Growth of nanocrystalline diamond protective coatings on quartz glass

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Transparent diamond films with a crystallite size well controlled below 70 nm were grown by hydrogen and methane microwave plasma-enhanced chemical vapor deposition on quartz glass substrates, which had been scratched with 0.5 μm diamond powder. A complementary set of analyzing tools was employed to study the microstructure, the optical and mechanical properties of the deposits. Transmission electron microscopy revealed a nucleation density generally larger than 1011/cm², which is of the same order of magnitude as the spotlike defects on the pretreated surface of the substrates. The Vicker’s hardness of the deposits scatters between 61 and 95 GPa. An optimal transmittance of 65% in the visible light range is achieved in coatings of 1.0 μm in thickness when the surface roughness measures about 10 nm or less. The nanocrystalline diamond films thus prepared can meet the requirements on transparent protective coatings for optical components.


I. INTRODUCTION

The multifarious potential applications of diamond as an engineering material originate in its extraordinary properties such as wide band gap (5.5 eV), high hardness, excellent thermal conductivity (20 W/cm K), and extreme chemical inertness. In addition, diamond is transparent over a very wide spectral range, and it is suitable for the fabrication of assorted devices subjected to harsh conditions such as high pressure, prohibitive temperature, and strong acid. The preparation of high-quality diamond films has attracted the interest of researchers for many decades, yet the enthusiasm toward diamond synthesis with various different methods continues unabated, as evidenced in many recent progresses.1–4 Notably, the accessibility of modern analyzing tools has considerably promoted our understanding of the growth mechanisms and facilitated to some extent the controlled growth of diamond films.

Exploiting the attractive features in thin-film applications requires the diamond film to be transparent when, for instance, used as protective coatings for optical components. Owing to the large grain size in the order of several microns, the polycrystalline diamond films often exhibit a rough surface and consequently are unsuitable for immediate optical or tribological applications. Polishing of polycrystalline diamond with either chemical or mechanical methods seems impractical because of its extreme hardness and chemical inertness. On the other hand, a compromising between crystallinity and surface roughness by tuning the process parameters may degrade the film quality via the promotion of the sp²-bonded structures.5 Therefore, to meet the requirements imposed upon diamond film in applications such as transparent overcoat, efficient approaches have to be exploited to prepare the films with a very smooth surface through reducing the diamond grain size down to nanometer dimension.5–7

Nanocrystalline diamond films have been successfully grown with a microwave plasma using both the hydrogen-methane and the fullerene-argon mixture as a precursor.8 Also the growth of nanocrystalline diamond by hot-filament chemical vapor deposition (CVD) with a small amount of Ar in methane has been reported.9 It is well known that the crucial factor for the attainment of a smooth diamond surface is the primary nucleation density. In the case of diamond growth on silicon substrates, a handful of rather efficient methods have been discovered by the trial and error process for the enhancement of nucleation density. These include the scratching of substrates with diamond powders, positive or negative biasing of the substrates, direct ion-beam deposition, passivation of the silicon surface with I or Br, and also the compound operations of these techniques.1,10,11 Today, a maximum nucleation density of 1×10¹²/cm² can be achieved and smooth diamond surfaces with a root-mean-square roughness even less than 2 nm have been accomplished. Although the nucleation enhancement mechanisms are not well understood, the researchers nowadays are nevertheless able to grow nanocrystalline diamond films even on substrates of noncarbon affinity such as copper and glass by applying the aforementioned methods.

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This article reports on the preparation of highly transparent nanocrystalline diamond coatings on quartz glass substrates by the microwave plasma-enhanced chemical vapor deposition (MW-CVD) method using the hydrogen-methane gas mixture. The effect of substrate pretreatment on the nucleation and the process parameter dependence of the deposit features were investigated. We provide the experimental confirmation that the deposits are compact, hard, and highly transparent, and they are thus competitive for the applications as protective coatings for the optical components. To this end, a complementary set of spectroscopic and microscopic techniques has been employed for the characterization of the film properties.

II. EXPERIMENT

A custom-designed MW-CVD system built after the Astex-2150 prototype has been employed for conducting the diamond growth. The substrates are optical grade quartz glass of 1.5×2.0 cm in dimension and of 0.5 mm in thickness. They are characterized by three material parameters, namely, a thermal expansion (0–300 °C) of 2.56×10⁻⁷/°C, a softening temperature at 1200 °C, and a refractive index (589.3 nm) of 1.45. The substrate pretreatment involves the ultrasonical polishing in acetone for 30 min with a diamond powder of grain size 0.5 μm, and after that the polished substrates were cleaned in acetone and rinsed using the deionized water to remove any residual diamond particles. The substrates were further cleaned in the pure hydrogen microwave plasma for another 30 min prior to the film growth. Film growth proceeded under the following conditions: sample temperature 500 °C, working pressure maintained at 0.2% oxygen would be introduced after the two-hour nucleation and the process parameter dependence of the deposition time. The microwave power was regulated at 1.5 kW in order to achieve a typical film thickness of 1.0 μm in 4 h.

The film thickness was determined using a stylus method (Dektak 3030). The surface morphology of the pretreated substrates and the deposits was determined on an atomic force microscope (AFM, Digital Instruments, Nanoscope). The scratched surface of the quartz glass substrates was inspected with an AFM. Figure 1 displays a typical height image obtained in an area of 10×10 μm on the polished surface. It is clearly seen that the surface landscape comprises randomly oriented scratches and dense spotlike damages. The nominal root-mean-square (rms) roughness $R_{\text{a}}$ was determined from the load versus displacement curve obtained on a nanoindenter (Nanoindentor™ II, MTS) at a maximum displacement of about 100 nm.

III. RESULTS AND DISCUSSION

The scratched surface of the quartz glass substrates was examined with the Raman technique. Figure 2 displays typical Raman spectra for the diamond films prepared with methane fractions of (a) 1.0%, (b) 2.0%, (c) 3.0%, and (d) 4.0%. The film thickness was determined using a stylus method (Dektak 3030). The surface morphology of the pretreated substrates and the deposits was determined on an atomic force microscope (AFM, Digital Instruments, Nanoscope). The scratched surface of the quartz glass substrates was inspected with an AFM. Figure 1 displays a typical height image obtained in an area of 10×10 μm on the polished surface. It is clearly seen that the surface landscape comprises randomly oriented scratches and dense spotlike damages. The nominal root-mean-square (rms) roughness $R_{\text{a}}$ was determined from the load versus displacement curve obtained on a nanoindenter (Nanoindentor™ II, MTS) at a maximum displacement of about 100 nm.

<table>
<thead>
<tr>
<th>Methane fraction (%)</th>
<th>Raman data (cm⁻¹)</th>
<th>Roughness (nm)</th>
<th>Grain size (nm)</th>
<th>Transmission (%)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1334</td>
<td>12</td>
<td>25.14</td>
<td>195</td>
<td>38</td>
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<tr>
<td>2.0</td>
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<td>1342</td>
<td>35</td>
<td>11.53</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>4.0</td>
<td>1359</td>
<td>38</td>
<td>8.99</td>
<td>52</td>
<td>61</td>
</tr>
</tbody>
</table>

aGrain size at the growth side.
bAveraged in the visible light range between 12 000 and 15 000 cm⁻¹.
cRange of the hardness value, 20 tests for each specimen.
50.772 nm and the maximum height difference is 17.238 nm. The elongated scratches contribute the most to the surface roughness. In a zoomed-in image, less than ten bright spots, of which the maximum dimension is only 25 nm, were identified in a 500×500 nm region. Evidently, these bright spots cannot be attributed to the residual diamond particles. It is therefore concluded that the diamond powders simply scratch the glass surface without leaving behind a perceptible amount of diamond particles embedded in the glass. This explicitly excludes the possibility of diamond growth on the seeding particles.

In the present paper, the diamond film growth proceeded straightforwardly on the scratched quartz glass substrates. With a methane fraction varying up to 4.0%, some 30 samples have been prepared. For those samples that grew for 4 h, the thickness generally scatters within 1.0 to 1.2 μm. They all exhibited a compact smooth appearance, and the transparency of the specimens in the visible light range can be judged immediately by the naked eye.

Raman spectroscopy is a conventional technique for the confirmation of diamond phase, which also provides various information such as the secondary sp² phases, the grain size, and the accumulated stress in film, etc. Raman spectra for the deposits obtained with a methane fraction of 1.0%, 2.0%, 3.0%, and 4.0% are shown in Fig. 2; they all exhibit three distinct peaks, namely, the diamond peak at the vicinity of 1332 cm⁻¹, a peak centered at about 1500 cm⁻¹ indicating the presence of some nondiamond carbon, and a peak centered at 1140 cm⁻¹. The origin of the latter has once been attributed to the nanocrystalline nature of the diamond deposit, but it is now still subjected to furious debate. For the deposits from 1.0% and 2.0% methane, the diamond peak manifests a full width at half maximum (FWHM) of only 12 and 10 cm⁻¹, respectively, only about four times wider than that of natural diamond (3.3 cm⁻¹). At the methane fraction 3.0%, the FWHM of this peak measured a value as large as 35 cm⁻¹, implying a sudden reduction of the grain size in the resultant deposits. A further reduction in the grain size was achieved at the methane fraction 4.0% as concluded from the broadened diamond peak. At the same time, the peak at 1500 cm⁻¹ turned out obviously intensified implying an ever-increasing presence of nondiamond phases in the deposit.

The increased content of nondiamond carbon is essentially responsible for the worse transmittance of the deposits obtained in this case, as will be clear later. It is also noted that with increasing methane fraction the diamond peak shifts constantly towards a larger wave number due to the accumulated compressive stress in the deposits, though the continu-

FIG. 3. Bright-field TEM images at (a) the nucleation side and (b) the growth side. In (c) a typical SAED pattern is shown.

FIG. 4. SEM image (3.5×3.5 μm) of a deposit grown for 4 h with 3.0% methane.
ally fining grain size initiates concomitantly a peak shift in the reversed direction, see Table I.

Bright-field TEM images were taken at both the nucleation side and the growth side to investigate the microstructure of the films. The plan-view images in Fig. 3 show a uniform grain-size distribution in a specimen obtained with a methane fraction of 3.0%. At the nucleation side, the fine crystallites in the aggregates have a grain size, taken as the averaged grain dimension along an arbitrary line across the image, less than 30 nm. The crystallites at the growth side have grown larger; the averaged grain size measures circa 65 nm. Figure 3(c) displays a typical SAED pattern that reveals the polycrystalline nature of the deposits. No diffraction due to the nondiamond carbon phases can be identified. All the sharp diffraction rings can be indexed to the diamond structure with a lattice constant $a = 0.367$ nm, which falls within the experimental error for this type of measurement. In comparison to the situation for bulk diamond where generally four reflections are registered, here seven diffraction rings are discernible from the diffraction pattern. The (222) reflection that is absent in bulk diamond emerges due to the large compressive stress in film. The presence of other two weak
Highly transparent nanocrystalline diamond coatings have been prepared on quartz glass substrates using the conventional MW-CVD method. Scratching of the substrate with 0.5 μm diamond powder resulted in a nucleation density over $10^{11}$/cm$^2$. The grain sizes on the growth side in specimens deposited for 4 h under given conditions can be approximately 70 nm.

V. CONCLUSIONS

Optical transmittance of the deposits was measured in two steps in a range between 4000 to 15 000 cm$^{-1}$, as shown in Fig. 6. The discontinuity at 9000 cm$^{-1}$ was caused by replacing the Si detector with a PbSn detector for the large wave-number range. The transmittance oscillates due to the multiple interference of the incident light in film. From the transmittance curve for the specimen deposited with 3.0% methane, a maximum value of 91% was measured at 6740 cm$^{-1}$. The transmittance in the part of visible light (12 600 to 15 000 cm$^{-1}$) averages about 65%. As compiled in Table I, the transmittance can be significantly improved by reducing the surface roughness; however, the smoother specimens obtained with 4.0% methane exhibit nonetheless a poorer transmittance due to the presence of the secondary carbon phases.

The hardness of the deposits was determined from the load versus displacement curve in a complete load/unload cycle. The loading was carefully programmed such that the maximum displacement was regulated at slightly less than one tenth of the film thickness, yet larger than 80 nm. This is critical for obtaining reliable hardness data since both the very shallow indentation and the deep indentation that affects the soft substrate may result in an underestimated hardness value. A typical load/unload curve is displayed in Fig. 7, which was obtained on a sample prepared under conditions referring to Fig. 4. From this curve, a Vicker’s hardness of 71 GPa was calculated. For over 20 samples deposited with a varying methane fraction, the hardness scattered between 61 and 95 GPa, which is definitely larger than the low limit for natural diamond. The diminishing grain size has given rise to an only slightly enlarged hardness; it is the presence of soft secondary phases that partially cancels out the hardness enhancement by finer grains, as specified by the Hall-Petch relation.

FIG. 6. Optical transmittance measured on the specimen referred to Fig. 4. The inset shows a photo of the films on a printed background.

FIG. 7. A typical load vs displacement curve obtained in a complete load/unload cycle.
well controlled below 70 nm. By a methane fraction of 3.0\%, the deposits demonstrated an optimum quality as protective coating for optical components, namely, a surface roughness of 11 nm, averaged transmittance over 65\% in the visible light range and a hardness within 61 and 95 GPa. Further increase in the methane fraction, though it may give rise to finer grains and consequently a smoother surface, may deteriorate the hardness and in particular the transmittance owing to the presence of augmented nondiamond carbon phases. The film quality regarding the application as protective coatings is expected to be significantly improved by growing the film at higher methane fractions, when an effective approach is applied to suppress the formation of the nondiamond phases.

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