Electron beam controlled restructuring of luminescence centers in polycrystalline diamond

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Abstract

Color centers in diamond are becoming prime candidates for applications in photonics and sensing. In this work we study the time evolution of cathodoluminescence (CL) emissions from color centers in a polycrystalline diamond film under electron irradiation. We demonstrate room temperature activation of several luminescence centers through a thermal mechanism that is catalyzed by an electron beam. CL activation kinetics were measured in realtime and discussed in the context of electron induced dehydrogenation of nitrogen-vacancy-hydrogen clusters and dislocation defects. Our results also show that (unintentional) electron beam induced chemical etching can take place during CL analysis of diamond. The etching is caused by residual H_2O molecules present in high vacuum CL systems.

KEYWORDS: diamond, nitrogen vacancy, dislocations, grain boundaries, cathodoluminescence, electron beam induced etching

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1 Introduction

Optical properties of materials, particularly of point defects in solids, are increasingly important to our understanding of single photon emitters. The negatively charged nitrogen vacancy (NV) center in diamond is an example of a color center that has been the subject of intense research due to its photophysical properties.[1–7] However, having a wide optical band gap, diamond hosts many optically active defects and the interplay between them is still a subject of debate. The behavior of various color centers under electron beam irradiation has not been fully explored. An understanding of such phenomena will inform future work on deterministic, nanometer-scale processing of diamond-based devices, and may become useful in the context of bio-sensing and correlative microscopy.[8] Here we investigated the luminescence kinetics of several optical centers, including the nitrogen vacancy, in a polycrystalline diamond (PCD) film during exposure to 20 keV electrons.

The majority of prior work has focused on luminescence properties of single crystal diamonds that have undergone high-energy irradiation to add vacancies.[9–13] In our work, we study as-grown polycrystalline diamond that had not been subjected to ion-bombardment or annealing processes which are commonly used to induce the formation of nitrogen vacancy defects. The time evolution of cathodoluminescence (CL) spectra from a PCD film and several single crystal diamond control samples suggest that electron-catalyzed, thermally-driven restructuring of extended defects activates luminescent NVs and A-band centers at room temperature, without the need for thermal annealing. The defect restructuring can be explained by electron beam induced dehydrogenation[14–17] of non-luminescent dislocations, and NVH_x centers located at extended defects.

2 Methods and materials

A PCD thin film was deposited on a silicon substrate by microwave plasma-assisted chemical vapor deposition (MWCVD) using a microwave power of 900 W, a H_2:CH_4 ratio of 99:1, and a total pressure of 8 kPa. The film had a thickness of $\sim$ 400 nm and a grain size of $\sim 250 \pm 50$ nm. After synthesis, no further cleaning, annealing, or ion bombardment was performed. The sample was analyzed in the as-grown state.

Three single crystal diamond samples were used for control experiments: a bulk CVD sample purchased from Element 6, a high-pressure high-temperature (HPHT) diamond (Sumitomo Inc.) and individual microdiamonds (Microdiamant). The HPHT diamond was sputter-coated with a 12 nm film of silver to suppress charging artifacts during CL analysis.

Cathodoluminescence characterization was carried out using an environmental scanning electron microscope (SEM)[18] with a base pressure of $\sim 10^{-4}$ Pa, equipped with a liquid nitrogen cooling stage. A parabolic mirror situated over the sample directed light through an ex-situ focusing lens onto a 600 nm optical fiber coupled to a spectrometer (OceanOptics QE65000) with a bandpass of 6.5 nm. CL spectra were recorded continuously using an integration time of 10 s per spectrum while exposing a sample area of $\sim 20\ \mu\text{m}^2$ to 20 keV electrons using the beam currents shown in figure captions. The area sampled during CL analysis was significantly larger than the grain size of the PCD film. Hence, each dataset reflects the mean response of a number of individual crystallites and grain boundaries. Each raw CL spectral kinetics profile was normalized and expressed as a color map (2(a), 3-5). A CL generation depth-profile (calculated using standard Monte Carlo techniques[19] for 20 keV electrons incident on a 400 nm diamond film on Si) is shown in 1. The CL generation rate is approximated by the total energy deposition rate[20] (the dashed line shows the energy deposition depth profile in the substrate).

Individual CL kinetics profiles were obtained for the A-band and H3 emissions (attributed to dislocations, and nitrogen-vacancy complexes, respectively),[21] and the NV^0 emission from the PCD film. 2b shows typical CL spectra and the corresponding peaks used to fit the three emissions, while 2c shows the time evolution of the corresponding peak areas during electron irradiation. The silicon vacancy (SiV) emission at 1.68 eV and an emission at 2.56 eV were excluded from peak fitting because of their relatively small contributions to the total integrated intensity. In the PCD film, the H3 center was difficult to resolve individually because of peak overlaps. Hence, a sample of CVD microdiamonds showing only the H3 emission (5c) was measured and the resulting spectra fit to an exponentially modified gaussian. The resulting coefficients were used to estimate the contribution of this defect to the PCD film emission spectrum. This method of H3 fitting is similar to that utilized by Tizei et al.[22,23]

3 Results

The intensities of several luminescence centers varied with electron beam exposure time. We first characterized the CL kinetics measured from the PCD film under various ambient conditions. At room temperature, electron irradiation caused the NV^0 luminescence intensity to increase with time (3a). When residual water vapor was present in the high vacuum CL chamber, this initial increase was followed by a subsequent decrease with continued electron exposure (3a). However, when a liquid nitrogen cold trap was used to reduce the residual H_2O pressure, the subsequent decrease was suppressed (3b)[a]. Conversely, when the water vapor pressure was increased to 47 Pa,[18] the intensity of all CL emissions rapidly decreased with irradiation time (3c).

The A-band luminescence exhibited two general trends during electron irradiation of different regions of the PCD film. The signal intensity would either decrease with exposure

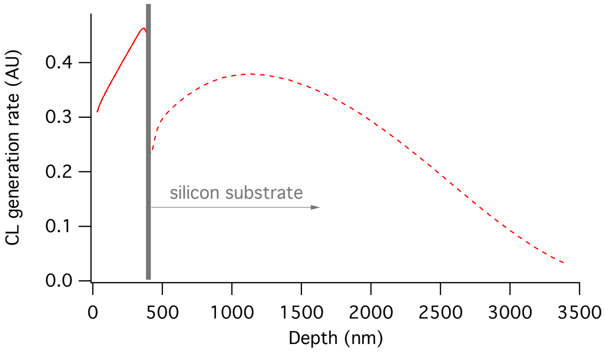

Figure 1: CL generation rate in diamond calculated as a function of depth for 20 keV electrons incident on a 400 nm diamond film on a silicon substrate. The dashed line shows the electron energy deposition depth profile in the substrate.

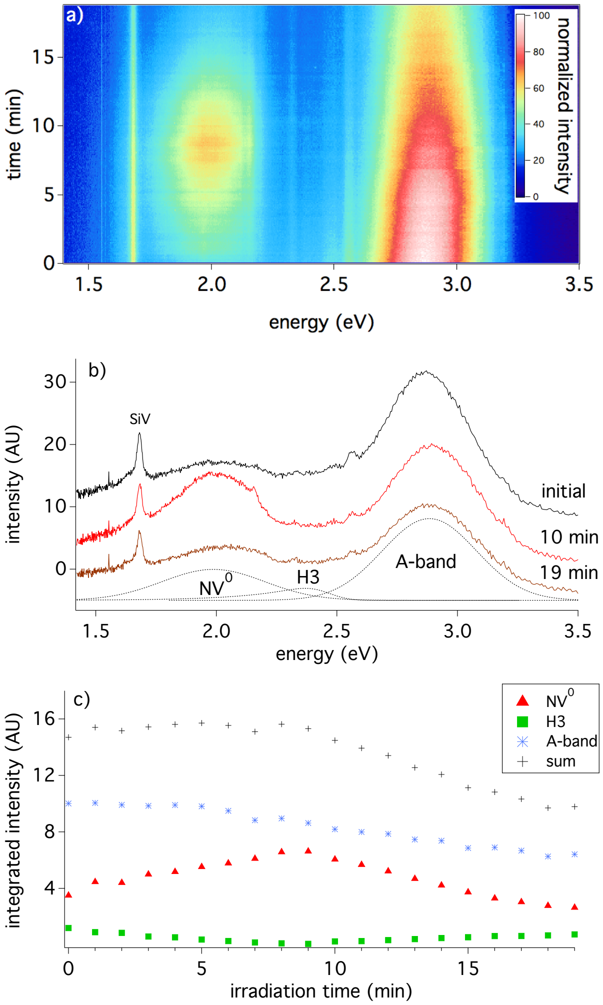

Figure 2: CL kinetics profiles recorded from a PCD film during a 20 min electron beam irradiation treatment: a) a normalized color map representation of CL spectra acquired as a function of time, b) corresponding CL spectra at electron exposure times of 0, 10 and 19 min, and c) time-evolution of the A-band, NV^0, and H3 emissions, plotted as the area of each of the peaks shown in (b) versus time. [Beam current = 23 nA.]

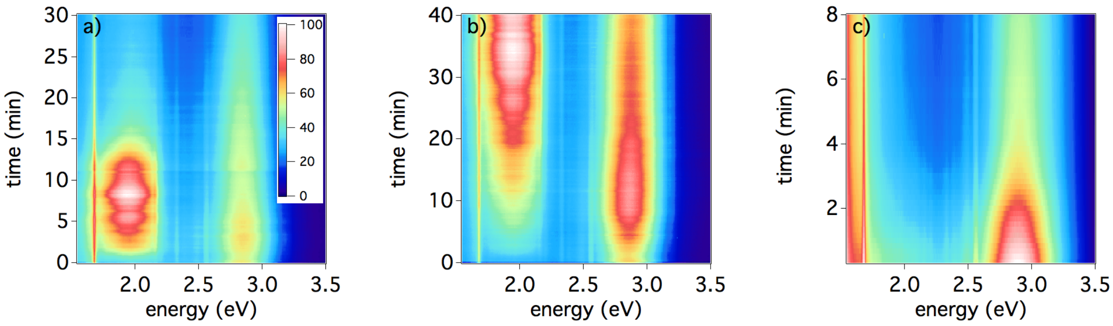

Figure 3: CL kinetics profiles obtained from a PCD film under the following conditions of temperature and humidity: a) room temperature with no measure taken to remove residual water molecules from a high vacuum CL analysis chamber, b) room temperature with an in-chamber liquid nitrogen-cooled trap used to cryo pump residual water vapor, and c) room temperature with a water vapor pressure of 47 Pa. [Beam current = 52 nA (a), and 43 nA (b, c).]

time (2), or an initial increase in intensity was followed by an eventual decay (3a, 3b, 4b). We attribute this variability accross the PCD surface to a non-uniform distribution of the sp^2 species associated with dislocations responsible for A-band luminescence[21,24] in the as-grown PCD film, and variations in the number of grain boundaries within the probed volume. All other trends in CL kinetics profiles reported here for the polycrystalline sample were observed in multiple locations and did not vary across the PCD film.

To characterize the effects of sample temperature, CL kinetics were measured at -25° C and -177° C (4). Sample cooling to -25° C reduced the magnitude of the electron beam induced increase in the intensity of the NV^0 CL emission. At -177° C, the effect was suppressed to below the detection limit and the entire CL spectrum decayed with electron exposure time [b].

Figure 5 shows reference data collected at room temperature from single crystal control samples, each containing only one of the three CL emissions of interest: (a) bulk CVD diamond enriched with NV centers, (b) HPHT diamond that exhibits A-band luminescence, and (c) a single microdiamond that contains H3 centers. In single crystal diamond (i.e. in the absence of grain boundaries), the NV^0 emission did not change with electron exposure time (5a). The A-band intensity shows an increase with irradiation time (5b), but the eventual

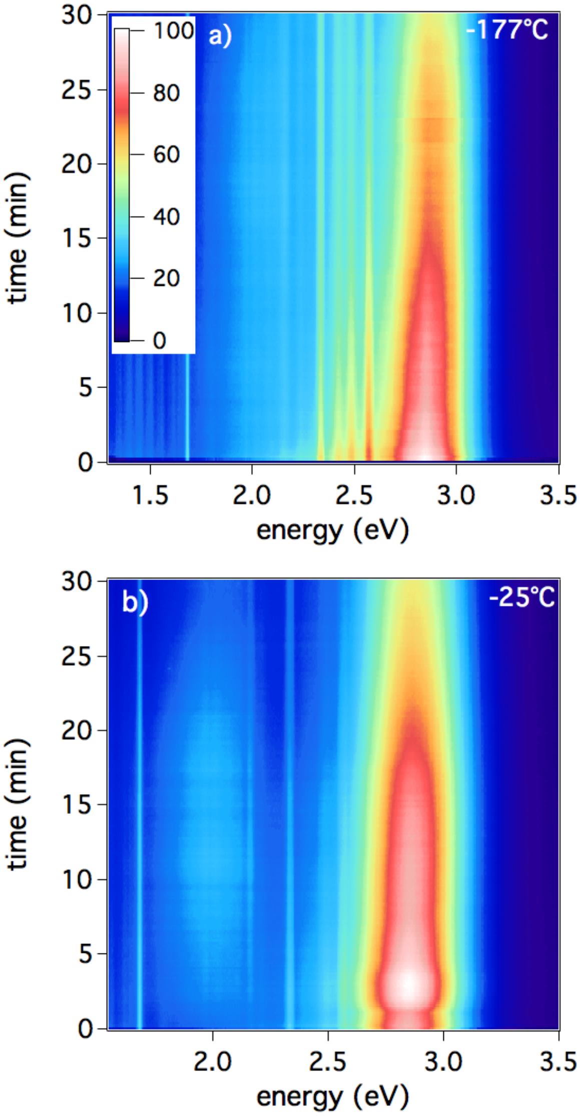

Figure 4: CL kinetics profiles obtained from a PCD film cooled to: a) -177°C, and b) -25°C. [Beam current = 33 nA (a), and 52 nA (b).]

decrease in A-band intensity observed in the PCD film was not observed in the bulk, single crystal diamond, due to negligible electron beam-induced etching (see discussion) of the bulk diamond relative to that of the polycrystalline film. The H3 emission intensity exhibits an initial decrease followed by an increase with time in both single-crystal microdiamonds (5c) and the PCD film (2c). These results show that the H3 kinetics can occur in the absence of NV^0 kinetics, and are therefore not necessarily the consequence of competitive recombination. We note that, in 5(c), the narrow line at 1.4 eV is associated with a Ni-related defect[21,25,26] and decreases marginally with electron exposure. It serves as an internal control, showing that the change in H3 CL intensity with irradiation time is not caused by an experimental artifact such as beam drift or fluctuations in beam current.

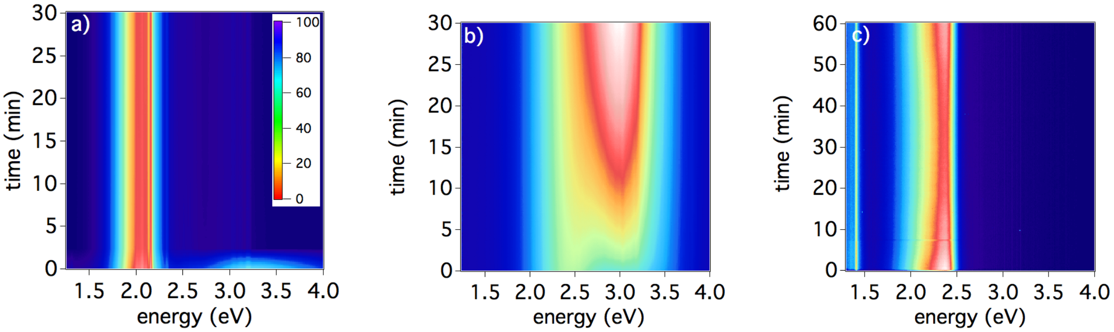

Figure 5: CL kinetics profiles recorded from control samples that exhibit specific luminescent features: a) bulk CVD single crystal diamond showing NV^0 luminescence, b) HPHT single crystal diamond showing A-band luminescence, c) single microdiamond showing H3 luminescence. [Beam current = 45 nA (a, b), and 3 nA (c).]

In all cases, the intensity of the SiV emission in the PCD film decreased with electron irradiation time, as seen in 2b (the apparent increase seen in 3 is caused by an overlap between the SiV and NV^0 peaks). While uninteresting in isolation, this behavior acts as an effective control for experimental artifacts, analogous to the aforementioned Ni defect in the microdiamond.

4 Discussion

We now discuss possible mechanisms behind the changes in luminescence caused by electron irradiation of the PCD film. In particular, we focus on the initial increase in the NV^0 and A-band intensity, and the eventual decay of most emissions caused by prolonged electron exposure. The latter is attributed primarily to efficient electron beam induced etching (EBIE) of polycrystalline diamond,[27–31] mediated by residual H_2O molecules present in the high vacuum SEM chamber[32] used for CL analysis. EBIE is a dry etch process that proceeds through electron induced dissociation of surface adsorbed precursor molecules (in this case H_2O). Dissociation yields fragments (e.g. O radicals) that react with the surface, producing volatile species (e.g. CO) that desorb from and thereby etch the substrate.[33,34] The most direct evidence for the role of EBIE in CL kinetics is shown in 3b, where a liquid nitrogen cold trap was used to reduce the residual H_2O pressure in the high vacuum CL analysis chamber. The cold trap was not in contact with the sample, but nonetheless caused a significant reduction in the long term decay rate of most emissions (SiV, NV^0 and A-band) present in the PCD CL spectrum. Conversely, when the water vapor pressure was increased to 47 Pa (in the absence of a cold trap; 3c), the CL decay rates increased dramatically, resulting in rapid quenching of the entire CL spectrum with electron irradiation time. Furthermore, in this extreme case, an etch pit was clearly visible in electron images of the sample region that had been irradiated by the electron beam. The correlation between H_2O pressure and the CL decay rate is consistent with EBIE because the etch rate scales with precursor adsorbate coverage[28,33] at the diamond surface.

The long term decay of CL emissions ascribed to EBIE is not evident in CL kinetics profiles acquired from bulk, single crystal diamond samples (5a,b). We attribute this to the fact that the EBIE rate of polycrystalline diamond is greater than that of single crystal diamond[27,28] (i.e. etching is most efficient at grain boundaries), and that etching has no significant effect on the thickness of the bulk, single crystal diamond. We note that when the etch rate is low (as in the case of single crystal diamond), etching can be terminated entirely by a competing process of contamination buildup under the electron beam caused by electron induced decomposition of hydrocarbon contaminants that are present in most vacuum systems.[32,35]

The long term decay of CL emissions ascribed to EBIE is also not evident in the H3 CL kinetics profiles acquired from the PCD film (2b) and the microdiamond (5c). In both cases, the H3 CL intensity exhibits an initial decrease followed by an increase with irradiation time, even when etching was observed in electron images taken after electron exposure. The mechanism behind the increase in H3 CL intensity is not understood.

We now turn to the initial increase in NV^0 and A-band CL emission intensities with electron exposure time (see, for example, 3a,b). First, we exclude a number of potential mechanisms that can not explain our results. The electron beam energy (of 20 keV) was well below the threshold for knock-on generation of vacancy-interstitial pairs in bulk diamond.[36,37] Direct generation of vacancies in bulk diamond (through knock-on or electron excitation mechanisms[15,38–41]) is also inconsistent with the data presented in 5b. Such a process is expected to create NV centers in HPHT diamond which contains nitrogen impurities but few vacancies. Similarly, nitrogen diffusion within or into bulk diamond is not supported by our data, which show no indication of a direct relationship between the NV^0 and H3 emissions (H3 centers are associated with nitrogen aggregates[21]), and no change in the NV^0 emission intensity in single crystal diamond.

Electron induced dissociation of residual H_2O adsorbates can, in principle, give rise to oxidation[42] of as-grown, H-terminated diamond surfaces. A change in surface termination from H to O has been shown to switch the charge state of near-surface NV^0 centers, causing an increase the ratio of NV^- to NV^0 centers.[43,44] However, this effect can not explain the increase in NV^0 intensity reported here because the NV^- emission is invisible in CL spectra. Hence, if this process dominated CL kinetics, we would expect a decrease rather than an increase in NV^0 intensity with electron exposure time.

Electron beam heating is negligible[13] because of the high thermal conductivity of diamond, and good thermal contact between the PCD diamond film, the Si substrate and the specimen holder.

The last mechanism that we exclude as the cause of the observed CL kinetics is electromigration[45–48] of point defects in the PCD film. The temperature dependencies seen in 4 show that sample cooling suppressed the magnitudes of the increase in the NV^0 and A-band CL intensities[b]. This behavior is the opposite of that expected for electromigration (since thermal detrapping suppresses the charging effects that cause electromigration[45–48])[c]. The observed temperature dependencies are, however, consistent with thermal restructuring or diffusion of defects in the sample. We therefore suggest that electron beam catalyzed, thermally driven dehydrogenation activates NV and A-band luminescence centers, noting that:

- We expect hydrogen to be present at the grain boundaries and dislocations of the as-grown PCD film, due to the nature of the CVD growth process.[49,50]
- Introduction of hydrogen into a sample containing bright NV centers has been shown to quench NV luminescence.[51]
- The A-band luminescence originates from certain types of dislocations[21] and has been associated with sp2 carbon,[24] which can form upon hydrogen desorption due to the restructuring of dangling bonds.[52]

Removal of hydrogen from NVH_x centers located at or near grain boundaries, and from non-luminescent dislocations is the simplest explanation that is consistent with our CL data, and the aforementioned literature. Electron irradiation likely lowers the energy barrier for thermal dissociation of the hydrogenated complexes, thereby catalyzing the dehydrogenation process.

It is well known that electron beam irradiation in an SEM (and electron injection by a scanning tunneling microscope) can give rise to the dissociation of hydrogenated complexes in several materials.[53–57] In the case of diamond, the dissociation kinetics of boron-hydrogen and boron-deuterium complexes have been characterized by CL analysis, and ascribed primarily to cumulative vibrational (rather than electronic) excitation,[14–17] a process whose efficiency scales inversely with temperature.[17] In contrast, the CL activation process reported here is suppressed by cooling, indicating a different excitation pathway. The data can not, however, be used to deduce the exact nature of the excitation mechanism.

5 Conclusions

To summarize, we observed CL kinetics in a PCD film irradiated by a 20 keV electron beam. The intensities of NV^0, A-band, H3, and SiV CL emissions were shown to change with time. To explain the increases in the intensities of NV^0 and A-band emissions, we propose electron beam induced dehydrogenation of CL centers at dislocations and grain boundaries as a possible mechanism. Our results also show that CL emissions from diamond can be quenched by electron beam induced etching caused by H_2O molecules present in high vacuum CL chambers. This effect is generally undesirable and can be suppressed by minimizing the partial pressure of residual H_2O.

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Notes

[a] We note that, in Fig. 4, the cold trap appears to decrease the NV center activation rate. This effect is not real, and is a consequence of the fact that each spectral CL kinetics profile was normalized (in order to show clearly the changes in each dataset). The absolute change in NV^0 intensity seen in Fig. 4b is much greater than the corresponding change in Fig. 4a

[b] The rapid decay of all CL emissions seen in Fig. 4a is attributed to electron beam induced etching, accelerated by a high coverage of H_2O molecules at the cold diamond surface

[c] Charging effects were minimized by the use of a 20 keV electron beam. The electron range was ~ 3.5 μm, and the beam therefore penetrated through the 400 nm PCD film, into the conductive Si substrate (see Fig. 1)

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Graphical TOC Entry