Quality Assessment of In Situ Plasma-Etched Diamond Surfaces for Chemical Vapor Deposition Overgrowth

Julia Langer,* Volker Cimalla, Mario Prescher, Jana Ligl, Björn Tegetmeyer, Christoph Schreyvogel, and Oliver Ambacher

In situ plasma etching is a common method to prepare diamond substrates for epitaxial overgrowth to effectuate higher quality. However, there is no feasible direct qualitative method established so far to assess the performance of the etching pretreatment. An optimization of the pretreatment process on grounds of high-resolution X-ray diffraction measurements is proposed to judge the structural quality gain of the diamond substrates and the effectiveness of the polishing-induced subsurface damage removal. The obtained data shows that parameters such as thickness and misorientation angle of the diamond substrates seem to have no clear-cut influence on the gain of structural quality. The process duration, however, is an important key factor when the amount of material removal and the arising roughness are discussed. Furthermore, the impact of the oxygen-to-hydrogen ratio is examined. With rising oxygen percentage, the structural quality gain remains similar; only the overall as well as local mean roughness increases strongly. Within the utilized reactor setup, the best results are obtained after a 20 min in situ hydrogen plasma-etching step. The optimal pretreatment process, however, changes for each reactor type and will always embody a trade-off. Due to the introduced method, a better evaluation and comparison of the achievements is accomplishable.

1. Introduction

For the realization of diamond-based optical as well as electronic devices, reproducible and affordable high-quality standards are demanded. Homoeptaxial microwave plasma-enhanced chemical vapor deposition (MW-PECVD) is currently the most adequate method to prepare tailor-made diamond with precisely defined composition, purity, and structural quality. To meet the required demands, the reactor setup as well as the growth conditions needs to be optimized. Yet another important criterion within this production chain is the starting material itself. The dislocations within the bulk crystal can thread through the growth layer and surface defects can additionally cause nucleation of dislocations.[6–9] In this connection, it is necessary to ensure the substrate quality of the diamond bulk and its surface finish. Over the past two decades, different kinds of diamond materials suitable for CVD overgrowth were investigated for their defect densities and structural quality.[10,11] Pristine diamond substrates with a very low concentration of undesired crystal impurities and a very high structural quality are, however, rather rare and only accessible to a certain extent. The issue in general hereby is the lack of defined quality standards on the commercially available diamond substrates, which are fluctuating largely in their structural quality as well as their impurity concentrations. Polishing is a common method to provide at least a reproducible surface for epitaxial overgrowth. It induces, however, additional subsurface damage, which can be controlled by an optimized polishing process with low damage infliction[9] and can further be reduced with an optimized pretreatment etching process of the substrates. Over the years of research, different methods for the pretreatment of diamond substrates were proposed. Methods such as reactive ion etching (RIE), electron cyclotron resonance (ECR), and inductively coupled plasma (ICP) etching were investigated and major improvements for the CVD overgrowth were demonstrated.[6–9] An in situ pretreatment process, however, features several advantages over the previously mentioned methods, such as reduced expenditure of time, energy, and cost as well as prevention of exposure to air and therefore contaminants during transfer. Thus, the literature states an in situ plasma-etching step as an essential pretreatment process prior to a high-quality CVD overgrowth.[10,11] Unfortunately, only a few results of systematic approaches to better understand the influence of different parameters on the pretreatment process have been published so far: The prevalent findings are that the etching rate exponentially increases with rising substrate temperature and an additional incline in the misorientation angle as well leads to an increase of the etching rate.[12,13] The importance hereby is the actual evaluation of the effectiveness of the polishing-induced...
subsurface damage removal. Usually, it is indirectly performed by subsequent epitaxial overgrowth,\cite{6, 8, 14} however, this method implicates various collateral factors of influence, which cannot be accounted for. Therefore, a direct method to assess the performance of the etching pretreatment would lead to a significant improvement and simplification on its optimization. In addition to in situ low-coherence interferometry,\cite{13} the only applied direct evaluation approach on in situ plasma etching of diamond substrates is to determine the saturation of the etch pit density,\cite{14} which, however, implies using a method that produces a very rough surface. Thus, this work proposes omega scans by high-resolution X-ray diffraction (HRXD) as a nondestructive tool to effectively optimize the in situ plasma etching pretreatment process of diamond substrates on grounds of structural quality gain. This technique is already an established method to evaluate the polishing-induced subsurface damage removal in fields of research on other material systems such as silicon carbide,\cite{15} silicon,\cite{16} as well as aluminum nitride.\cite{17}

Within this study, first the effect of pure hydrogen-plasma etching depending on the run duration is studied. Furthermore, etching experiments with substrates varying in thickness and misorientation angle are performed. In the end, the impact of adding oxygen to the hydrogen plasma is evaluated. For the process optimization, it is important to see if and how significantly these parameters influence the resulting crystal quality of the diamond substrates after etching.

2. Results and Discussion

2.1. Hydrogen Plasma Etching Pretreatment

The process duration of the plasma-etching step is an important aspect of an optimization process. Several successive etching steps were performed on one high-pressure high-temperature (HPHT) substrate to obtain data on the etching rate and the evolution of the quality over the time of etching.

The effective etching rate monotonically decreases from \(~1\mu m h^{-1}\) after 5 min of etching to less than 100 nm h\(^{-1}\) after 40 min. It should be noted that these measurement results are subject to large tolerances due to the limitation of thickness determination by weighing. Nevertheless, they show a clear trend and are in a good qualitative agreement to the observation of increased initial etching of a “defected layer” by Yurov et al.\cite{13}

It implies that a near-surface region of the diamond has a substantially higher defect density than the bulk diamond, which amplifies the etching. The equilibrium etching rate of the bulk diamond after longer etching times is below 100 nm h\(^{-1}\), consistent with literature data.\cite{13}

The removal of the “defected layer” was further investigated by HRXD measurements. In Figure 1a, the black omega scan of the 004 reflection displays the crystal quality of the (001) substrate as received. The sample was pretreated by pure hydrogen-plasma etching steps in the following time intervals: 5, +5, +10, +20, +560 min; adding up to 600 min of etching time in total. The well-addressed full width at half maximum (FWHM) of the omega scan measurements provides an indication on the mosaic spread of the diamond, including dislocations and stacking faults. Within this etching experiment, the FWHM did not change substantially:

The original substrate exhibited a FWHM of 11.0” and was slightly reduced to 10.1” after 40 min of hydrogen etching and marginally increased to 11.1” again with the final etching step.
(Figure 1b). However, observing the diffuse scattering at the slopes around the 004 reflection of diamond provides additional information on the crystal lattice distortion such as point defects.[18] For a rough quantification of the diffuse scattering, the full width at ten thousandth of the maximum (FWTMM) was analyzed. The data are displayed in Figure 1c, which shows an exponential decline, allowing us to deduce a significant reduction of the subsurface damage. The results illustrate that the longer the sample is etched the steeper the slopes get and therefore the quality of the sample surface increases. Furthermore, the mean roughness (Ra) of the sample increases strongly with longer etching duration (Figure 2). Therefore, when considering both the structural quality gain and the unwanted, overall roughening of the diamond sample, a reasonable compromise lies in between. Within our reactor setup, an optimal tradeoff for the pretreatment process is reached after 20 min of in situ hydrogen plasma etching, where the measurable structural quality gain begins to saturate, whereas the surface roughness only doubles.

Continuing with the optimized duration of the etching process, the influence of the thickness, meaning how far the substrate reaches into the plasma, as well as the misorientation angle of HPHT diamond substrates on the surface-quality gain due to the pretreatment process, was investigated. This is of interest because these two properties are predefined by the purchased diamond substrates and are not easily controllable during an additional polishing step. The selected substrates for the experimental series cover the fluctuation ranges of the received standard substrates, which deviate from 300 to 350 μm in thickness and 0.1° to 5° in their misorientation angle. The results on the predominance of the effect from these parameters should enable an estimation on accuracy for further etching experiments. The two experimental series were conducted on diamond substrates with rather poor quality of the surface finish, ensuring the sensitivity of the method when evaluating the arising tendencies. However, no correlation between the thickness of the sample and the etching rate nor the quality gain could be substantiated. The same findings apply for the data of the misorientation-angle series. It should be noted that Ivanov et al.[12] found a strong dependence of the etching rate on the misorientation angle for bulk diamond, which was substantially lower than the etching rate of the “defected layer.” Thus, it is probable that the high density of the polishing-induced subsurface defects was dominating the etching of the diamond substrates and obscured the actual impact of the misorientation angle. In our case, the only determinable trend was the correlation between the structural quality given by the FWHM and the FWTMM of the omega scan measurements before and after the etching process. The data are displayed in Figure 3a, b. The quality gain of the pretreated substrates from the thickness and misorientation-angle series calculated by a linear fit through the FWHM data averages out at around 35%. The comparable reference data point from the duration series, however, is located way above the trend line. This outlier can be explained by the higher surface finish of this sample, which was achieved due to an optimized polishing process with a
lower damage infliction. For the FWTTM, the data follow a similar trend, putting emphasis on the findings from the FWHM data that the original substrate quality, including its surface finish, plays a major role on the quality gain attained through an in situ plasma etching pretreatment. However, this time the reference data point from the duration series follows the same trend as the samples from the thickness and misorientation-angle series. Because of this, it can be hypothesized that the defects, responsible for the diffuse scattering around the omega scan of the 004 reflection, are introduced to the diamond lattice via any polishing process. At the same time, these defects can again be reduced via an optimized etching pretreatment. Therefore, through the FWTTM value a more reliable statement about the reduction of the polishing-induced subsurface damage can be given than on grounds of the FWHM.

2.2. Oxygen–Hydrogen Plasma-Etching Pretreatment

The literature shows that the quality gain through a decent plasma pretreatment process can be even further enhanced by adding oxygen as an additional etchant to the plasma\[4,6,14,19\]. To prove this working hypothesis, a series with varying oxygen-to-hydrogen ratios was conducted: starting out from 0% up to 1.5% oxygen in hydrogen. These pretreatment experiments with oxygen were conducted on a batch of well-polished, high-quality CVD substrates with FWHM below 8.5°. The FWHM of the omega scans did not change; slight variations of minimal FWHM values are solely due to the resolution limits of the diffractometer. However, when correlating the omega scan data from before and after the etching experiment, a peak sharpening due to a reduction of the diffuse scattering can again be observed despite the already high structural quality of the diamond substrates displayed by the very low FWHM (Figure 4). This tendency can be noted in all the results throughout the whole oxygen–hydrogen etching series. Ultimately, the quality gain seems to be consistent although independent of the oxygen percentage used in the pretreatment process.

The difference in the etching experiment series with an increasing oxygen-to-hydrogen ratio becomes only visible during optical characterization and the determination of the etching rate. The latter is contrasted with the rising oxygen percentage of the different pretreatment processes in Figure 5. The data illustrate a strong increase of the etching rate with higher oxygen-to-hydrogen ratios. Figure 6a–d displays microscope images with differential interference contrast (DIC) of four plasma-pretreated substrates. From these images, it is evident that the influence of oxygen rises with its percentage: The higher the oxygen concentration, the more etch pits appear. The mean roughness (Ra) of the in situ oxygen–hydrogen plasma-etched pretreated substrates, excluding the etch pits, is shown in Figure 7, supporting the impression of an increasing roughness with higher oxygen concentrations from the DIC microscopy images shown in Figure 6a–d. However, not only is the overall roughness affected based on the rising amount of etch pits, but also the depth of the single etch pits becomes greater. With 1.5% oxygen in the plasma, the resulting etch pits are already up to 13 μm deep. Oxygen as an etchant within the plasma is affecting the surface more locally in contrast to pure hydrogen plasmas. This leads to the finding that oxygen within the plasma pretreatment process may not certainly result in a higher quality gain, but in this case only in a rougher surface.

3. Conclusion

The etching rate of the diamond substrates with polishing-induced subsurface damage is substantially higher than for bulk diamond, indicating an extended density of defects. The occurrence of such extended defect densities can be investigated through omega scan measurements by HRXD. Depending on the initial quality of the substrates, an optimization can be achieved with the reduction of the FWHM. Speaking in terms

![Figure 4](image-url)  
**Figure 4.** Omega scan data of an untreated CVD diamond substrate (black) in comparison to pretreated ones, which are plasma etched with different oxygen-to-hydrogen ratios (green to yellow).

![Figure 5](image-url)  
**Figure 5.** Evolution of the etching rate as a function of the oxygen percentage within the plasma.
of FWHM improvement, a quality gain up to 35% can be obtained within our reactor setup. Especially for well-polished, high-quality samples, however, the determination of the FWHM is not informative enough. The displayed data show that the increasing steepness of the omega scan slopes, approximately quantifiable by the FWTTM, is in addition very significant.

Generally, the FWTTM decreases during etching until it reaches an equilibrium state, which indicates the entire removal of the polishing-induced subsurface damage. Within the utilized reactor setup, the best tradeoff between etching duration, mean roughness, and structural quality gain is attained after 20 min of etching without the addition of oxygen to the plasma. Oxygen as an admixed etchant only increases the etching rate and the overall as well as local surface roughness without further improving the structural quality of the diamonds. Furthermore, the thickness and misorientation angle of the diamond substrates only show a negligible impact on the removal of the polishing-induced subsurface damage. The dominant factor on the resulting structural quality after an in situ etching pretreatment process is the polishing-induced subsurface damage of the diamond substrates prior to etching depending on the executed polishing process.

The displayed data show that HRXD is a valid direct qualitative method to determine the reduction of the polishing-induced subsurface damage on diamond substrates by an in situ plasma etching process and offers a possibility to establish a quality assessment criterion. This proposed evaluation method further enables more detailed studies about the impact of the subsurface damage on the homoepitaxial growth of high-quality diamond.

### 4. Experimental Section

The pretreatment process was optimized by using (001) HPHT and CVD diamond substrates. These substrates were carefully precharacterized by HRXRD omega scan measurements of the 004 reflection. A PANalytical X’Pert Pro MRD system equipped with Cu radiation (\(\lambda = 154.06\) pm) was used for these measurements. On the primary beam side, a multilayer mirror and a double bounce Ge (220) monochromator was inserted into the beam path, and for the diffracted beam side a triple bounce Ge (220) analyzer was installed. The mean roughness (Ra) of the samples after polishing was determined via white-light interferometry to be mainly well below 3 nm Ra (WYKO NT1100). In addition, optical microscopy was conducted with and without crossed polarizers (Leica...
DMRM. Afterward, the substrates were sorted by their thickness and misorientation angle to be assembled for different experimental series regarding process duration, thickness variation, misorientation-angle variation, and variation of the oxygen content in the total gas flow.

Prior to etching, all substrates underwent an extended cleaning process, which included boiling them in nitro sulfuric acid and successively several steps of organic solvent cleaning. It is of great importance that the substrates are spotless before mounting them into the reactor because any residue of metal or other contaminants can influence the plasma interaction with the substrate and cause additional unpredictable quantities of local etching.

The plasma etching experiments were performed in an ellipsoidal-shaped CVD reactor with a 2.45 GHz microwave frequency and equipped with a 6 kW microwave generator.[20] The postcharacterization was executed with the same measurement setups and parameters to receive comparable results from before and after the plasma etching pretreatment process. The etching rate was calculated from the weight difference of the sample measured by an ultramicrobalance (Mettler Toledo UMX5).

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

chemical vapor deposition, in situ etching, pretreatment process, structural analysis, synthetic diamond

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