Characterization of MBE grown diamond structure on Ti/sapphire

M Asghar¹, K Mahmood¹, Noor ul Ain¹, W Stiputra² and R Tsu²
¹Department of Physics, the Islamia University of Bahawalpur, 63100, Pakistan
²Department of Electrical and Computer Engineering, UNC-Charlotte, 28223, USA
E-mail: mhashmi@iub.edu.pk

Abstract. Diamond crystallites were found on titanium/sapphire surface as a result of evaporation of C₆₀ from effusion cell in molecular beam epitaxy (MBE) reactor. Substrate temperature, effusion cell temperature and base pressure of the MBE chamber were set as 1050 °C, 650 °C and 1×10⁻⁹ Torr, respectively. Raman scattering of the as-grown layers revealed the existence of diamond and graphite at 1337 cm⁻¹ and 1592 cm⁻¹, respectively. Moreover, x-ray-diffraction pattern, micrographs exposed from scanning electron microscopy and optical microscopy also confirmed the evidence of MBE diamond crystallites.

1. Introduction
Diamond and diamond like carbon is an active area of research because it has some exceptional properties such as hardness, low coefficient of friction, chemical inertness, wide electrochemical working potential window, good electron emitting characteristics, high transmittance near infrared region and especially the highest resistivity in its pure form [1-4].

Despite of these promising applications, the growth of pure diamond is however very difficult by the frequently used methods like chemical vapor deposition. The reason behind that is the incorporation of hydrogen in diamond films during CVD growth. In fact, hydrogen has been reported to induce detrimental effects on the tribological and optoelectronic properties of diamond [5]. Single solid source molecular beam epitaxy (MBE) has evolved as a best alternate for the conventional growth methodologies for high purity synthesis of diamond. Molecular beam epitaxy is versatile technique due to ultra-high vacuum conditions, highly controlled conditions and low growth temperature. In this perception we used fullerene (C₆₀) as a single source to grow diamond on titanium surface. Raman scattering revealed a well-defined peak of diamond at 1337 cm⁻¹ along with a graphitic line. The apparent shift from the pure diamond line has been discussed with the help of literature.

2. Experimental
MBE chamber (SVT MBE system) with C₆₀ effusion cell was prepared for the growth of hydrogen-free diamond on Ti/ c-plane sapphire Al₂O₃ substrate. The substrate was loaded into the MBE chamber. During the 3 hours growth procedure, the chamber pressure, substrate temperature and C₆₀ cell temperature were set as 1.4×10⁻⁹ Torr, 1050 °C and 650 °C respectively. It is pertinent to mention here that an amorphous layer of C₆₀ was deposited for about half an hour while maintaining the substrate temperature at 400 °C. Characterization of the as-grown film was performed by following equipment: XRD by PANALYTICAL-Philips, SEM/EDAX by JEOL 6430 and Micro Raman.
spectroscopy from HORIBA excited by optical source having wavelength 532.14 nm. All the measurements were carried out at room temperature.

3. Results and Discussion

3.1 SEM/EDAX Measurements
Figure 1 displays the SEM/EDAX images of sample taken at different magnifications. The picture clearly demonstrates the crystallite-growth of diamond. The large scale EDAX measurements of the as-grown layer revealed that the concentration (by at %) of carbon in as-grown film is 95% (c.f. inset). Whereas the interior of the same crystallite at higher magnification revealed a 100% carbon at% as depicted by figure 1b. The same crystallite was further investigated using the Raman microscopy.

![Figure 1](image_url)

**Figure 1.** SEM images of MBE diamond crystallite on titanium surface (background) under different magnifications to witness 100% carbon by at%.

3.2 X-ray diffraction
X-Ray diffraction was performed to confirm the phases of diamond. Figure 2 reveals a typical XRD pattern showing diamond peak P5 at 43.21° which is related to the diamond plane (111) [6, 7], the small intensity reflects the amorphousness of diamond cluster. Other XRD peaks P1-P4 at 20.49°, 37.43°, 39.39° and 41.69° are associated with C$_{60}$, Ti and sapphire, respectively. The most intense signal is from c-plane sapphire indicating the highly oriented and crystalline structure along [0 0 6] plane. Titanium being an orthorhombic system therefore it is hardly observed with the XRD and therefore its small intensity is justified [8]. Ratio of the integrated intensities of diamond peak to carbon peak i.e. $A_{\text{Diamond}}/A_{\text{Carbon}} = \sim 0.5$, indicates that almost half of carbon is available in the chamber has been used for the diamond growth.
Figure 2. X-ray diffraction pattern of as-grown to demonstrate presence of diamond structure on Ti/Al₂O₃ surface.

3.3 Micro-RAMAN mapping
Diamond is a monoatomic system having first order phonon with the symmetry T₂g which is the only Raman active mode. That is why for more than two decades Raman spectroscopy is used for the detection of synthetic and natural diamond in the carbonaceous materials [9].

Micro Raman spectrum of the typical diamond crystallite is shown in figure 3 exposed on the portion of the film optically displayed in the inset. In the figure, we can see two Raman lines at 1337 cm⁻¹ and 1592 cm⁻¹ respectively. With the information from the literature, we assign 1337 cm⁻¹ to diamond and 1592 cm⁻¹ line to graphite [10]. A higher frequency shift of the diamond line i.e. from 1332.5 cm⁻¹ (theoretical) to 1337 cm⁻¹, is attributed to the compressive stress between the diamond and substrate [11, 12]. Similarly the apparent broadening of the diamond peak is related with the presence of defects sites in the crystal, to be discussed later. We understand stress-induced frequency shift is due to film-substrate mismatch of lattice constant and thermal expansion coefficient [13]. Quantitatively, the stress-induced frequency shift was calculated by following formula:

\[ V_s - V_r = \sigma \alpha \]  

where \( V_s \) is the measured frequency of Raman line i.e. 1337 cm⁻¹; \( V_r \) is the position of stress-free Raman line i.e. 1332.5 cm⁻¹; \( \alpha \) is the stress present in the film and \( \sigma \) is the coefficient of stress induced frequency shift. The reported value of \( \alpha \) is 2.88 ±0.17 cm⁻¹/GPa [14]. By incorporating all values in the above equation, the diamond crystal is found to be under a compressive stress of ~1.5-1.7 GPa which is consistent with the reported data [12].
Figure 3. Raman spectroscopy data (Investigated portion is shown in the inset) recorded with argon ion 514.5 nm laser line.

The broadening of Raman peak is also utilized to get information about the crystal quality and stress present in the sample. Generally the sources of Raman line broadenings are crystal disorder and/or crystal size. Since the lifetime of the phonon in the crystal is shortened by scatter at the defect site and hence results in the broadening of the FWHM of the Raman. The observed FWHM of Raman line is 169 cm\(^{-1}\), indicating that the phonon lifetime is very short (50 µSec). Therefore, the broadening of Raman line in diamond (ours) is justified.

|                             |               |
|-----------------------------|---------------|
| Diamond peak                | 1337 cm\(^{-1}\)|
| Graphite G peak             | 1592 cm\(^{-1}\)|
| FWHM of Diamond peak       | 169 cm\(^{-1}\)|
| FWHM of Graphite G peak     | 78.94 cm\(^{-1}\)|

\[
\frac{I_{\text{Diamond}}}{I_{\text{Graphite}}} = 0.9071
\]

\[
Purity \text{ Index (PI)} = \frac{I_{\text{Diamond}}}{I_{\text{Diamond}} + \frac{I_{\text{Carbon}}}{50}} = 0.656688
\]

\[
\text{Figure of Merit (FOM)} = \frac{I_{\text{Diamond}}}{I_{\text{Diamond}} + I_{\text{Carbon}}} \times 100 = 48.8858 \%
\]
Moreover Raman parameters were used to find the quality and purity of the grown crystallites. Using Sails ET. al. [15] method, we calculated the figure of merit (FOM) and quality factor for MBE diamond. Similarly, purity index (PI) was worked out with the help of formula found in Braga et.al and Guo and Chen papers [16, 17]. As-calculated parameters for as-grown diamond crystallite are listed in Table 1.

4. Conclusion
In summery we have successfully grown diamond on titanium/sapphire by Molecular Beam Epitaxy (MBE) using C\textsubscript{60} as a single solid source. Different diagnostic techniques were employed to verify that the grown film was diamond. Micro Raman spectrum of a carbon rich region of the as-grown layers revealed the existence of diamond and graphite at 1337 cm\textsuperscript{-1} and 1592 cm\textsuperscript{-1}, respectively on Ti/Al\textsubscript{2}O\textsubscript{3}. The possible reason of the higher-frequency shift of Raman line with respect to the theoretical one (1332.5 cm\textsuperscript{-1}) was compressive stress: ~1.7-1.5 GPa on the diamond crystallites induced by lattice mismatch and/or thermal expansion coefficient of the hetero-substrate. Micrographs exposed from scanning electron microscopy demonstrated well defined crystallites of diamond. The composition of the SEM image was ~ 100% carbon (EDAX data).

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