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Deposition of CVD diamond onto GaN

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Abstract

A series of experiments have been performed to deposit continuous layers of CVD diamond onto epitaxial GaN films. Such diamond coatings would be useful to enhance the light extraction and heat dissipation in GaN LEDs. A hot filament CVD reactor utilising a CH₄/H₂ gas mixture was used to deposit the diamond. The substrates consisted of an epitaxial layer of GaN grown onto a sapphire base. It was found that at deposition temperatures >600 °C the GaN decomposed, evolving gaseous N₂ which created pinholes in the growing diamond layer or caused it to delaminate. Lowering the substrate temperature below 600 °C resulted in a prohibitively low growth rate and poor quality diamond. Results will also be presented from a further series of experiments performed using N₂ addition to the CH₄/H₂ gas mixture, with the idea that a high background partial pressure of N₂ would slow or prevent the decomposition of GaN.

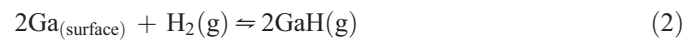
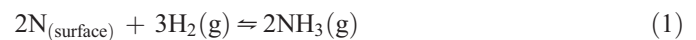
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Keywords: Diamond growth and characterisation; CVD diamond; Hot filament; GaN

1. Introduction

Due to its excellent mechanical and electronic properties, such as high hardness, wide band-gap, chemical inertness and high thermal conductivity, diamond is currently one of the most promising materials for use in electronic and optoelectronic devices. Devices fabricated using chemical vapour deposited (CVD) diamond thin films have been proposed for high-temperature, high-power and high frequency operation. Another promising material is GaN, for use in power FETs, blue lasers and LEDs. Hexagonal GaN (h-GaN) can now be grown as layers onto sapphire substrates, and this offers the possibility of utilising the specific advantages of both diamond and GaN layers in one device. For example, a microcrystalline CVD diamond layer with a surface roughness of the order of 1 μm, deposited onto a GaN surface, would be useful to enhance the light extraction and heat dissipation from the GaN layer, and improve the efficiency of the LED. This is because the roughness of the polycrystalline diamond surface would prevent light from leaking out of the GaN layer and channel it to the ends of the device where it can be extracted.

One of the major issues limiting diamond CVD onto GaN is the lack of high temperature stability of GaN under typical diamond CVD process conditions. Although its normal melting point is around 2500 °C [1], GaN reacts with hydrogen at temperatures around only 800 °C [2], decomposing to volatile products via the following reactions:



Thus, the usual deposition conditions for diamond CVD of a substrate temperature close to 800–900 °C would result in etching of the GaN. Another reaction which can occur is:



although this requires temperatures >800 °C due to the high barrier for the formation of liquid Ga droplets [3]. These three reactions are perhaps one of the reasons why, to date, there have been very few reported attempts in the literature to combine layers of diamond with GaN. Hageman et al. [4] reported that a thick layer of h-GaN had been grown onto a (110) single crystalline diamond substrate using an AlN nucleation layer and a metal-organic chemical vapour deposition (MOCVD) method. But the only reports of attempts to deposit CVD diamond onto GaN are by the group of Oba and

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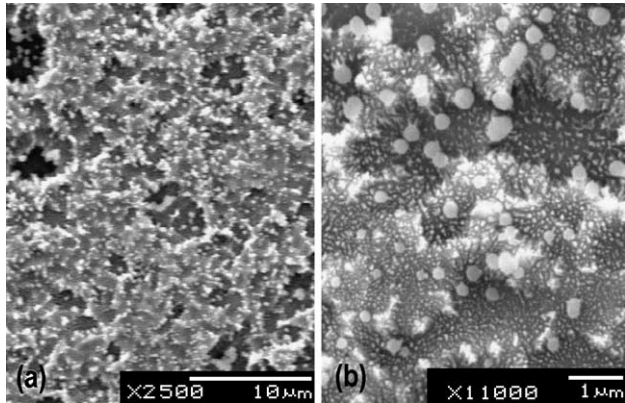


Fig. 1. SEM micrographs after diamond deposition using 1% CH_4/H_2 and a filament distance of 5 mm, at (a) low and (b) higher magnification. The GaN surface is partially decomposed, and individual lumps of resolidified Ga can be seen.

Sugino [5,6], who deposited diamond onto 1- μm -thick (0001)-oriented GaN films on an $\text{AlN}/\text{Al}_2\text{O}_3$ substrate using MW plasma CVD. They reported that to prevent etching of the GaN surface, they needed to carburize and treat the surface using a bias-enhanced nucleation method prior to diamond growth. The growth of oriented, heteroepitaxial isolated diamond crystals on the GaN surface was achieved, but the crystals did not coalesce into a continuous film due to the low nucleation density.

In this paper we report the results of attempts to grow continuous layers of diamond on top of GaN layers using a hot filament CVD technique. We found that there was a competition between the rate of diamond deposition and the rate of GaN decomposition, and this determined whether net deposition or etching occurred. Various experiments were performed in an attempt to limit the GaN decomposition while maintaining an acceptable diamond deposition rate, first by lowering the deposition temperature, and secondly by addition of N_2 to the gas mixture.

2. Experimental

The unintentionally doped GaN epitaxial layer used in this study was grown on 2-in. *c*-face (0001) sapphire substrates using an Aixtron 200HT metal-organic chemical vapour deposition (MOCVD) system. First, a 25-nm-thick GaN nucleation layer was deposited onto the substrate at 500 °C, followed by 2- μm -thick undoped GaN layer. The single crystalline GaN epitaxy layer was (0001)-oriented with average surface roughness of few nm. The FWHM of the (002) reflection rocking curve measured in ω - 2θ geometry was ~ 324 arc-seconds. The defect density, measured by the etch pits density method, was around $5 \times 10^8 \text{ cm}^{-2}$.

Prior to deposition the films were manually abraded with 1–3 μm diamond grit, and then cleaned with propan-2-ol. Diamond deposition occurred in a standard hot filament CVD reactor, using 1% CH_4 in H_2 (total flow 200 sccm) as input gases, maintained at a process pressure of 20 Torr. Later experiments involved additions of a few % N_2 to the gas

mixture. Deposition time was ~ 8 h, with a diamond deposition rate around $0.5 \mu\text{m h}^{-1}$ depending upon the filament temperature and its distance from the substrate. The filament was made from 0.25-mm-diameter Ta wire, coiled into a 3-mm-diameter helix of length 15 mm. The height of the filament was varied between 5 and 15 mm from the substrate surface, and this was used to control the surface temperature. ~ 6.75 A of alternating current was used to raise the temperature of the filament to 2400 °C, as measured by a two-colour optical pyrometer.

Films were analysed by SEM and laser Raman spectroscopy (514 nm excitation). The main diagnostics peaks used for the diamond layer occur at 1332 cm^{-1} corresponding to sp^3 carbon (diamond), and the D and G bands at ~ 1347 and $\sim 1585 \text{ cm}^{-1}$ corresponding to disordered and ordered sp^2 (graphitic) carbon, respectively [7,8]. Crystalline GaN has a strong characteristic peak from the $\text{A}_1(\text{LO})$ phonon at 734 cm^{-1} [9]. Absence of this peak suggests either the overlying diamond layer is too thick to allow the laser beam to penetrate through the substrate to the sample GaN, or that the crystallinity of the GaN has been disrupted, for example by partial decomposition followed by resolidifying into gallium droplets.

3. Results

3.1. 1% CH_4/H_2 with varying filament distance

Using the standard filament distance $d_{\text{fil}}=5$ mm would normally result in growth of good quality diamond at a rate of $\sim 0.5 \mu\text{m h}^{-1}$ on Si substrates. However, for GaN substrates, the decomposition rate of the GaN was so high that the surface

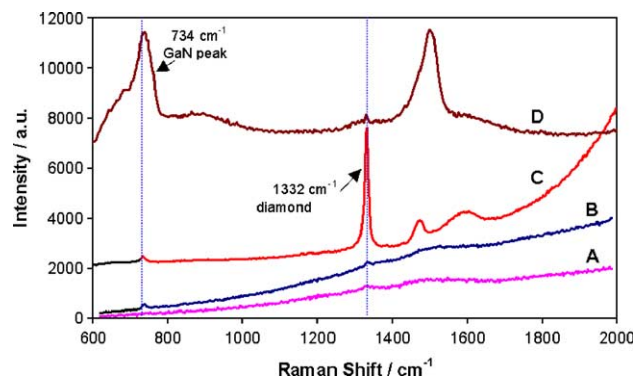


Fig. 2. 514 nm laser Raman spectra from the films shown in Figs. 1, 3–5. Each spectrum has been offset vertically and rescaled for clarity. (A) SEM photos in Fig. 1. Only a small diamond peak is apparent at 1332 cm^{-1} and no GaN peak is seen at $\sim 734 \text{ cm}^{-1}$, suggesting that the crystallinity of the GaN has been destroyed. (B) SEM photos in Fig. 3. This shows a slightly larger 1332 cm^{-1} diamond peak, plus a small 734 cm^{-1} GaN peak, indicating that the GaN surface did not undergo substantial melting or decomposition. (C) SEM photos in Fig. 4. Now we see a strong diamond peak, along with a graphitic G band around 1580 cm^{-1} , indicative of a lower quality of diamond. Also visible is the GaN 734 cm^{-1} peak and its second order peak at $\sim 1470 \text{ cm}^{-1}$. (D) SEM photos in Fig. 5. The 734 cm^{-1} GaN peak is also strong showing that the deposition conditions have not affected the crystallinity of the substrate. The diamond peak is now very weak, and there is a large G band (underneath the second order of the GaN band), showing that the films are now becoming highly graphitic.

153 did not remain stable enough for a diamond film to develop.
 154 Fig. 1 shows the SEM photograph of the etched GaN surface
 155 with isolated lumps of Ga, which have solidified from the
 156 liquid droplets upon cooling. Raman spectroscopy (Fig. 2,
 157 curve A) showed neither a 1332 cm^{-1} peak for diamond nor a
 158 734 cm^{-1} peak for crystalline GaN. This suggests that under
 159 these conditions the rate of GaN decomposition exceeds the
 160 rate of diamond growth.

161 Increasing d_{fil} to 9 mm reduces the surface temperature,
 162 which should lower the GaN decomposition rate. But it will
 163 also affect the concentration of growth species (CH_3 , H atoms,
 164 etc.) close to the surface, which will lower the growth rate. Fig.
 165 3 shows that in this case, we now see net diamond deposition,
 166 but the film is porous and appears to be composed of many
 167 isolated spheres of diamond only loosely joined together. This
 168 may be a result of the products of the GaN decomposition (N_2 ,
 169 NH_3) diffusing from the substrate, through the diamond later,
 170 and etching the grain boundaries of the diamond crystallites,
 171 thus preventing them from fusing together properly. The
 172 Raman spectrum (Fig. 2, curve B) shows a slight increase in
 173 the diamond peak intensity, and a small GaN peak. Thus the
 174 lower temperature conditions deposit diamond at a slower rate,
 175 but there is also less decomposition of the GaN.

176 Further increasing d_{fil} to 13 mm enabled a continuous
 177 coating of diamond to be formed on the substrate. However the
 178 surface of the diamond layer was covered in $\sim 0.2\text{-}\mu\text{m}$ -diameter
 179 holes and pits (see Fig. 4). This is again believed to be due to
 180 etching from the gaseous decomposition products for the
 181 underlying GaN. The Raman spectrum (Fig. 2, curve C) shows
 182 a large diamond peak, and also a GaN peak. This suggests that
 183 for these conditions the rate of diamond deposition slightly
 184 exceeds that of GaN decomposition.

185 Finally, increasing d_{fil} to 15 mm allowed a continuous film
 186 to be deposited with minimal decomposition of the GaN
 187 substrate (Fig. 5). However the diamond deposition rate was
 188 prohibitively low ($<0.1\text{ }\mu\text{m h}^{-1}$) and the film surface showed
 189 cracks and fissures, presumably due to the etching effect of
 190 escaping decomposition gases. The small, broad 1332 cm^{-1}
 191 Raman peak (Fig. 2, curve D) showed that the crystal quality
 192 was poor, while the large GaN peak shows that substrate
 193 decomposition was minimal.

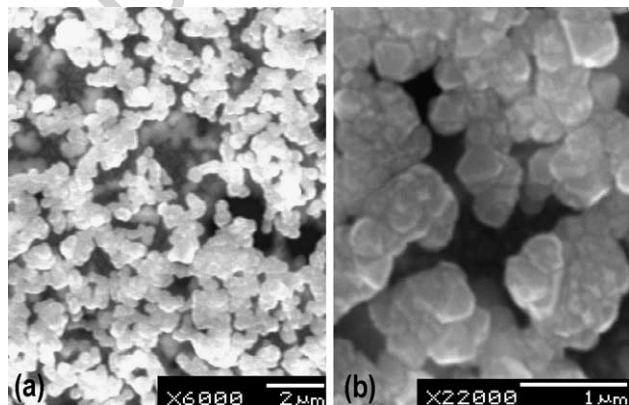


Fig. 3. SEM micrographs after diamond deposition using 1% CH_4/H_2 and a filament distance of 9 mm, at (a) low and (b) higher magnification.

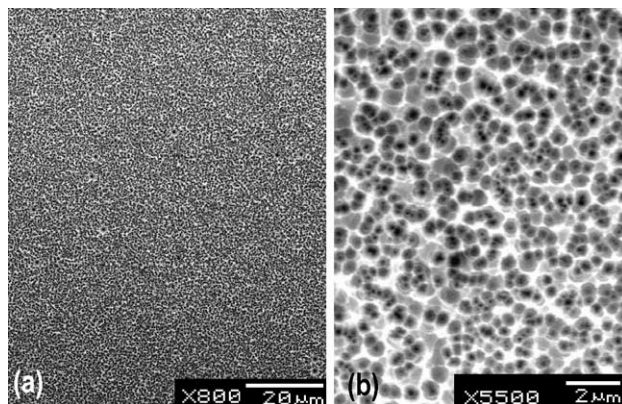


Fig. 4. SEM micrographs after diamond deposition using 1% CH_4/H_2 and a filament distance of 13 mm.

194 Increasing d_{fil} beyond 15 mm did not result in diamond
 195 deposition. Therefore, 12–14 mm was adopted as being the
 196 optimum geometry for further experiments, since this mini-
 197 mised the GaN decomposition rate while still providing an
 198 acceptable growth rate for good quality diamond.

3.2. Higher CH_4 concentrations

199
 200 The next idea was that if the GaN surface could be quickly
 201 covered in a continuous layer of diamond, by using a high
 202 growth rate process, then the surface might be protected from
 203 decomposition for the remainder of the deposition. However, to
 204 achieve a high growth rate at low substrate temperatures, it is
 205 necessary to increase the methane concentration in the gas
 206 mixture, but this substantially reduces the quality of the
 207 deposited diamond. Therefore, the deposition was performed
 208 in two stages. First there was an initial ‘rapid growth’ stage, in
 209 which the methane concentration was raised to 2–4% for 0.5–
 210 3 h. Then the gas mixture was changed back to the standard 1%
 211 CH_4/H_2 growth conditions for the remaining 7 h of growth. A
 212 number of experiments were performed with varying methane
 213 concentrations, times, and filament distances for the initial step.
 214 The results were all broadly similar, with continuous diamond
 215 films being deposited. However, the diamond remained porous

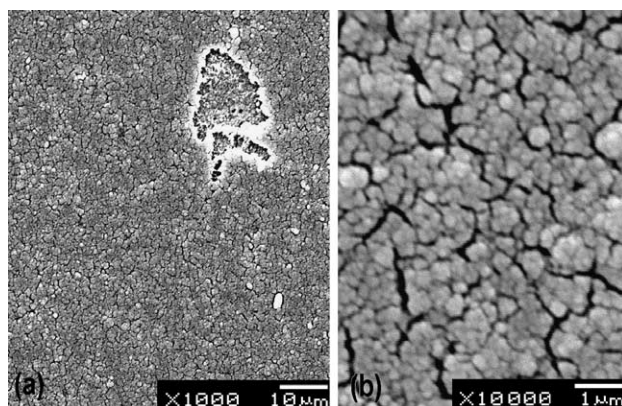


Fig. 5. SEM micrographs after diamond deposition using 1% CH_4/H_2 and a filament distance of 15 mm. The GaN surface is partially melted and becoming amorphous in nature.

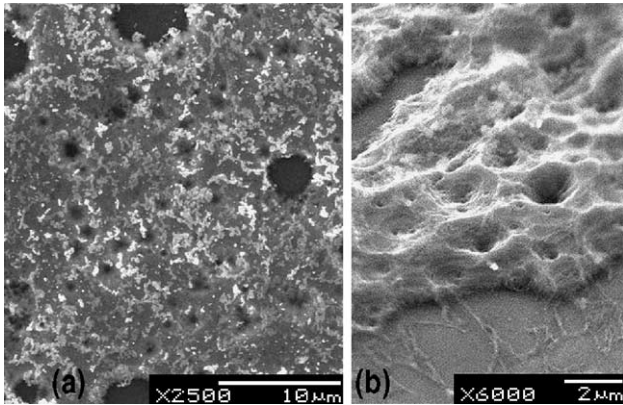


Fig. 6. SEM micrographs after diamond deposition using 3% CH₄/H₂ for 1 h with $d_{\text{fil}}=14$ mm, followed by 1% CH₄/H₂ for 7 h with $d_{\text{fil}}=10$ mm.

and pitted (see Fig. 6), and the 2-stage growth process did not seem to be effective in preventing etching of the GaN. The Raman spectrum (Fig. 7, curve A) showed a strong diamond peak, plus a weak GaN peak. There was also the hint of a peak around 1150 cm⁻¹ which might indicate the presence of nanophase diamond, which is to be expected given the high methane concentration.

3.3. 1% CH₄/H₂ with additional N₂

A possible way to suppress reactions (1) and (3), above, would be to add a few percent of the reaction products (NH₃ and N₂, respectively) to the gas mixture. In theory, this should drive the equilibria toward the left-hand side, reducing the tendency for GaN decomposition. Adding NH₃ to a 1% CH₄/H₂ process would not be beneficial, as previous work [10] has shown that gas phase ammonia reacts with methane to form CN radicals, which then act as a stable sink for C, locking it up and preventing its incorporation into the diamond lattice. However, addition of <3% N₂ to the gas mixture [11] actually increases diamond growth rate without substantial decrease in

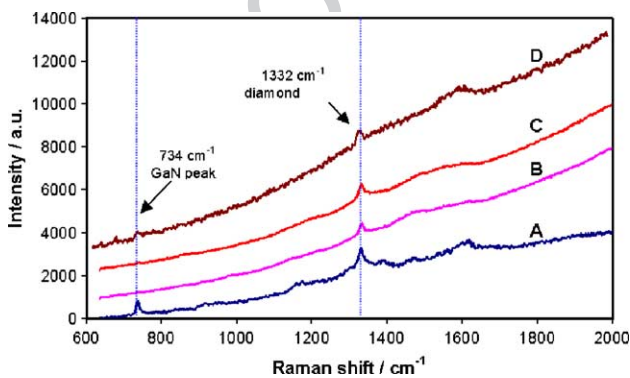


Fig. 7. 514 nm laser Raman spectra from the films shown in the SEM images in Fig. 6, 8–10. Each spectrum has been offset vertically and rescaled for clarity. (A) SEM photos in Fig. 6. There is a reasonably intense diamond peak, along with some D and G bands, as well as a slight band around 1150–1180 cm⁻¹ possibly indicating nanoscale diamond. (B) SEM photos in Fig. 8. The Raman spectrum shows a strong diamond line, however the GaN line at 734 cm⁻¹ is absent. (C) SEM photos in Fig. 9. There is a strong diamond line, but the GaN line is again absent. (D) SEM photos in Fig. 10. The diamond line is now quite weak, while the G band is relatively intense.

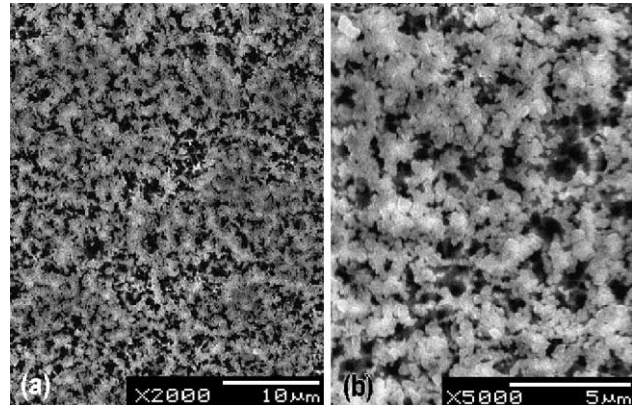


Fig. 8. SEM micrographs after diamond deposition using 1% CH₄/1% N₂/H₂ for 7 h with $d_{\text{fil}}=12$ mm.

film quality. Therefore, the next set of experiments involved addition of 0.5–5% N₂ to the 1% CH₄/H₂ input. For all experiments, a continuous thick layer of good quality (prominent 1332 cm⁻¹ Raman peak) diamond was obtained, although the layers remained very porous with a surface covered in holes and pits. An example is shown in Fig. 8. These porous diamond films exhibited very poor adhesion to the GaN surface, and would often spontaneously flake or delaminate upon removal from the chamber. The Raman spectrum (Fig. 7, curve B) showed a large diamond peak, but no GaN peak. This was possibly because the diamond layer was too thick to allow the substrate to be sampled by the laser.

3.4. 2-Step process

Experiments were attempted which combined the ideas from (b) and (c). A 2-step process was employed in which the initial fast-growth step was used to rapidly produce a continuous layer of (poorer quality) diamond on the GaN surface. This time N₂ was added during this step to help prevent GaN etching. The second stage involved standard growth chemistry, except with added 1% N₂. The results can be seen in Fig. 9. A continuous, but porous 2-μm-thick diamond film was deposited, but adhesion was still poor. Although there were still some holes and fissures present, these comprised only ~5% of the film

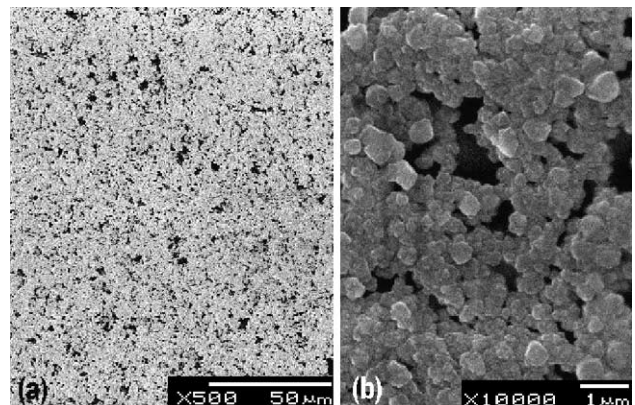


Fig. 9. SEM micrographs after diamond deposition using (a) 3% CH₄/1% N₂/H₂ for 30 min, then (b) 1% CH₄/1% N₂/H₂ for 8 h, with $d_{\text{fil}}=12$ mm.

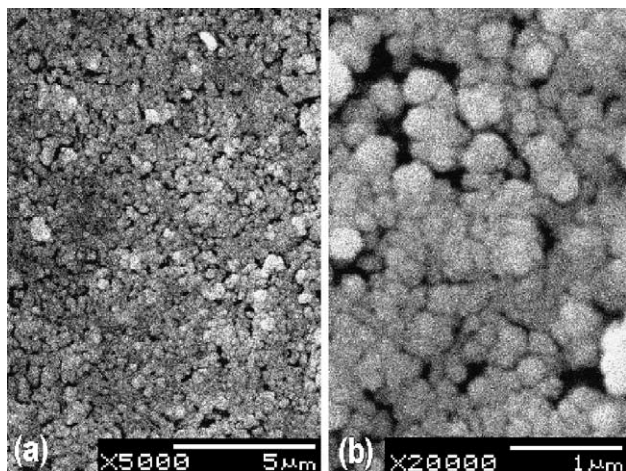


Fig. 10. SEM micrographs after diamond deposition using alternating cycles of (a) 1% CH₄/H₂ for 20 min, then (b) 1% N₂/H₂ for 20 min, for a total of 8 h, with $d_{fil}=12$ mm.

274 surface area. The Raman spectra (Fig. 7, curve C) showed a
275 strong diamond line, but the GaN line is again absent,
276 presumably due to the thickness of the overlying diamond film.

277 3.5. Alternate growth and ‘healing’ steps

278 Further experiments were performed in which the nitrogen
279 and methane flows were alternated periodically throughout the
280 deposition. The duty-cycle between on–off periods was varied,
281 with a typical deposition run consisting of 20 min of 1% CH₄/
282 H₂ followed by 20 min of 2% N₂/H₂, and these 2 steps would
283 be repeated up to 12 times through the 8 h deposition run. The
284 idea was that during the ‘nitrogen-free’ steps, the diamond
285 growth would continue normally, but the GaN substrate would
286 begin to decompose. But during the subsequent ‘methane-free’
287 step the nitrogen would react with the GaN surface and ‘heal’
288 any fissures before they had a chance to grow too large and
289 disrupt the integrity of the surface. The results were promising,
290 in that continuous films were deposited onto the GaN surface
291 with a significant reduction in holes and fissures observed.
292 However, the quality of the diamond was poor, with the
293 crystallites having a ‘cauliflower’ morphology (see Fig. 10).
294 Adherence of these films to the substrate appeared to be better
295 than previous films, but it was still unsatisfactory. The Raman
296 spectrum (Fig. 7, curve D) showed that the diamond line is now
297 quite weak, while the G band is relatively intense. This
298 indicates that the diamond quality has been reduced, although
299 the small intensity of the GaN peak suggests that the film
300 thickness is quite large.

301 4. Conclusions

302 We have demonstrated that it is possible to deposit
303 continuous diamond films onto GaN substrates, using multi-

step processes involving nitrogen addition to inhibit decom- 304
position of the GaN. However, the diamond films are low 305
quality, porous and have poor adherence. Decomposition of the 306
GaN remains a major problem, but our findings suggest a 307
number of avenues for further exploration. Appropriate choice 308
of gas chemistry to lower the deposition temperature substan- 309
tially is one approach. Additions of chlorinated gases to the 1% 310
CH₄/H₂ mixture have been shown to allow lower temperature 311
diamond growth [12,13], however this probably would not be 312
viable in the presence of GaN, which is known to be rapidly 313
etched by Cl₂ [14]. Microwave plasma-activated CO₂/CH₄ gas 314
chemistries have been found to facilitate low temperature 315
diamond growth [15], and ‘ultrananocrystalline’ diamond, 316
using Ar/CH₄/H₂ gas chemistries, can be deposited at 317
temperatures as low as 400 °C [16]. Both of these processes 318
would probably be compatible with GaN substrates, and so 319
would be worthwhile to investigate. An alternative approach 320
would be to protect the GaN surface with a suitable barrier 321
layer, such as Si. 322

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