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Investigation of residual stress in structured diamond films grown on silicon

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ABSTRACT

Thin diamond strips on Si with the thickness of approx. 0.5 and 1 μm and two different widths (100 and 200 μm) were fabricated in two different ways: i) selective ion etching of the continuous diamond films and ii) selective area diamond growth. The stress induced in the films was measured by Raman spectroscopy. The measured values were in the range from −0.7 to −0.1 GPa. It was found that the stress was compressive and independent of the film thickness. In the films deposited at 950 K, more compressive stress than at 1100 K was measured. The thermal part of the stress as a consequence of heterostructure cooling from high deposition temperature down to room temperature was calculated by Finite Element Method (FEM) simulations and compared with the measurement. It was found that the calculated thermal stress of the continuous film was rather close to the stress values measured for the etched films. The qualitative distribution of the stress measured from the diamond strip center to its edge coincided very well with the FEM simulations. It was shown that relevant stress studies can be made with a relatively low spatial resolution of the Raman measurement in combination with qualitative results of FEM simulations.

1. Introduction

Diamond is considered a highly attractive material for many applications. Its extreme hardness, high thermal conductivity, high electrical resistivity and low friction coefficient in combination with its chemical inertness, high optical transparency, radiation hardness, makes this material superior to traditional semiconductor materials. Moreover, the diamond surface can be relatively easily covered by different kinds of functional groups and thus be made capable for various chemical interactions. This surface functionalization also significantly alters the surface electrical conductivity, electron affinity, and wettability. Thus, devices, like gas sensors [1,2], biosensors [3,4] or selective electrodes [5] may be tuned for desired applications. The chemical vapor deposition (CVD) of thin diamond films enabled expensive bulk diamond crystals to be replaced and easy combining of diamond with other materials. The advanced methods of nucleation, above all the ultrasonic seeding, are significant for the covering of low-adhesion materials and preparation of structured (discontinuous) films [6]. The structured films are required for applications like protective layers on transistors [7] or advanced hybrid MEMS devices [8]. The micro-structured diamond films are also used for tissue engineering [9–11].

When any material covered by the diamond film is exposed to temperature variations, stress is induced due to different thermal expansions and elasticities of diamond and the substrate material. Such temperature changes occur when the diamond-covered component works under a high thermal load, like in an aircraft engine, space vehicle, or when the component itself produces large heat (HEMT transistors) [7]. The CVD itself is this kind of situation, since the produced structure is finally cooled down from the deposition temperature (700–900 °C) to room temperature. In the fabrication process, not only thermal, but also the intrinsic growth stress contributes to the mechanical behavior of the diamond-covered component, depending on the deposition process conditions. The character of the nucleation process and the substrate properties then govern if the component becomes bent (the stress is relaxed to the shape change) or even damaged (cracking and delamination of the diamond film).

Simulations of the mechanical behavior of solid materials often accompany experimental studies. The Finite Element Method (FEM) simulations of thermal stress in diamond films have been presented by several authors [12–15]. Edwards et al. [12] calculated a bow of circular silicon wafer covered by diamond film varying the ratio of diamond to Si thickness. Michler et al. [13] simulated the stress distribution in isolated diamond islands of different aspect ratios (island width to height) on Si. They found that for a smooth film, the stress gets close to the theoretical value of the infinitely-thin film, if the aspect ratio of the island is higher than 100. They also found that a higher surface roughness relaxes to some extent the thermal stress. When the measured and calculated stresses are compared, large discrepancies may be found which are usually explained by the intrinsic stress component in a real sample which is not modeled [16]. However, the calculations are also very sensitive to the used values of thermal expansion coefficient (TEC) of the substrate

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and diamond, including their temperature dependence. For example, a large difference between the experimental stress and values calculated from the analytic expressions by Fan et al. [16] may be caused not only by the intrinsic stress component missing in the calculation, but also by using too small a value of average TEC for diamond. Some important aspects of the stress simulations are briefly summarized in Section 3 of this paper.

In our previous work [17], we simulated a post-deposition thermal stress in the circular GaN HEMT structure covered by the diamond film. The dependence of the thermal stress and/or the structure bending on the substrate properties was studied. The influence of the diamond and GaN film thickness on the thermal stress was studied as well. In the present work, we conducted a more basic study of the stress in thin diamond films on silicon. We combined the simulations of thermal stress with the evaluation of the total stress by means of Raman spectroscopy. Moreover, we compare and discuss in detail the measured and the simulated stress induced in discontinuous diamond-on-silicon structures (diamond strips) prepared by two different techniques.

2. Experimental details

2.1. Fabrication of diamond strips

Sets of diamond strips of 100 and 200 μm in width with gaps of the same width were fabricated on one-side polished Si (100) substrates of the area 10 × 10 mm^2 by two different methods.

The top-down (TD) approach (Fig. 1a) is based on the after-growth etching of continuous diamond film [18]. In this approach, clean Si substrates were treated by applying ultrasonic agitation in a water-based diamond powder suspension (4–5 nm particles) for 40 min followed by the diamond growth using focused microwave plasma [19]. Next, by using a photolithography the Ni metallic mask was deposited onto diamond films. Afterwards, the diamond structures were realized by reactive ion etching in oxygen with 4% of CF_4. The etching was performed at the pressure of 20 Pa and the power of 100 W for 20–40 min till the diamond layer was etched up to the substrate. Finally, the metallic mask was removed by wet chemical etching in HNO_3 acid solution and the samples were washed in deionized water and dried by nitrogen gun.

The bottom-up (BU) approach (Fig. 1b) involves the before-growth modification of the seeding layer, i.e. the selective area nucleation/deposition. This approach included a fabrication of UV-sensitive-polymer/seeding-layer/UV-sensitive-polymer sandwich-like structure. Then, the isolated areas of diamond seeds were made by the photolithography process [6]. The subsequent short (150 s) reactive ion etching removed residual diamond seeds. Finally, the diamond strips were grown on remaining seeded areas by employing the same plasma CVD process as in the TD case.

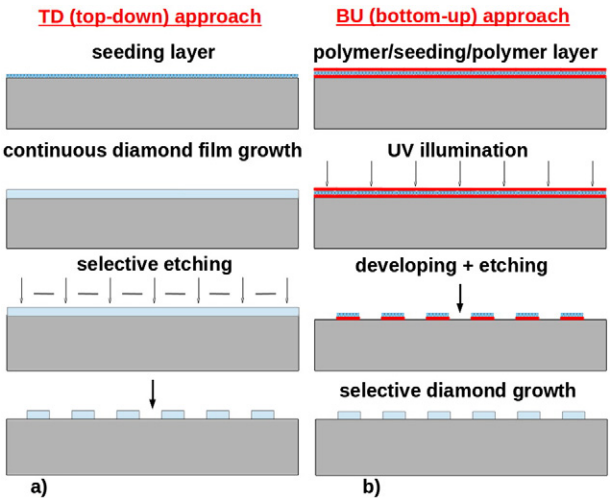

Fig. 1. Schematic description of the (a) top-down and (b) bottom-up approaches.

Three sets of TD and BU samples were grown at the parameters summarized in Table 1. The first two sets of samples of each approach (i.e. BU1, BU2 and TD1, TD2) were deposited at 1100 K. They differed in the deposition time (1 and 2 h) which resulted in different diamond film thicknesses (i.e. approx. 0.45 μm and 1 μm for samples 1 and 2, respectively). The third set of samples (BU3 and TD3) was grown at a lower temperature (950 K), but for a longer time (6 h) to achieve a similar thickness to BU1 and TD1. The lowering of temperature was controlled/achieved by lowering the microwave power.

After the deposition, the surface morphology of the fabricated diamond structures/strips was characterized by Scanning Electron Microscopy (SEM) using the MAIA 3 FESEM microscope (Tescan, Ltd.).

2.2. Stress measurement

The Raman spectra of the grown structures were measured by the Renishaw inVia Reflex Raman microscope using the excitation wavelength of 442 nm (He–Cd laser, output power 80 mW) with grating of 2400 lines/mm and corresponding spectral resolution of 1.5 cm^{-1}. All spectra were measured in back scattering setup with 50× objective in confocal mode. For Raman mapping, computer controlled motorized sample stage with step size of 0.1 μm was used. The Raman map was performed on a 14 × 60 μm^2 area (including the edge of the diamond film strip) by the step of 200 nm. Moreover, the single Raman spectra were measured on the central strip of each sample at two points: lateral center and 10 μm from the strip edge. In every point the Raman spectrum was collected by silicon CCD detector for 10 s. The laser spot size was approx. 5 μm in diameter. However, the Raman mapping near the strip edge showed that the spectra were collected from a somewhat larger area. Accordingly, the spot size for evaluating (averaging) the simulation results was set to 8 μm. For each measured sample, a new wavenumber calibration was made using a single crystal diamond reference sample with the Raman shift of 1332.0 cm^{-1}.

The diamond peak of the collected spectrum was fitted by the Voigt function and the error of evaluating the centerline frequency was estimated to be ±0.1 cm^{-1}. Since the error of wavenumber calibration is ±0.25 cm^{-1}, we estimated the total error in the centerline wavenumber evaluation to ±0.35 cm^{-1} (sum of the fitting and the wavenumber calibration errors), which corresponds to ±0.2 GPa in stress, according to Eq. (1) (see below).

The evaluation of the stress by Raman spectroscopy is based on the fact that the optical phonons of diamond crystals change their frequency in dependence on the applied strain [20,21]. From the dynamic equations [21], the relationships between the applied uni- or biaxial stress and the shift of the appropriate Raman phonon mode frequency can be derived. An averaging over the 4 most common diamond crystal orientations and assuming one common spectral band for both singlet and

Table 1
Diamond growth conditions and diamond film properties. The gas composition was constant for all depositions: 5% CH_4 and 1.5% CO_2 in H_2. The temperature was measured by IR pyrometer.

Sample[a]	MW power [kW]	Pressure [Pa]	Temperature [K]	Duration [h]	Thickness [μm]	Grain size [μm]
BU1	3	7×10^3	1100	1	0.47	0.35 ± 0.1
BU2	3	7×10^3	1100	2	1.04	0.50 ± 0.1
BU3	2.5	5×10^3	950	6	0.47	0.35 ± 0.1
TD1	3	7×10^3	1100	1	0.44	0.28 ± 0.1
TD2	3	7×10^3	1100	2	0.98	0.40 ± 0.1
TD3	2.5	5×10^3	950	6	0.44	0.30 ± 0.1

[a] BU and TD means samples prepared by "bottom-up" or "top-down" approach, respectively. The samples are further in the text distinguished by the strip width, e.g. BU1-100 for 100 μm width, etc.