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Evolution of surface morphology and optical transmittance of single crystal diamond film by epitaxial growth

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ABSTRACT
The single crystal diamond (SCD) has great potential in the application of optical windows, photoelectric devices, semiconductors and other fields owing to its excellent performance in optics, mechanics, and thermotics. The SCD was homoepitaxially deposited on High Pressure and High Temperature (HPHT) seed substrate through microwave plasma chemical vapor deposition (MPCVD) method using CH$_4$/H$_2$ as the reaction gas. Hydrogen plasma treatment was proposed to pretreat the seed crystal. The top surface of the epitaxial layer of SCD has a creased morphology and no polycrystalline rim growth on the side. The results showed that the transmittance of the epitaxial SCD film was primarily affected by the surface roughness, which was mainly influenced by the growth time. The photoluminescence at 738 nm was attributed to the silicon color center in the grown SCD, suggesting the application in optoelectronic devices.

I. INTRODUCTION

Diamond has many unique properties, including high carrier mobility, high dielectric breakdown threshold and unique chemical inertness, as well as excellent broadband optical transmission performance. Single crystal diamond (SCD) has entered the commercial market as jewelry and has potential applications as optical window and photoelectric material, such as the next generation optical devices including optical window, laser material and monochromator.\cite{1-3}

In 2009, Liang and Meng et al. prepared the SCD of gem-quality using microwave plasma chemical vapor deposition (MPCVD) method. The optical property of the SCD at high growth rate was developed dramatically by low pressure high temperature treatment, and the UV-visible absorption decreased by 2-6 times after the treatment.\cite{4,5} Shreya Nad et al. prepared the SCD with the usage of modified “pocket substrate”, which benefited the growth of thick SCD, and also suppressed the growth of poly-crystalline edges. Compared to the seed crystal, the lateral size of the SCD was expanded by 2.5 times. In addition to the growth of SCD with a large size,\cite{6,7} impurities and defects must also be investigated when SCD is used as power semiconductors, spintronics, sensors and quantum computing devices. In 2018, Sergey A. Malykhin et al. studied the photoluminescent properties of single crystal diamond microneedles and found that silicon-vacancy centers were concentrated at the crystallites apex while nitrogen vacancy centers are distributed over the whole crystallite. N- and Si-vacancy centers are the most attractive for quantum information processing and optical sensing.\cite{8-10}

In the present paper, the SCD was homoepitaxially deposited on a HPHT seed crystal through microwave plasma chemical vapor deposition (MPCVD) method. Since the surface of the seed crystal has grooves owing to cutting process, a pretreatment must be performed. As is well known, the diamond has a high hardness, and the normal pretreatment such as polishing will raise cost. Thus, a simple pretreatment by hydrogen plasma etching was proposed to investigate the surface morphology and defects in SCD after this pretreatment. Also, what factors affect the transmittance of the SCD was studied and the quality control strategies of the epitaxial SCD were explored.
II. EXPERIMENT

All SCD layers were homoepitaxially grown on (100) oriented HPHT seeds (3×3×1 mm³). Firstly, the seed crystal was ultrasonically cleaned in acetone and ethanol successively to get rid of the surface contaminations. Next, the seed crystal was placed in the homemade MPCVD reaction chamber and etched at 1000 °C for 30 min with the hydrogen plasma to eliminate the substrate contamination and the surface damage caused by mechanical processing. After the etching process was finished, the growth procedure of the epitaxial SCD was performed. In the present study, the optimized process parameters were as follows: methane concentration was 6%, growth temperature was 1000 °C, growth pressure was 15 kPa, and growth time was 12 h, 36 h and 84 h, respectively. After the preparation, the SCD sample was boiled in the nitric acid and sulfuric acid mixture, aiming to remove graphite on the SCD surface.

The surface roughness and morphology of the grown substrate was characterized by Atomic force microscope (Brook MultiMode8) with PeakForce Tapping Mode, and images were then collected using Bruker ScanAsyst mode. The Raman and photoluminescence (PL) spectroscopy measurements were performed at room temperatures using a Renishaw InVia Raman microscope operated at 532 nm (Nd:YAG laser) and 40 mW. The transmittance of SCD layers on seeds were measured by Agilent Cary 5000 UV-Vis-NIR. The monochromatic light was generated by the deuterium arc, and the PbS detector was used to collect signals.

III. RESULTS AND DISCUSSION

Fig. 1 shows the AFM images of seed substrate and SCD films grown on single crystal seeds after 12 h, 36 h, and 84 h at 1000 °C, respectively. The measurement area is 50 × 50 μm² (except for seed,

![AFM images of SCD films with different growth times](image-url)

**TABLE I. Roughness of SCD films with different growth times.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ra (nm)</th>
<th>Rq (nm)</th>
<th>Rmax (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seed</td>
<td>3.63</td>
<td>4.56</td>
<td>33.2</td>
</tr>
<tr>
<td>12 h</td>
<td>100</td>
<td>123</td>
<td>643</td>
</tr>
<tr>
<td>36 h</td>
<td>107</td>
<td>133</td>
<td>833</td>
</tr>
<tr>
<td>84 h</td>
<td>420</td>
<td>489</td>
<td>2100</td>
</tr>
</tbody>
</table>

![Raman spectra of SCD films with different growth time](image-url)

![PL spectra of SCD films with growth time for 36 h and 84 h](image-url)
When the growth time increased from 36 h to 84 h, photoluminescence remains visible, confirming that the SCD layer is still of good quality. The first-order diamond Raman increases over time, and the nitrogen related signal from the seed rather than the epitaxial layer. The thickness of the epitaxial layer increases near 1332 cm$^{-1}$, which is mainly due to the seed surface. Therefore, it is believed the peak at 1420 cm$^{-1}$ is mainly due to the seed rather than the epitaxial layer. The thickness of the epitaxial layer increases over time, and the nitrogen related signal from the seed gradually disappears. As the growth time prolongs, the nitrogen-related peak weakens significantly. It appears that the thick epitaxial layers cover the signal from the seed. Hence, the transmittance of SCD film with growth time 36 h is improved by nearly 20% after acid treatment. Fig. 4(b) demonstrates the transmittance of the 36 h and 84 h SCD films after acid treatment. The inset in Fig. 4(b) is an optical image of the SCD-84 h layer where there is no polycrystalline rim growth, and the yellow seed at the bottom can be seen through the epitaxial layer. The transmittance of the 36 h SCD sample is slightly lower than that of the seed by 10% because the diffuse reflection caused by the surface roughness increases after film growing. In addition, the surface roughness of SCD increases continuously when further prolonging the growth time. So the enhanced surface reflection leads to the decrease of 10-20% in transmittance. The transmittance of the SCD-84 h layer reduces by 10% at a longer wavelength and decreases by 20% at a shorter wavelength. It seems that the longer the wavelength, the less the decrease in transmittance.

According to the transmittance theory, the main factors affecting the transmittance of materials are surface roughness, impurities, pores, and interface between phases. There are no pores in the CVD epitaxial film, and there would be no phase interface if the seed is removed. Hence, the transmittance of the CVD epitaxial film is primarily affected by the surface roughness, and then the absorption and scattering caused by impurities. Based on the test results, the impurities in the present study are mainly non-diamond phase and silicon. The non-diamond phase can be removed by post treatment at 612 nm with a side peak at 660 nm increased significantly. The weak peak at 738 nm related to Si appears in the PL spectrum. It accounts for that the Si essentially originates from the quartz windows and previous contamination from Si-containing materials, which would gradually enter into the SCD film in the long deposition process.

IV. CONCLUSIONS
In summary, SCD layer without polycrystalline rim was grown on HPHT seed using the simple hydrogen plasma pretreatment. The creased morphology, derived from the initial morphology of crystal seed surface, is a unique morphology on the surface of the SCD. With the rising of growth time, the number of the zigzag decreases significantly. When the growth time increases, the nitrogen-related peak weakens significantly. It appears that the thick epitaxial layers cover the signal from the seed. Therefore, it is believed the peak at 1420 cm$^{-1}$ is mainly due to the seed rather than the epitaxial layer. The thickness of the epitaxial layer increases over time, and the nitrogen related signal from the seed gradually disappears.
accompanied by the increase of their size. Also, the surface roughness of the SCD samples elevates significantly under the same conditions, which could be regarded as the main cause of the decline of the transmittance that can be improved by post-polishing. In addition, a trace amount of Si was introduced into SCD due to its long growth time and had a little negative effect on its transmittance.

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