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Abstract. Results of stress analysis of macroscopic growth defects (hillocks) on the surface of homoepitaxial diamond films produced by microwave plasma assisted CVD are presented. Local stress was evaluated by analyzing the position and splitting of the 1332 cm⁻¹ diamond Raman peak to build 2D stress maps for pyramidal hillocks and hillocks with a flat top.

1. Introduction

Due to its unique characteristics, homoepitaxial single crystal (SC) diamond produced by microwave plasma-assisted chemical vapor deposition (MPCVD) is considered a potential material for advanced applications such as radiation-hard detectors [1], Raman lasers [2,3], power electronic devices [4], and quantum technologies [5]. In particular, diamond electronic devices possess a high breakdown characteristic and a high carrier mobility, and can operate at high temperatures and in a harsh environment. One of the factors affecting the diamond component performance is the presence of crystal defects. Due to the formation of growth defects on the surface and in the bulk, the deposited homoepitaxial CVD diamond films rarely have a smooth and perfect morphology. Such defective surfaces are detrimental for engineering applications, because they induce surface roughness and stress, and facilitate incorporation of impurities, crystalline imperfections, and non-diamond phases, which limit the use of the epitaxial diamond layers not only in electronics [6], but also in nanophotonics and quantum optics.

Growth hillocks and unepitaxial crystallites are often observed on homoepitaxial CVD diamond films. The reason for the formation of unepitaxial crystals is the instability of the deposition process [7]. There is no correlation between the location of crystals on the growth surface of the diamond film (DF) and the imperfections on the substrate [7-8], which is typically a synthetic HPHT (grown at high pressure and high temperature) SC diamond. As for the hillocks, there is a very obvious correlation with the defects of the substrate [7]. The hillock formation is believed to be caused by stacking faults or dislocations that nucleate at the interface between the surface and the epitaxial layer from lattice defects or propagate from the substrate into the CVD layer [7]. The hillocks could be responsible for the dielectric breakdown effect and current leakage in diamond-based electronic devices, which are the main limitations for their development and improvement of device properties [9]. The features of the formation mechanism and stress state of the growth defects in CVD homoepitaxial films are still debatable. Some authors believe that the mechanism of defect growth is related to the dislocation exits to the DF surface [8]. Others [10] state that hillocks originate in the places where etching pits form during the preparation of the HPHT substrate, which in turn are formed at the points where the dislocations (dislocation bundles) exit to the surface of the HPHT substrate.
There are several techniques available to examine the strain fields around dislocations in diamond. The express method for stress analysis is the birefringence technique [11-13], although it is not quantitative. For measurements of the birefringence, it is necessary to separate the diamond film from the HPHT substrate, and the resulting picture gives information from the entire film thickness. Although the fine birefringence image structure of dislocation has been reported with the stress-strain calculation [11], it is difficult to determine the type of dislocation by using only one birefringence image because optical inhomogeneities in the film produce signals which overlap the birefringence image. In [12], birefringence patterns from single dislocations were investigated, but it was not possible to achieve complete agreement between the experiment and the model calculations. The reason for this was found in [14], where it was shown that the dislocation beam propagates from the substrate to the surface of the film not vertically, but in a zigzag manner due to the instability of the deposition conditions. A strong correlation between the change in the direction of dislocation propagation and the varying stress state was found in [15] using X-ray diffraction and transmission electron microscopy for (111) oriented diamond epitaxial layers. The formation of anisotropic stress, which correlates with the anisotropy of the dislocation slope, was confirmed by transmission microscopy in plan-view and two perpendicular cross sections.

In the present work, information on the presence of stresses in the vicinity of two types of hillocks on the surface of homoepitaxial diamond films is determined from the position and splitting of the diamond Raman peak. The point-by-point mapping of the Raman spectra using confocal spectroscopy allows non-destructive studies of structural features on the surface and in the bulk of diamond [16-17], making it possible to assess the strain patterns across the hillocks.

2. Samples and experimental

The epitaxial diamond film was synthesized in a hydrogen/methane gas mixture on an SC diamond substrate using an ARDIS-100 microwave plasma CVD system (2.45 GHz, 5 kW) [17] with the following parameters: pressure of 130 Torr, substrate temperature ~ 1000 °C, microwave power of 2.3 kW, and total gas flow rate of 500 sccm (H₂:450/CH₄:50). For the growth time of 6 h, the resulting epilayer thickness was 210 μm. The purity of source gases was 99.99999% for H₂ and 99.9995% for CH₄. Before the diamond deposition, the substrate was pretreated in H₂/O₂ microwave plasma (70 Torr, 2300 W, 2 h) to etch away surface defects such as dislocations and those caused by polishing [19-20]. The substrate temperature was determined by a two-color IR pyrometer (Micron Instruments, model M770) looking at the edge of the sample via a side quartz viewport of the CVD chamber (with a diameter of the thermal emission probed area of ≈2 mm).

A JSM7001F (JEOL) scanning electron microscope (SEM) was used to examine the film surface morphology. The Raman and PL spectra excited at a 473 nm wavelength were measured at room temperature with a LabRam HR800 (Horiba Jobin-Yvon) spectrometer in a confocal configuration with a spectral resolution of 0.5 cm⁻¹ and a spatial resolution of ~1 μm. The spatial mapping of the PL and Raman spectra over the hillock surface area was performed by placing the sample on a motorized table (Märzhäuser Wetzlar) with a positioning accuracy of about 0.5 μm.

3. Results and discussion

Growth defects such as hillocks, the local elevations of a few tens of micrometers above a macroscopically flat surface, often appear on the surface of epitaxial CVD diamond [7, 9, 21, 22]. The hillocks can be classified into three types: pyramidal hillocks, hillocks with a flat top, and unepitaxial crystals [7]. The pyramidal hillocks consist of four triangle-shaped sidewalls. The hillocks with a flat top display a top flat (001) face and four sidewalls. Unepitaxial crystals exhibit a random shape and appear not to have an epitaxial relation to the substrate crystal [7].

3.1. Raman mapping of a pyramidal hillock

Figure 1(a) shows the SEM image of a pyramidal hillock with a base of approximately square shape ≈ 70×60 μm² with sides parallel to the ⟨011⟩ and ⟨0T1⟩ directions in shown in figure 1(a). The
formation of hillocks on {100} face proceeds in step-growth mode and can be accompanied with the appearance of polycrystalline inclusions on the top [23]. The growth steps on the hillock’s sidewalls are shaped like an unwinding spiral [21-22]. It is a common shape of the upper part of the hillocks, because they are formed due to preferential spiral growth at the site of screw dislocation in seed substrate, which are invariably present [7, 22]. The SEM images at higher magnifications (figures 1(b,c)) show that the facets of the pyramid reveal numerous square growth pits of about 250 – 300 nm in size due to preferentially etching of dislocations by the plasma during the growth [24]. Such pits are typically observed when using high-power conditions [8], because the dissociated dislocation core and its intrinsic stacking-fault ribbon contain weaker C–C bonds.

Figure 1. (a-c) SEM images of a pyramidal hillock. (a) Low-magnification panoramic view. The white square indicates the area mapped with Raman spectra; (b) Higher magnification of the hillock’s tip; (c) Pyramidal pits on the facets of the hillock. (d) The stress map at the top of the hillock in an area of 40×40 μm². The stress values are calculated from the diamond peak position in the Raman spectra measured with a 0.5 μm step. Two regions with compressive and tensile stress co-exist within a top central 20×20 μm² area. Dashed white lines designate the edges of the hillock.

Figure 1(d) displays the stress map taken for a selected area (shown by the white quadrant) of the pyramidal hillock presented in figure 1(a). Information on the internal stresses generated in the near-surface diamond layer has been derived from the Raman spectroscopy analysis of the triply
degenerated first-order diamond Raman line. For the surface outside of the hillock, the diamond Raman peak position was close to 1332.5 cm\(^{-1}\), corresponding to unstressed material, and the peak half-width (FWHM) was rather narrow, \(\Delta \nu \approx 4\) cm\(^{-1}\). The diamond Raman peak measured at the top of the hillock is asymmetrically broadened with FWHM increasing up to 7 cm\(^{-1}\) at the center of the hillock. Such a behavior of the Raman spectra is due to the presence of anisotropic internal stresses, extended defects or point defects near the center of the hillock, where dislocation bundles form [7, 22]. It is known [25] that, depending on the stress configurations, the diamond Raman peak can be shifted relative to the unstressed diamond phonon frequency \(\nu_0 = 1332.5\) cm\(^{-1}\) and split into two or three components. To calculate the stress \(\sigma\), we used the relationship [26]:
\[
\sigma = 470 \times \sum \frac{I_n (\nu_n - \nu_0)}{\sum I_n \nu_n} \text{MPa},
\]
where \(I_n\) and \(\nu_n\) are the intensities and positions of the components.

Two regions with stress as high as 1 GPa with dimensions of about 8 × 8 \(\mu\)m\(^2\) each can be observed on the stress map around the top of the hillock (figure 1(d)). These regions are located on the opposite inclined triangle facets of the hillock pyramid. One of them exhibits compressive stress, while the second region has tensile stress, while two other facets show no significant stress.

3.2. Hillocks with a flat surface

An example of a hillock with a flat (100) oriented surface is shown in figure 2(a). The edges of the top face of the quadrant (they go along the sides of the white quadrant selected for Raman mapping as depicted in figure 2(a)) are directed in <110> crystallographic axis, while the diagonals of the quadrant are <100> directions. The stress map of the top surface, obtained by Raman mapping over an area of 500×500 \(\mu\)m\(^2\), reveals the presence of elongated narrow regions with compressive stress (figure 2(b)). Those linear stressed domains with a length up to 200 \(\mu\)m are directed at a 45° angle to the top facet edges. They indicate the locations of accumulation of structural defects, which, upon further growth, may concentrate on the tip of the pyramidal hillock, as demonstrated in figure 1. The stress amplitude within the hillock (figure 2(b)) is relatively low, less than 400 MPa, which indicates the high quality of the film. In contrast, the regions with tensile stress, which is up to 300 MPa, are small (several tens of micrometers), and located more or less randomly across the studied area.

![Figure 2](https://example.com/figure2.jpg)

**Figure 2.** (a) SEM image of a flat hillock and (b) stress map around the top region. (a) Low-magnification panoramic view. The white square indicates the area mapped with Raman spectra; (b) The stress map at the flat part of the hillock in an area of 500×500 \(\mu\)m\(^2\). The stress values are calculated from the diamond peak position in Raman spectra measured with 10 \(\mu\)m steps.
4. Conclusion
The confocal Raman spectroscopy mapping of epitaxial diamond films has shown that the stress distributions over the two types of growth hillocks, in the form of a pyramid and a truncated pyramid, turned out to be quite different in shape, dimensions and stress magnitude. This reflects the difference in accumulation of defects, presumably dislocation bundles, in the hillocks. The stress of up to 1 GPa was detected on the surface in the regions with a typical size of a few tens to several hundred micrometers. We note that an enhanced concentration of impurities, like nitrogen [28], results in diamond Raman peak broadening, therefore the Raman mapping could be used to study spatial inhomogeneities of the impurity distributions. It was also reported [23] that the Si impurity atoms can form enhanced concentration of color centers silicon-vacancy (SiV) within hillocks, so the mapping of photoluminescence of the color centers such as SiV or N-V [16], could be a useful tool to study stress and impurity-related defects within the hillocks, and may shed light to the hillocks origin.

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