most optical applications.

Presented paper is aimed at studying the kinetics of diamond growth on quartz substrates seeded with 0.25 μ m diamond powder in terms of growth rate and activation energy of the process. The paper deals with structural properties of diamond-on-quartz structures (morphology, roughness, UV–VIS transmittance) deposited in the moderate-temperature regime of about 500 °C. The diamond films were grown by means of the

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Microwave Plasma CVD method from one of the following gas mixtures: (1) methane and hydrogen (undoped films), or (2) methane, hydrogen and trimethylboron (boron-doped films). Prior to the deposition process quartz substrates were mechanically seeded with diamond powder onto a vibrating plate in order to increase the density of diamond nuclei.

2. Experimental details

Quartz plates of the thickness of 1 mm have been chosen as substrates for diamond deposition. The substrates were subjected to 4-h mechanical seeding with 0.25 µm diamond powder on a vibrating plate (Vibromet), and followed by ultrasonication in a bath of isopropyl alcohol and deionised water. Neither implantation with Ti ions nor additional seeding with a diamond/titanium slurry has been used to increase the diamond nucleation density on guartz substrates. The growth process was carried out in a 3 kW ASTeX microwave plasmaassisted CVD system using standard gas mixture for diamond growth containing methane diluted with hydrogen and optionally enriched with small amounts of trimethylboron ((CH₃)₃B, TMB) as a source of boron dopants. The deposition parameters were as follows: hydrocarbon concentration [CH₄] ranged from 1 up to 5% (vol.), TMB concentration less than 50 ppm (vol.), substrate temperature T_{sub} =500-860 °C measured by a twocolor pyrometer (Williamson Pro 92-40), gas pressure p=7.33 kPa (55 Torr), microwave power $P_{\rm MP}=3$ kW and deposition time $t_{dep}=2$ h.

The crystalline structure of the films was identified using Raman spectroscopy (Jobin-Yvon U1000 spectrometer with 488 nm Ar-ion laser) in a scattered light configuration, and Xray diffraction (XRD, Siemens D5000 diffractometer with Cu (K_{α}) radiation) in a theta–2theta mode scanning within a plane perpendicular to the sample surface. Morphology of the films was studied using atomic force microscopy (AFM, Veeco Dimension 3100 Scanning Probe Microscope) working in a tapping mode.

Growth rate of diamond films was calculated from the interference fringes seen as variations of the apparent temperature measured *in-situ* by the pyrometer [6-8]. The idea behind such indirect temperature measurement was that the intensity ratio at two neighbouring wavelengths in a gray body emission spectrum (non-absorbing and relatively thick quartz substrate heated by the plasma ball) might be directly related to its temperature according to the Planck's law. It turned out, however, that despite the constant microwave power, the ratio observed over a period of the deposition process was highly oscillating that resulted in apparent variations of the sample temperature. The reason was that with increasing thickness of the diamond film, the optical path lengths of multiply reflected beams observed by the pyrometer were increasing as well, but not to the same degree. Using Fresnel equations and taking into account the chamber geometry, oscillations of the pyrometric temperature have been successfully modelled, and their peaks were assigned to the thickness of the diamond film.

The regular transmission spectra at a normal incidence angle (*i.e.* with no diffuse transmission included) were recorded in a

range between 200 and 1100 nm using a double beam Lambda 2 UV–VIS spectrometer (Perkin-Elmer), with the quartz substrate facing the illuminating beam.

3. Results and discussion

Fig. 1 shows tapping-mode AFM images of quartz substrates before (A), and after (B) mechanical seeding. The untreated substrate in Fig. 1(A) was found unintentionally pre-scratched, but several measurements of the surface roughness over $50 \times 50 \ \mu\text{m}^2$ squares consistently resulted in the root-meansquare (RMS) surface roughness less than 0.5 nm. In turn, mechanical seeding left behind homogeneously distributed residual diamond grains, which increased the RMS roughness to 2.0 nm. It should be noticed, however, that although 250-nm diamond seeds were used, a vast majority of residual particles observed in Fig. 1(B) did not exceed 100 nm in diameter, which suggests that large diamond grains were first crushed into smaller pieces and then hardly pressed into the quartz substrate where they withstood subsequent ultrasonic vibrations in a bath. This was particularly important for the deposition process as the nucleation density obtained after 4 h of such a pre-treatment procedure was found at about $2.0 \cdot 10^8$ cm⁻², with the smallest particles contributing to about 92 % of the overall nucleation detected in Fig. 1(B). After all, obtained nucleation density, although 2 orders of magnitude lower than the highest reported so far [4,9], appeared to be sufficient for continuous, optical quality diamond films described in the following paragraphs.



Fig. 1. Tapping-mode AFM micrographs of quartz substrates before and after seeding with 0.25 μ m diamond powder: (A) untreated surface with remarkable unintentional pre-scratches, and the RMS roughness of 0.5 nm, (B) seeded surface with the RMS roughness of 2.0 nm, and the nucleation density of $2 \cdot 10^8$ cm⁻². Note that the majority of the seeds are particles smaller than 100 nm.

In Fig. 2, AFM images of undoped (A), and doped with 50 ppm of boron (B) diamond films are shown, deposited for 2 h at 500 °C, and 4.8% of methane concentration in the gas mixture. They do not differ significantly in their surface morphology. Both films exhibit grain density of about $1.3 \cdot 10^8$ cm⁻², which is comparable to the density of diamond seeds, and corresponds to the average grain diameter of about 0.98 µm assuming the model of surface filled with circles. Grains are distributed homogenously (Fig. 1(A)), and hence directional pre-scratching of the substrate does not affect the grain alignment in any way. Therefore, it is actually seeding which helps the diamond deposition on quartz, whereas previous works have stressed significance of the scratching procedure [9].

XRD patterns of the films from Fig. 2 are shown in Fig. 3(A). Three distinct peaks located at $2\Theta \approx 44.04^{\circ}$, 75.30°, and 91.70° could be identified as reflections from (111), (220), and (311) planes of diamond polycrystals, respectively. To determine the average size of the coherently diffracting domains (CDD) in diamond, numerical fit of the Debye–Scherrer equation to the peak positions and their widths has been carried out [10,11]. It yields a value of 24, and 20 nm for diamond films doped with 0, and 50 ppm of B atoms, respectively, which is 50 times smaller than the grain diameter estimated from AFM micrographs. It strongly suggests that a single diamond grain usually contains hundreds CDDs (subgrains) without any predominant orientation.

In Fig. 3(B), Raman spectra of diamond films containing (from top to bottom, respectively): 0, 3, 6, 12, 25, and 50 ppm of boron atoms within their lattice sites are shown. In order to investigate their phase purity, spectral features characteristic of



Fig. 2. Tapping-mode AFM micrographs of the diamond films: (A) undoped, and (B) doped with 50 ppm of boron. Obtained grain density of about $1.3 \cdot 10^8$ cm⁻² is comparable to the nucleation density on the seeded substrate.



Fig. 3. (A) XRD patterns of the films doped with 0 and 50 ppm of boron atoms (top and bottom, respectively); (B) Raman spectra of CVD diamond films on quartz with increasing content of boron atoms (from top to bottom): 0, 3, 6, 12, 25 and 50 ppm, respectively. Let us notice the disappearance of the 1332 cm⁻¹ line caused by increasing absorption of light, and the 1370 cm⁻¹ line in low-doped films, attributed to compressive strains within sp³ clusters.

carbon atoms in tetrahedral (diamond) and trigonal (graphite) configurations need to be taken into consideration. Therefore, prominent peaks at around 1332 cm⁻¹ are unambiguously attributed to diamond crystals, but they are found strongly dependent on the dopant concentration. In fact, the peak position shifts from 1331 to 1322 cm⁻¹ with boron content increasing from 0 to 50 ppm. In the light of the harmonic oscillator model proposed by Fitzer and Rozploch [12], such a red-shift is a consequence of elongation of sp³-hybrydized carbon bonds due to structural defects from 0.1542 to 0.1547 nm, i.e. less than 1%. In turn, the peak intensity falls down to zero for samples doped with 50 ppm of boron, which, in connection with XRD data, suggests an increase in the light absorption coefficient. This observation is additionally supported by similar behaviour of a wide peak at around 1600 cm⁻ (graphitic inclusions in the diamond structure), which disappears in heavily doped films.

Apart from that, tiny peak around 1370 cm⁻¹, and a shoulder at 1480 cm⁻¹ are also visible, first of which is connected with sp³ clusters under compressive stress [12], while the latter is

speculatively assigned to carbon–hydrogen bonds in the grain boundaries [13]. It is not clear, however, why the 1370 cm⁻¹ line is not accompanied by another hydrogen-related peak at 1120 cm⁻¹ observed both in nanocrystalline [13] as well as in polycrystalline diamond films [14]. On the whole, Raman scattering measurements prove very good quality of obtained films, since the volume fraction of non-diamond carbon phase Φ_N , calculated according to the expression proposed by Vorlicek et al. [15], varies between 1 and 2%.

In Fig. 4, the measured growth rate of undoped films as a function of the deposition temperature is shown in the form of the Arrhenius plot. The growth rate is found to increase from 0.48 μ m/h at low temperature (475 °C) to 3.6 μ m/h at 860 °C. Obtained values are slightly higher than those measured in similar configuration for diamond films on silicon [6], presumably because of lacking carburization of the substrate. On the other hand, the growth rate is at least double of those reported elsewhere for quartz substrates [3,9,16]. Observed difference is likely to stem from the pre-treatment procedure, and more precisely from the prolonged seeding, which decreased the incubation period necessary for the seeds to overgrow. Unambiguous determination of the incubation time is hardly possible, however, an overestimation has been made by defining the incubation as a period over which the apparent temperature peaks for the first time, which in a given set-up is equivalent to a 151 nm thick diamond film. The incubation is found to vary from 25 min at 475 °to 2 min at 860 °C. Furthermore, plotted data are found to follow the straight line, and hence they obey the Arrhenius law with an activation energy $E_A = 322$ meV. In such a case, however, the energy is higher than that measured for diamond on silicon [6], which suggests that, apart from hydrogen desorption from diamond surface under atomic hydrogen flux, additional thermallyactivated processes are involved in diamond growth.

Fig. 5 shows the variation of the film thickness (A) and corresponding growth rate (B) of diamond films as a function of the growth time, calculated from the oscillations of apparent



Fig. 4. Arrhenius plot of the growth rate *vs.* reciprocal temperature function for the undoped diamond sample, that exhibits activation energy of the deposition process of about 322 meV.



Fig. 5. (A) Film thickness, and (B) the growth rate evolution for undoped (open circles), and doped with 50 ppm of boron (closed circles) diamond films, respectively. It turns out that both the growth rate and the incubation time are suppressed under boron addition.

temperature measured with the pyrometer. As a rule, the growth rate of the undoped film (open circles) is approximately double that doped with 50 ppm of boron (closed circles), but is not constant throughout the deposition process. It gradually increases over a period of 3000, and 4000 s for undoped, and the heaviest B-doped film, respectively, which could be due to the overgrowth of the residual diamond seeds and incubation of new diamond nuclei until a continuous diamond film is completed. Note, however, that the same pre-treatment procedure gives rise to different growth kinetics which suggests changes in the plasma chemistry under boron addition, and needs to be addressed in further work. Such an observation is supported by the fact that both incubation process is suppressed and growth rate is reduced in experiments with boron-enriched gas mixtures.

Systematic analysis of the boron effect on the overall growth rate has been carried out and is presented in Fig. 6. As seen in Fig. 6(A), the growth rate plotted against boron content follows the straight line and decreases every 5 nm/h per 1 ppm of a dopant concentration. Similar tendency can be seen in Fig. 6(B), where the film roughness as a function of increasing boron content is presented. The roughness of the undoped film approaches 90 nm, but falls down to 75 nm for the film doped with 50 ppm of boron. As a rule, obtained films exhibit surface roughness smaller than films seeded with μ m-size diamond powder [2], and equal to those seeded with nm-size powder [2]. Fig. 6(B) proves that every 1 ppm of boron added to the gas mixture decreases the RMS roughness of the surface by about 0.3 nm, which actually proves very weak dependence. The effect of boron atoms is not clearly understood, but it might be seen as a process of filling of structural defects in the diamond lattice by relatively light dopants. Unfortunately, optical transmittance data given in the following paragraph suggest that smoother surface goes hand in hand with increasing absorption of light within investigated structures making them useless for many optical applications.

Fig. 7 presents regular optical transmittance data of undoped and B-doped films on quartz substrates, and the spectrum of an untreated quartz given as a reference. Observed tailing in the transmittance of the films in the UV limit, *i.e.* near the fundamental absorption edge of diamond, clearly points at their continuity, although some contribution from structural defects



Fig. 6. (A) Growth rate, and (B) surface roughness *vs.* boron concentration plots showing the decrease in the growth rate with increasing boron content and simultaneous reduction in the surface roughness.



Fig. 7. The regular transmittance spectra of undoped, and B-doped diamond films on quartz (with respect to the air), together with the spectrum of quartz given as a reference. Gradual increase in the transmittance is seen in case of undoped sample, although a wide shoulder centered at about 700 nm is seen for B-doped sample. The latter is brought by the tail absorption of boron centers introduced to the diamond lattice.

and phase contaminations is possible as well. The oscillations of the transmittance of the undoped film seen near the IR limit come from the Fresnel interference in the thin layer. In this case, the absolute transmittance is lower than reported elsewhere [2,17], although for reliable data comparison the difference in the film thickness as well as the light scattering on diamond surface and diamond/quartz interface (diffuse transmission) need to be taken into account.

Fig. 7 shows that the transmittance of the undoped film on quartz gradually increases from UV to IR spectral range and approaches T=45% at 1100 nm. Having the transmittance of the quartz substrate measured, however, one might expect that the transmittance of a diamond film removed from its quartz substrate would be increased by a factor of 1.5 up to T=70%, which is comparable to the transmittance of much thinner films reported in [2,17]. On the other hand, the regular transmission of the film doped with 50 ppm of boron is very low, and peaks at 5% at 700 nm. Observed shoulder results from the tail absorption of B-centers in boron-doped diamonds, located at about 0.37 eV (3.3 µm) above the valence band maximum, and extending up to 2.2 eV (0.6 µm) into the bandgap.

4. Conclusions

Deposition of continuous diamond films on quartz substrates seeded with diamond particles at a density exceeding 10^8 cm^{-2} is demonstrated in the paper. Despite the seeding with 0.25 µm diamond powder, seeds smaller than 100 nm contribute to over 90% of the nucleation density, and subsequently account for the diamond growth due to comparable density of obtained diamond polycrystals. Considering the regular transmittance of the films it appears that the nucleation density of the order 10^8 cm^{-2} is high enough for most optical applications. In addition, growth rates are found similar to those reported for diamond deposition on silicon in the same system, and at least 2

times higher than previously reported for quartz substrates. Unexpectedly, the growth rate appears to decrease with increasing boron addition, but this effect is compensated by decreasing RMS roughness of the surface. In such a case, filling in the vacancies in diamond is suggested that suppresses the surface irregularities. Optical transmittance of the films on quartz substrates is found lower with respect to the highest reported so far, however, when the contribution of the quartz substrate is removed it turns out that the diamond transparency might be sufficient for most optical applications.

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