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# Reduced Plasma-Induced Damage to Near-Surface Nitrogen-Vacancy Centers in Diamond

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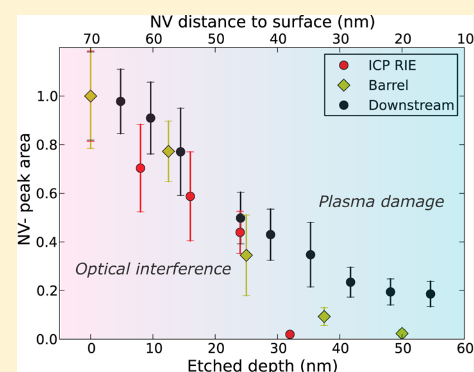
Supporting Information

**ABSTRACT:** Understanding plasma etch damage on near-surface nitrogen vacancy (NV) centers in diamond is essential for preserving NV emission in photonic structures and magnetometry systems. We have developed a methodology to compare the optical properties of ensemble NV centers initially 70 nm from the surface brought closer to the surface through etching with $O_2$ plasmas in three different reactors. We employ a conventional reactive ion etcher, a barrel etcher, and a downstream etcher. We find that, irrespective of the etcher used, NV luminescence dims steadily as NVs are brought closer to the surface due to optical and surface effects. When NVs are less than 40 nm from the surface, differences in damage from the three different plasma processes affect the NV emission intensity in different ways. Diamond that is etched using the conventional etching method shows a greatly reduced NV luminescence, whereas NVs 15 nm from the surface still survive when the diamond is etched in the downstream reactor. As a result, downstream etching provides a possible alternative method for low damage etching of diamond for preservation of near surface NV properties.




**KEYWORDS:** *nitrogen vacancy, plasma damage, etching, optics*

The nitrogen vacancy (NV) center, a luminescent point defect in diamond, is an important emerging system for sensing nuclei[1,2] and magnetic fields[3] on the nanoscale. To achieve high sensitivities to the external target sample, the NVs need to be as close as possible (<10 nm) to the surface. Initially produced through ion implantation or the growth of single crystal diamond, NV centers are often brought even closer to the surface by etch removing the top few nanometers of diamond through oxygen annealing[4] or through the use of gas-phase, ion-assisted etching (loosely termed "plasma etching").[5] Although etching diamond through oxygen annealing is a promising method, the etch rate is difficult to characterize and control. Plasma etch processes, however, are widely incorporated by the semiconductor electronic device industry and are well understood. In addition to etching the diamond surface, plasma processes may be used to clean or controllably prepare the diamond surface.

Experience in working with plasma-based processing of semiconductor materials reveals concomitant process-associated device damage to be a continuing challenge.[6,7] Near-surface NVs are especially sensitive to ion-based and plasma-based damage. It is therefore important to characterize the effect of plasma etching on NVs and consider alternative, lower-damage etch processes, especially for bringing the NVs closer to the surface for external spin sensing. Because the optical (photoluminescence, PL) signature of the NV is so critical for the read-out and the initialization of the local spin states, we monitor the relative health of ensembles of NVs through the intensity of their luminescence. In this work, we study NV emission as a function of its distance from the surface. The surface is brought closer to the NVs by etching the diamond in oxygen, utilizing three different reactors: an inductively coupled plasma reactive ion etcher (ICP RIE), a barrel reactor, and a downstream reactor.

Due to the small etch distances involved and the atom-like character of the NV emitters, several careful experimental design considerations and calibrations are mandatory for these comparative studies: (1) The NVs should be located at a uniform distance from the surface to extract meaningful correlations between NV depth and NV luminescence. Such a sample was achieved by "delta-doping" NVs, a process in which a very thin layer (4 nm) of NVs is incorporated during a controlled and slow growth process[8−10] [more detail in Supporting Information]. (2) Awareness of the initial depth of the NVs before any etching occurs is important in order to know when the layer of NVs has been etched through. Even for

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the controlled delta-doped growth, the absolute depth of the NVs can vary significantly, depending on the diamond growth rate. Thus, we cross-calibrated the NV depths through spin lifetime measurements, which have also been found to have a dependence on depth from the surface [more detail in Supporting Information]. (3) To accommodate the lateral variability in luminescence from these ensembles of discrete NVs, we created PL maps of the etched surfaces and tracked the luminescence at the same ($x$, $y$) positions after each etch step. (4) To ensure sufficient precision in determining etched depths, we masked our diamond substrate with a thin film of chemical vapor deposited $SiO_2$. Atomic force microscopy (AFM) was used to measure etched depths. The dielectric mask provided us with an unetched reference for the material thickness and NV luminescence and also served to protect the rest of the sample such that multiple experiments could be carried out.

The same delta-doped diamond substrate, selectively masked into various regions, was etched in an oxygen plasma in the three different plasma reactors: an ICP RIE reactor (Unaxis), a benchtop resist stripper (Technics), and a downstream system (Matrix). The three reactors are shown schematically in Figure 1. ICP RIE, the most commonly used method for etching diamond[11,12] is characterized by high ion densities at low plasma pressures, and the capability of utilizing relatively low ion energies, thereby minimizing ion-related damage. As with all RIE processes, a largely chemical process (i.e., removal of carbon−oxygen species) is enhanced by the physical bombardment of ions on the surface from an applied bias between the sample and the plasma. This ion-bombardment augments the etch rate and provides both directionality and uniformity. However, such ion bombardment can also result in damage to the substrate, such as the creation of vacancies and the introduction of ions into the material itself.[13] In contrast, barrel reactors operate at higher plasma pressures, without a deliberately applied bias, and the resulting low voltage reduces the energy of the ions and, hence, the degree of damage. Finally, the gentlest of etching techniques is the downstream reactor, where the plasma is generated in a separate chamber from the sample. Because the most reactive ions collide with the chamber walls and only low energy radicals and neutral species interact with the target, "downstream etching" holds promise as a low-damage process.

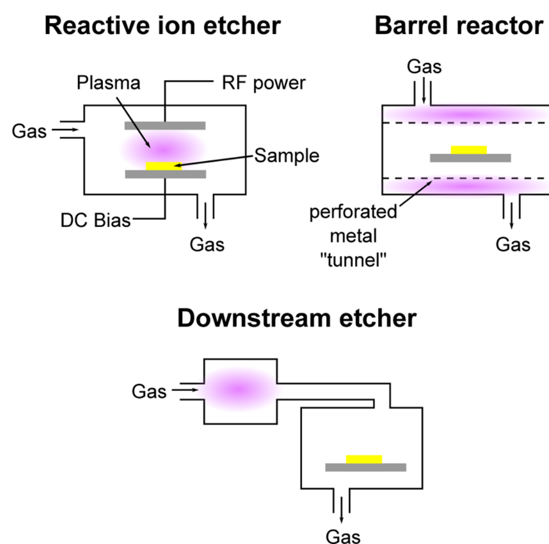


**Figure 1.** Simplified schematic of three etch reactor geometries used in this study.

After etch-removing a few nanometers of diamond in each reactor, the NV photoluminescence (PL) was collected via an objective (magnification of 100×, numerical aperture of 0.9) in a confocal setup utilizing a 532 nm laser excitation (Horiba Jobin-Yvonne). A typical PL spectrum [Figure 2a] consists of a diamond Raman peak (573 nm), $NV^0$ zero-phonon line (ZPL) peak (575 nm), and $NV^-$ ZPL peak (638 nm). The spectrum is collected at several points over ~300 × 100 $\mu$m area of the exposed diamond to account for variability in NV emission across the sample. The diamond is placed back in the reactor, and the subsequent PL map is taken over the same region using the same acquisition parameters. Figure 2b shows a map of $NV^-$ ZPL intensity after sequential etch steps. We repeat this process until the $NV^-$ ZPL emission is no longer observed. The total etch time in the ICP RIE, barrel, and downstream reactors was 2, 40, and 510 min, respectively. The mask is then removed, and the final step height is measured using AFM. The total etched depth in the ICP RIE, barrel, and downstream reactors was 32, 50, and 55 nm, respectively. This results in a diamond etch rate of 8 nm/30 s in the ICP RIE, 1.25 nm/min in the barrel reactor, and 0.11 nm/min in the downstream reactor [for more etch condition details, please see Supporting Information].

Equipped with an estimate of the final etched depth from the AFM data, assuming a uniform etch rate at each etch step, we can compare the relative change in NV luminescence between etching in the ICP RIE, barrel reactor, and downstream reactor. We compare $NV^-$ ZPL intensity at various etched depths for each instrument [Figure 3]. The plotted $NV^-$ signal (measured by integrating under the $NV^-$ zero-phonon line peak) is normalized by the initial $NV^-$ signal before any etching occurred. Each point represents the average and standard deviation of $NV^-$ signal across the multiple points seen in Figure 2b. In the analysis that follows, we will use the relative luminescence intensity as the correlation with etch damage: that is, if the luminescence intensity is preserved as the etch process proceeds, we will assume that no process-associated damage is incurred. There are obvious limitations to this assumption. In particular, when the surface is brought within a few nanometers of the NVs, interactions might take place between the $NV^-$ and surface states.[14] A diminished luminescence could ensue, irrespective of any etch process employed. In fact, the analysis described below will highlight initial reductions of luminescence that cannot necessarily be correlated with etch damage.

Most notably, the $NV^-$ photoluminescence intensity in Figure 3 shows two different regions of behavior: (a) within the removal of up to 30 nm of diamond (alternatively, when the NVs are within 40−70 nm from the surface), there is a clear reduction in $NV^-$ luminescence signal, with a *uniform* behavior for all three etch processes, and (b) as the etch proceeds further into the diamond, there is a clear distinction among the three processes.

In the removal of the first 30 nm of the diamond, all three reactors produce a steady reduction in $NV^-$ PL peak intensity at a comparable rate and range [Figure 3]. Because the details of ion energy and direct plasma immersion appear to make no difference in this regime, a reasonable assumption is that the decrease in collected $NV^-$ signal is simply related to the interactions of the emitter with the surface. Previous analogous


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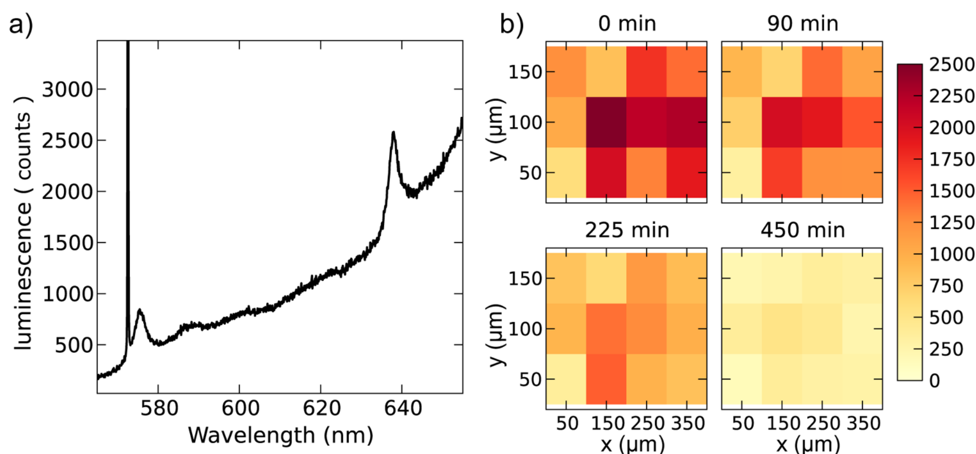


**Figure 2.** (a) A typical photoluminescence spectrum on diamond, taken at room temperature with 532 nm excitation, consists of a Raman peak and $NV^0$ and $NV^-$ zero-phonon line peaks. (b) A map of $NV^-$ zero-phonon-line luminescence at several time increments of etching in the downstream reactor. Heat map unit is total collected counts at 638 nm within 10 s acquisition. The $NV^-$ signal decreases uniformly as etch time (and therefore etch depth) increases.

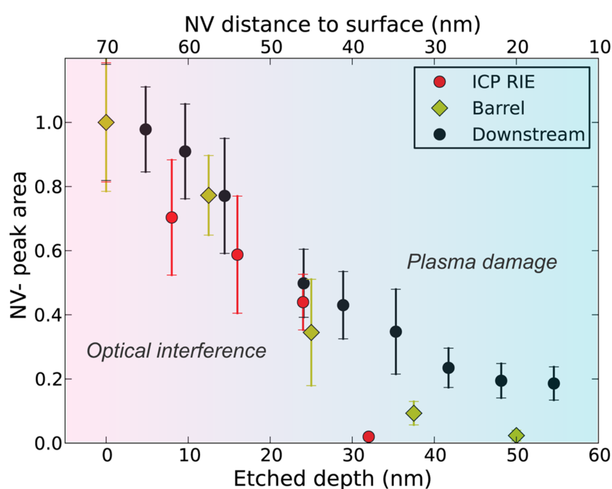


**Figure 3.** Normalized $NV^-$ luminescence signal as a function of etch depth. We normalize the $NV^-$ luminescence signal at each etch step to the signal before etching with each reactor system. $NV^-$ signals when using the ICP and barrel reactors are gone after etching ~32 nm and ~50 nm, respectively. The signal when using the downstream reactor remains after 55 nm of etching (NVs are ~15 nm from the surface). Uncertainty bars represent the standard deviation of $NV^-$ signal on the 3 × 4 grid in Figure 2b.

etch studies found pronounced PL degradation of GaAs quantum wells (QWs) within ~30 nm of the surface, which was attributed to interactions of the QWs with surface states.[13,15] Photobleaching and blinking due to surface states has also been reported for NVs < 10 nm deep, theorized to be due to delocalized image states, deep sub-bandgap states related to surface-termination, and localized acceptor states near the surface.[16,17] However, the NVs > 50 nm deep reported here are not expected to be affected by those surface states. Another explanation for the monotonic decrease in luminescence for NVs 70−40 nm from the surface may relate to the electromagnetic interaction with the surface. Early calculations and measurements carried out by Drexhage demonstrated a change in emitter lifetime for a dipole approaching the near-field of an interface or surface. The change in lifetime results from the interference between the emitted light and that light reflected by the dielectric interface.[18] This can lead to a substantial increase in lifetime of the emitter as it approaches the interface, which in turn can decrease the total light collected from that emitter. The interaction emerges for emitter−surface distances $d < \lambda/4n$, where $\lambda$ is the wavelength of emission and $n$ is the index of refraction of the dielectric. For the NV emitters considered here, $d \sim 65$ nm; thus, the interference effects are certainly applicable to the samples studied. Our initial simulations model the power emitted by a dipole in diamond either perpendicular or parallel to the surface, as a function of distance from the surface [see Supporting Information]. NVs aligned along the (111) direction, at an angle of 54.75° relative to the (100) direction, should exhibit behaviors associated with both the perpendicular and parallel components. Although the power from the parallel component does not change much as the dipole approaches the surface, the perpendicular component displays a dramatic decrease in power at a similar rate shown in the first region of Figure 3. Given the uncertainty in the precise distances of the NVs from the surface and the imperfections of the surface such as roughness, we believe that the perpendicular component dominates and models the decrease in power observed. Within the range of the error bars in Figure 3, the absence of significant differences between the three reactors on the rate of NV dimming suggests that the reduction in luminescence intensity is not primarily due to damage. Hence, this first half of the graph opens up many interesting questions about inherent NV dynamics and optics near surfaces.

For the second region shown in Figure 3, after more than 30 nm of etch removal of the diamond, there is a very clear difference in the result produced by the three reactors. After etching around 32 nm of diamond in the ICP RIE, when the NVs are still ~40 nm from the surface, NV emission is already annihilated. Acquiring spectra for longer periods of time or increasing the laser intensity still does not lead to any NV peaks. Similarly, after 50 nm of etching in the barrel reactor, when NVs are ~20 nm from the surface, no NV luminescence is seen. In contrast, after 55 nm of etching in the downstream system, the NV signal is still strong. In fact, continued etching does not seem to affect the PL emission any further. Downstream etching in particular relies entirely on isotropic chemical etching, which can lead to roughened surfaces and hence greater total surface area. Given the increased surface



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area, and the very slow etch rate of the downstream process, further etching results in an increased surface roughness, rather than incursion into a direction perpendicular to the original diamond surface [see Supporting Information]. Therefore, to minimize roughening of the diamond surface, it may be preferable to use downstream etching on NVs initially <20 nm from the surface.

There are several potential sources of damage resulting in the quenching of NVs before they are actually physically etch-removed: ion damage resulting in (1) increased vacancies, (2) ion implantation, or (3) damage from UV light associated with the plasma. Ion implantation and vacancy creation are especially problematic and likely when etching in an ICP RIE. Recently, a study showed that a short etch in $O_2$ plasma in ICP RIE resulted in the complete disappearance of NVs 20 nm deep.[19] However, this study demonstrated the ability to generate new NVs at higher densities after vacuum annealing at 800 °C, likely because of the additional vacancies introduced from the etch process. Vacancies near NVs can have a profound effect on NV dynamics, ionizing them to the neutral charge state, $NV^0$.[14] However, we did not notice any drastic change in the $NV^-/NV^0$ ZPL ratio in this set of experiments. It is possible that the NVs are ionized into a $NV^+$ state, but this is difficult to validate. Furthermore, even though there is no deliberate alignment of the diamond crystal to ion direction in the etch process, ions can be scattered into channeling directions, and those ions can subsequently penetrate far deeper (∼100 nm) into the material than typical SRIM[20] simulations would predict.[21] Finally, the high energy UV light generated in the plasma has been known to break chemical bonds and generate electron−hole pairs, resulting in the formation of crystalline defects, which are known to quench NV luminescence.[22]

In conclusion, we have quantified the damage effect on NVs when etched in three different reactors. We used an ICP RIE, a barrel, and a downstream reactor to slowly etch the diamond and bring NVs closer to the surface. We found the downstream method to be a promising alternative to ICP RIE for etching small distances into the diamond. The careful calibration of the material and the optical measurements was critical in analyzing what may appear to be subtle differences in the etch processes. This methodology will enable further studies and augmented understanding of near-surface NV dynamics. Further insight will be gained through probing the surface chemistry after plasma-assisted etching procedures and by studying the optics of single NVs approaching the diamond surface through further experiment and simulation.

## ■ ASSOCIATED CONTENT

### Supporting Information

Growth of delta-doped NV layer; etch process conditions and details; atomic force microscopy of surface roughness; estimation of actual NV depth; simulations of dipole embedded in diamond approaching a diamond−air interface. This material is free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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