Patterning of diamond with 10nm resolution by electron-beam-induced etching

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Received 22 March 2019, revised 7 May 2019
Accepted for publication 31 May 2019
Published 18 June 2019

Abstract
We report on mask-less, high resolution etching of diamond surfaces, featuring sizes down to 10 nm. We use a scanning electron microscope (SEM) together with water vapor, which was injected by a needle directly onto the sample surface. Using this versatile and low-damage technique, trenches with different depths were etched. Cross sections of each trench were obtained by focused ion beam milling and used to calculate the achieved aspect ratios. The developed technique opens up the possibility of mask- and resist-less patterning of diamond for nano-optical and electronic applications.

Keywords: diamond, gas-assisted etching, patterning, nano-structuring

(Some figures may appear in colour only in the online journal)

1. Introduction

Diamond is a material that possesses unique and attractive properties including ultrahigh hardness, chemical stability and mechanical strength, while it is highly transparent and an exceptional thermal conductor [1]. Furthermore, diamond is a wide-bandgap semiconductor with working temperatures up to 500 °C. It has a bandgap of 5.47 eV at room temperature and its surface can be functionalized to exhibit negative electron affinity. Due to these physical properties in combination with the capability of hosting nitrogen vacancy luminescence centers (NV), diamond is one of the most promising candidates as a platform for next generation sensing, nano-photonic and quantum information devices [1, 2].

The processing of diamond for its implementation in functional devices is, however, extremely challenging due to the very same physical properties that render it an excellent candidate for these applications. Currently, high resolution diamond structuring requires arduous masking techniques and ion bombardment [3, 4] or high power laser ablation [5], which often cause damage and material re-deposition artifacts [6, 7]. One of the most commonly used methods is reactive ion etching (RIE), which is compatible with lithographic techniques and gives the opportunity of selecting from a wide range of reactants. RIE provides increased etching rate, thus enabling the patterning of large areas of diamond for the fabrication of MEMS devices [8]. However, it requires the development of hard masks and it is a technique mostly implemented for micro-device fabrication [9]. Nevertheless, according to recent reports, by using a careful selection of etchant gases and their ratio [10] and in combination with hard masks [11], RIE can be utilized to etch diamond on the sub-micron level. At present, the prevailing method for the mask-less patterning of diamond is focused ion beam (FIB) milling. This method offers direct, mask-less, and precise patterning featuring sizes down to 15–20 nm [12]. However, the FIB limits the fabrication process due to extended surface damage that leads to graphitization, re-deposition of carbon and ion implantation [3, 13].

As a less-destructive patterning technique of diamond layers, gas-assisted electron-beam induced etching (EBIE) [14, 15] was proposed, which is a well-known technique being used for high resolution patterning of semiconductors such as GaAs [16] and Ge [17] as well as graphene [18]. Gas-assisted EBIE to pattern diamond was first proposed by Taniguchi et al [19] and we show here that is an alternative, low-damage method that opens the way for mask-less...
The best resolution reported so far on single crystalline diamond was ~100 nm [6]. In this work, we report the mask-less and high resolution patterning of hydrogen-terminated single crystalline diamond samples using water vapor assisted EBIE featuring sizes down to 10 nm.

2. Sample synthesis and experimental setup

2.1. Sample synthesis

The samples were grown in a microwave plasma-assisted CVD reactor based on a 2.45 GHz IPLAS CYRANNUS I-6 plasma source [27]. The single-crystal, (100)-oriented diamond samples were placed on the substrate holder and the chamber was pumped down to <10⁻⁷ mbar. Then a hydrogen plasma at 200 mbar, with a microwave power of 2.6 kW and a gas flow of 400 sccm for 45 min was used to clean the sample and sample holder prior to deposition. The deposition started at 120 mbar chamber pressure, with 1.26 kW microwave power. The H₂ flow was at 500 sccm with a purity of 7.0, while for methane CH₄ was 57 sccm with a purity of 9.0 and a substrate temperature of 810 °C. Deposition took 6 hours, resulting in an approximately 17 μm thin film with [100] orientation. These surfaces were used for the etching experiments as grown.

2.2. Experimental setup

For the EBIE, a FEI Helios 600 NanoLab DualBeam setup was used, which integrates an electron and an ion beam. This system implements a gas-injection system (GIS) for enhanced etching and material removal, as well as metal and insulator deposition. For the purpose of our study, only the electron-beam was utilized in combination with simultaneous injection of water vapor using a GIS needle in an ultrahigh vacuum (UHV) environment of 10⁻⁶ mbar. Low-pressure H₂O vapor is supplied by gently heating (29 °C) Magnesium Sulfate Heptahydrate (MgSO₄ · 7H₂O), and guiding it through a capillary into the microscopy chamber, where it is released a few μm above the sample surface. The working principle that governs the gas-assisted EBIE method, as presented in figure 1, is based on the dissociation of water vapor molecules due to impact ionization from the electrons. The resulting ions (e.g. OH⁻, H⁰) then create volatile compounds with the carbon atoms of the diamond surface such as CO₂, CH₄ (volatilization), which are then removed from the sample and eventually pumped out of the chamber [20, 24]. Subsequently, as described in the second part of the results section, the utilization of the FIB is necessary in order to mill a rectangular area across each trench, to obtain the corresponding cross section and measure the depth of each trench for the calculation of the aspect ratio. For this step, the stage is tilted by 52°. The FIB consists of Ga⁺ ions derived from a liquid metal ion source.
the setup instability leads to extensive broadening. The experimental system for etching times longer than 400 s, lies out of the general trend followed by all other data points. The last point of 10 kV corresponding to 656 s of exposure time, lies out of the general trend followed by all other data points. We believe this point indicates the instability of our experimental system for etching times longer than 400–500 s, where the setup instability leads to extensive broadening.

3. Results

3.1. High resolution parametric study

In order to achieve the highest resolution of 10 nm and the aspect ratio of 4.5 the influence of the e-beam acceleration voltage and current on the etching process was investigated. It was found that the hydrogen termination of the diamond samples is crucial for our study because it provides sufficient surface conductivity. Due to the two-dimensional hole gas (2DHG) that is established on the surface of the sample [28], charging effects can be avoided and thus, high resolution imaging and patterning can be achieved.

The single crystalline diamond sample was mounted on the sample holder, inserted in the FIB setup chamber and the system was pumped down to UHV region of 10^-6 mbar. For the trench series, the ultrahigh resolution mode (immersion) was implemented with the “Through The Lens” detector. Using this mode, trenches of 1 μm length and only a few nm width were patterned into the diamond surface with varying electron-beam current and acceleration voltage and the corresponding trench width was measured in each case. The dose of the e-beam was kept constant for every patterned trench in order to compare the effect of different SEM parameters on the etching process. Note that under constant dose, the variation of the beam current leads to different exposure times to the water vapor and the e-beam.

As shown in figure 2, an increase of the current of the electron-beam corresponds to reduction of the exposure and etching time, which results to better resolution of the patterned trenches. This indicates that the resolution is given by the temporal stability of the setup. The lowest acceleration voltage of 10 kV and a small current value of 43 pA for 11 min, yield a resolution of 54 nm, while increased current and voltage to 0.69 nA and 30 kV for 12 s respectively yields trenches of only 10 nm. For short exposure times, i.e. below 60 s, the acceleration voltage of 30 kV provides better resolution compared to 20 and 10 kV. However, for longer exposure times, 30 kV of acceleration voltage lead to broader trenches than the 10 and 20 kV.

3.2. Aspect ratio

In the second part of this study, taking into account the results presented in the previous section and using the beam current that resulted in the best resolution trenches (0.69 nA), a second series of trenches was patterned. The current of the electron-beam was kept at 0.69 nA, while the exposure time was increasing from 2 min to 5, 15, 30 and 45 min and the e-beam dose was calculated respectively. The linear distribution of the e-beam for the aforementioned exposure times correspond to 0.08, 0.2, 0.62, 1.24 and 1.86 μC μm^-1. The increase of the dose resulted in deeper trenches, however, with increased widths. This effect was investigated by calculating the aspect ratio of each trench.

For a stable current value of 0.69 nA and acceleration voltages of 10, 20 and 30 kV, 15 trenches were patterned in total for 2, 5, 15, 30 and 45 min of exposure time. The trench widths were measured and then the stage was tilted to 52° in order to employ the FIB to mill rectangular holes of 600 × 600 nm to 1 μm depth and measure the cross section of the trenches, see figure 3. Using the measured widths and cross sections, the aspect ratios for the different acceleration voltages were calculated and are presented in figure 4. The obtained aspect ratios are calculated to be between 1:1 and 1:5.

For small exposure times (5 and 15 min) the aspect ratio is around 1:1, while with increasing the exposure time, the depth of the trenches is increased up to 385 nm. However, by increasing the exposure time, a broadening is also observed in most trenches. This effect is attributed to increased number of passes in combination with a minor sample drift and external vibrations. The broadening resulted in increased widths and an asymmetry of trenches that lead to variations of the aspect ratios despite the increased depths. This side effect is also observed in figure 2, where the last data point of 10 kV (656 sec) does not follow the same trend as all the other data points. It is noteworthy, that the broadening of the trenches is not completely avoidable even if the drift is reduced. A possible reason for this is that the water molecules that are being adsorbed from a larger area around the etched trench, can also be dissociated by the secondary electrons created under the diamond surface. This could explain the reversed conical shape of the trenches that can be seen at figure 3. The latter effect of the cone-shaped broadened trenches should be also attributed to the reduced diffusion of the water molecules in the trench during etching process. Under the conditions maintained during etching (<10^-4 mbar), the fluid dynamics are described by the free molecular flow. As a consequence, the random movement of the water molecules inhibits their further diffusion in the etched trench, thus reducing the thickness gradually.

Figure 2. Width of etched trenches for the same dose of approximately 10 nC μm^-1 and different electron acceleration voltage and beam current. The current ranged from 43 pA to 0.69 nA and the acceleration voltages were 10, 20 and 30 kV. The trench widths range from 54 nm and go down to 10 nm, which is the highest resolution obtained for electron-beam-induced etching of bulk diamond. The last point of 10 kV corresponding to 656 s of exposure time, lies out of the general trend followed by all other data points. We believe this point indicates the instability of our experimental system for etching times longer than 400–500 s, where the setup instability leads to extensive broadening.
4. Conclusion

In conclusion, we have studied in depth the EBIE method on diamond. By systematically varying the etching parameters, we were able to obtain an exceptionally high resolution of only 10 nm for patterned trenches. The influence of the different parameters on the etching process was investigated in depth and defined accurately. Furthermore, the aspect ratio of the patterned trenches was calculated, in order to obtain an estimate about the removed material. Apart from the optimum choice of the etching parameters, the hydrogen termination of the diamond samples was of great importance to reach high resolution imaging and patterning, because it provided the necessary surface conductivity that minimized the charging effects. The reported results can be improved even further by reducing the number of e-beam passes over the patterned area, which will limit the observed broadening. Our results open up new ways of easier processing of diamond towards the fabrication of high precision devices at the nanometer range that exploit the unique properties of this special material.

Acknowledgments

This work was financially supported by the International Max Planck Research School for Interface Controlled Materials for Energy Conversion (IMPRS-SurMat).

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