# NV Formation through Repeated Annealing

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**We report on the observation of an increase in the concentration of negatively charged nitrogen-vacancy (NV⁻) defects in a sample of electronic grade single crystal, chemical vapor deposition (CVD) grown diamond after repeated annealing. The diamond sample is annealed at high temperature and under vacuum. Confocal microscopy is utilized to image the NV⁻ photoluminescence in the same region of the diamond after each anneal cycle. Rotation of linearly polarized 532nm laser excitation is used to record NV⁻ orientation. Comparison of these images allows us to track behavior of each individual NV⁻ center through nine annealing cycles at different temperatures and durations. Analysis reveals total number of NV⁻ in the region, individual appearances, disappearances and orientation changes. We observe a four fold increase in overall density of NV⁻ with no preferential orientation. Accepted theory points to vacancy migration as the source of NV formation. In the absence of extrinsic vacancy incorporation via irradiation prior to annealing, the origin of excess mobile vacancies that could result in increased NV density in our sample is unknown. Such behavior could provide a useful mechanism for increasing NV⁻ density without introducing additional lattice damage.**

## 1. INTRODUCTION

Nitrogen-vacancy centers are point defects in diamond that are promising candidates for quantum sensing as well as quantum information applications because of their long coherence time and optically accessible spin states at room temperature. To form a nitrogen-vacancy (NV) center in diamond, a carbon atom in the lattice is replaced with a substitutional nitrogen atom and an adjacent lattice site is missing a carbon atom (vacancy). An NV is depicted in Figure 1.

We are specifically interested in the negatively charged NV center, NV⁻, which we will refer to as simply NV throughout this paper.

The two primary methods of NV creation in diamond are irradiation followed by annealing[4] and incorporation as unit during chemical vapor deposition (CVD) growth[3]. Our experiment was conducted on an electronic grade single crystal diamond grown via CVD, sourced from ElementSix, a diamond company. It has very low impurity concentration. Material specifications include substitutional nitrogen concentration of less than 0.5 parts per billion. We do not introduce additional lattice damage via irradiation and hence low single vacancy concentration is assumed. All reports of NV formation due to annealing intentionally create vacancies (usually via irradiation) to promote the NV formation process [7].

The work outlined in this paper suggests that this step may not be necessary.

We subjected our diamond sample to multiple annealing cycles and performed confocal microscopy to identify and track each individual NV center in a large experiment volume. Annealing adds energy to the lattice and enables migration of mobile defect species as well as the formation of new species. Accepted theory for NV formation during annealing involves mobile neutral single vacancies trapped by substitutional nitrogen sites. Neutral vacancies are mobile above 700°C. [7].

Nitrogen-vacancies have eight possible orientations, meaning that the vacancy can be positioned one of eight ways relative to the substitutional nitrogen. Rotation of linearly polarized laser excitation enables us to selectively excite a specific subset of NV orientations. The anti-parallel orientations are optically indistinguishable and crystal orientation of our (100) diamond surface allows us to record two subsets of orientations (with two orientations in each subset). Theory suggests annealing could provide a means to control orientation when coupled with strain engineering[6]. Preferential NV orientation would greatly aid many NV applications. Quantum sensing would benefit from the increase in signal-to-noise ratio. Coupling between the NV dipole and cavities could
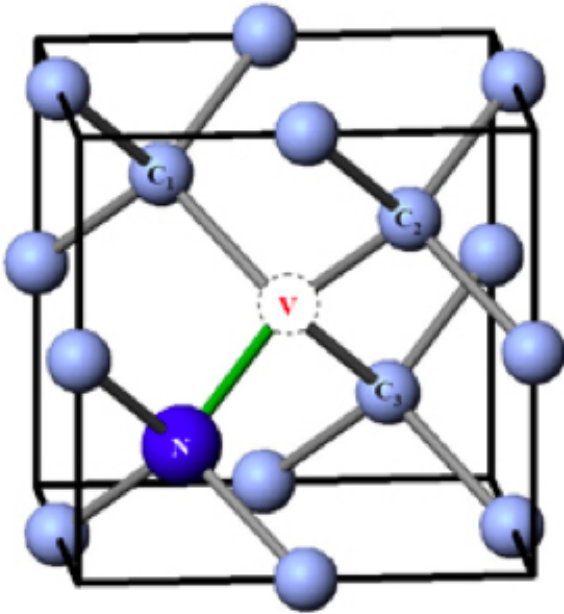
**FIGURE 1.** This images depicts a nitrogen-vacancy center in the diamond lattice.

be optimized facilitating enhanced NV photon emission and collection for quantum information applications.

Thus we were motivated to find a specific anneal temperature and duration to allow for preferential alignment of grown-in NV centers. Based on prior theoretical density-functional calculations, re-orientation involves a vacancy trapped by substitutional nitrogen, mobilizing and migrating to a different lattice site around it's parent substitutional nitrogen. This mechanism is quantified by the reorientation equation shown below

$$R = \nu e^{-\frac{W}{k_B T}}. \tag{1}$$

In Equation (1), $R$ represents the reorientation rate of a nitrogen-vacancy center, $\nu$ is the attempt frequency, $W$ is the energy barrier for reorientation of an NV center and $k_B T$ is related to the thermal energy of each atom. The reorientation rate is linearly dependent on time and exponentially dependent on temperature.

We annealed repeatedly in search of an anneal recipe that would yield preferential orientation of the NV centers. None of the anneal recipes we ran yielded any significant reorientation events, which is clear from comparing Figure 4 to Figure 5. However, we did see an almost four fold increase in overall concentration of NV centers. This result implies a large intrinsic source of mobile single vacancies which we found interesting and became the focus of this work.

The potential for annealing alone to be used for increasing total NV density in a sample could offer a way to increase the number of NVs while keeping the lattice intact. This has applications in ensemble based magnetometry in which a large number of NV centers with preserved quantum properties are required.

## 2. METHODS

### 2.1. Annealing

Our diamond sample is annealed at temperature between 800 and 1000°C in a quartz tube evacuated to $10^{-9}$ mbar to prevent graphitization. The furnace temperature is PID controlled and the ramp time is kept constant (2 hours). Utmost care was taken to prevent contamination. We cleaned the sample in a fuming tri-acid bath (sulphuric+nitric+perchloric acid) maintained at 200°C. Immediately following the clean the sample is transferred to the furnace. We conducted nine anneals in order of increasing temperature. A list of all these anneals can be found in Table 1.

| Anneal | Temp. (°C) | Time (hrs) | Anneal | Temp. (°C) | Time (hrs) |
|--------|------------|------------|--------|------------|------------|
| #1 | 800 | 2 | #2 | 800 | 10 |
| #3 | 950 | 10 | #4 | 960 | 10 |
| #5 | 960 | 10 | #6 | 970 | 2 |
| #7 | 970 | 10 | #8 | 970 | 20 |
| #9 | 980 | 2 | | | |

**Table 1.** This table lists all of the anneal recipes we conducted on the diamond sample in the order in which we conducted them.

Our criteria for deciding the recipe of every subsequent anneal was guided by the number of NV center changes observed in the previous anneal. We increased the anneal temperature by increments of 10°C. A similar experiment performed by our group on a sister diamond sample (unpublished) increased the anneal temperature by increments of 100°C and showed total depletion of NV centers going from 1000°C to 1100°C. The finer temperature increments in the current experiment should allow us to better probe this strange behavior. Most increases in temperature were accompanied by a short 2 hour hold time at the annealing temperature. This short anneal cycle gives us a peek at the NV kinetics. If we did not see many disappearances then we felt comfortable annealing again at that same temperature for a longer period of time.

### 2.2. Confocal Microscopy

After each anneal we used confocal microscopy to image and analyze changes in the NV centers in our diamond sample. We excited the NVs with a linearly polarized 532 nm green diode laser and collected filtered $637-750$ nm NV photoluminescence via a single photon counting module (SPCM). We did not collect $NV^0$ or $NV^+$ photoluminescence. Excitation polarization was rotated with a half-waveplate placed in front of the objective.

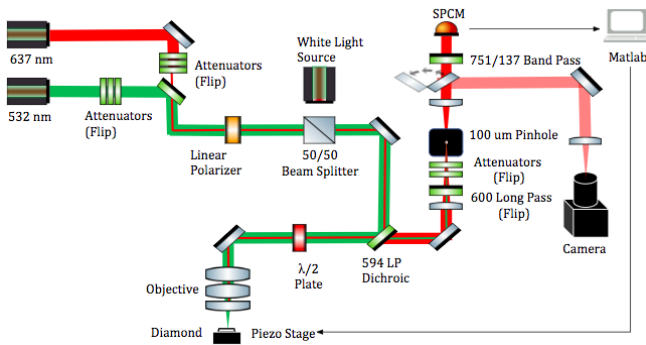To achieve the resolution required for single NV imaging, the diamond sample was placed on a precision

**FIGURE 2.** This is a schematic of our confocal microscope setup.



**FIGURE 3.** This figure shows the same region of a large scan image from two separate "large" scans, before and after the diamond was annealed at $970°C$ for 20 hours. The two scans were compared. The yellow circles indicate where NVs appeared and the red circle indicates where an NV disappeared. The green and purple represent the two different NV classes of orientation we can distinguish.

xyz-nano-positioning piezo stage with a range of $50um$ along each axis. This sat atop a larger micro-positioning stage. In addition to sample piezo stage, the microscope objective was mounted on a piezo z-axis stage with a range of $100um$. This combination gave us a z-axis range of $150um$ which translates to $360um$ after accounting for the refractive index of diamond.

The depth-of-field of the confocal microscope was $10um$ i.e. we could image NV centers in a $10um$ thick plane perpendicular to the $< 100 >$ axis. The size of each confocal scan was limited by the range of our piezo stage, $(50um)^2$. However, we could translate the sample by micrometers, run multiple scans and stitch them to obtain NV data over a much larger area. With this scheme we could locate over eight thousand NV centers in a scan area of $(350um)^2$ by stitching 81 individual piezo scans for each of the two orthogonal excitation polarizations. We set the "large scan" depth to $100um$ from the surface. At this depth the crystal lattice is isolated from extrinsic species, contamination and anomalous surface effects providing an excellently controlled environment for study of NV formation dynamics and kinetics.

In addition to the "large scan" we performed "depth scans", which allowed us to sample the NV density through the vertical cross-section of the diamond sample. A confocal scan, $(50um)^2$, was performed on five different regions in a quincunx pattern with $500um$ spacing. We needed to image NV centers through the entire cross-section ($500um$) of our diamond sample. However, due to limitation of our objective piezo z-axis stage ($100um$ in air; $240um$ in diamond). Two sets of depth scans had to be performed, one starting from the top surface and one starting from the bottom surface of the sample. The data was then collated to characterize NV centers through the full $500um$ depth with images every $10um$. The "depth scans" show the overall trend of NV density change throughout the entire sample in order to ensure that the relatively small area we analyzed with the "large scans"(corresponding to 3% of total diamond surface area) was reasonably representative of the entire sample.
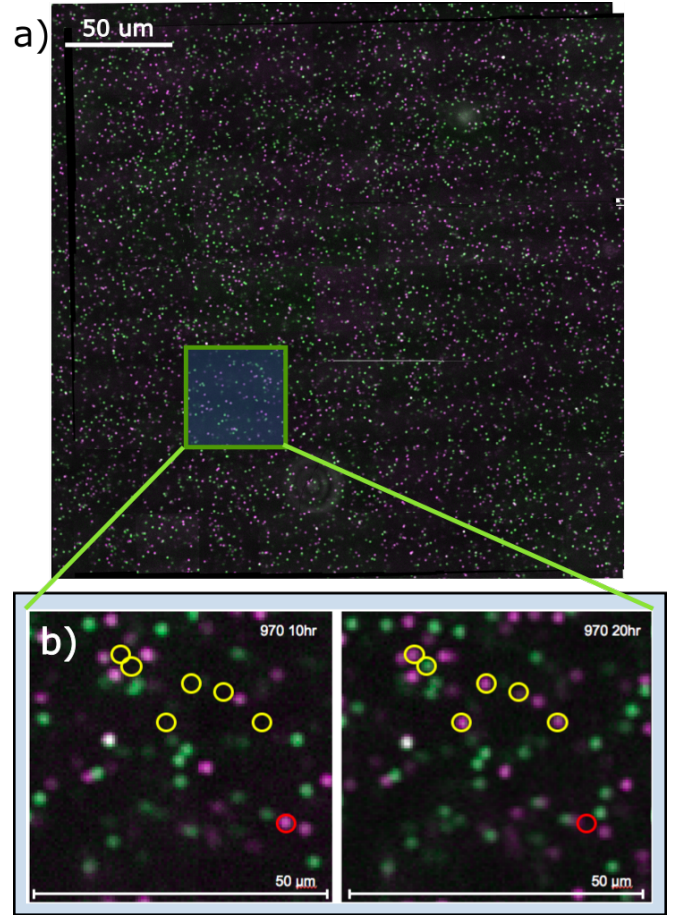
Pre-measurement calibration routines are performed to ensure data consistency. This involves manually locating the corners of the diamond sample while illuminated by a white light source. The corner coordinates serve as a rough guide for image registration of different "large scans". We use the laser reflection off the surface to calibrate the scan depth. This laser reflection measurement is automatically performed for every individual piezo scan in the "large scan" ensuring tilt of the diamond sample does not contribute to anomalies in NV center tracking. Once at scan depth, we optimize the rotation of the half wave plate so that the intensity of the light emitted from one orientation of the NV centers is maximized. This corrects for rotation of the diamond sample relative to the laser excitation polarization.

Every anneal cycle is followed by corresponding "large scan" and "depth scan" data acquisition.

## 2.3. Data processing

We always performed "large scans" in the same region of the diamond at the same depth of $100um$ from the top surface. The intensity of the detected photoluminescence from an NV center is determined by the dot product of the laser polarization axis with the NV symmetry axis. An area is imaged with the half wave plate positioned such that the polarization of the light is optimized to preferentially excite one subset of orientations of NV center. Then the wave plate is rotated $90°$ and the area is scanned again in order to detect the NVs with the orthogonal subset of orientations. Each of the $(50um)^2$ piezo scans were performed for two orthogonal excitation laser polarizations. In the scan images the two orientation subsets are encoded with green and purple coloration.

After acquisition and before data analysis we overlaid the "large scan" composite images with the scan data from the previous anneal. This is done in an image processing tool (GIMP). Image registration aided by persistent luminescent defects and local NV constellations is performed to match NV centers in the "large scan" data sets. Once matched and overlaid, the individual NV appearances, disappearances and re-orientation can be tracked. An example of the comparison process can be seen in Figure 3. The NV changes are recored manually, however the total NV counts per anneal are obtained through image processing algorithm (MATLAB) and validated manually. Figure 3 shows comparison scans of two anneals. The appearances/disappearances are marked in yellow/red. We compiled all of this data into graphs that can be seen in Figures 4 and 5. The total count data from each anneal can be seen in Figure 6.

Data from the "depth scans" are run through an image processing algorithm (MATLAB) to obtain the average NV density for depths from the top surface to the bottom surface with a step of $10um$. The graph of this data can be seen in Figure 7.

## 3. RESULTS AND ANALYSIS

The "depth scan" data in Figure 7 shows an overall increase in the number of NV centers throughout our sample after repeated annealing. It also appears that the rate of increase was higher in the center of the diamond than near the surfaces. This appears to indicate that whatever is causing an increase in NV centers in the sample is more densely concentrated or more likely to happen towards the center of the diamond than near either surface.

Though the changes in the concentration of NV centers in the diamond during each anneal were fairly unpredictable we do notice a few trends in the "large scan" comparisons. For both orientations we observe a significantly larger number of NV center appearances than disappearances after almost every anneal. We also noticed that a spike in disappearances
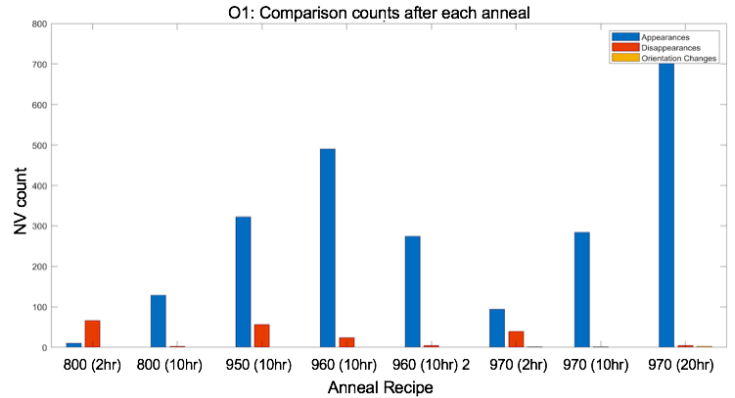


**FIGURE 4.** This is a graph showing the changes in the NVs with orientation one in a small area of the diamond after each anneal. These comparisons and counts were done by hand rather than with a code.
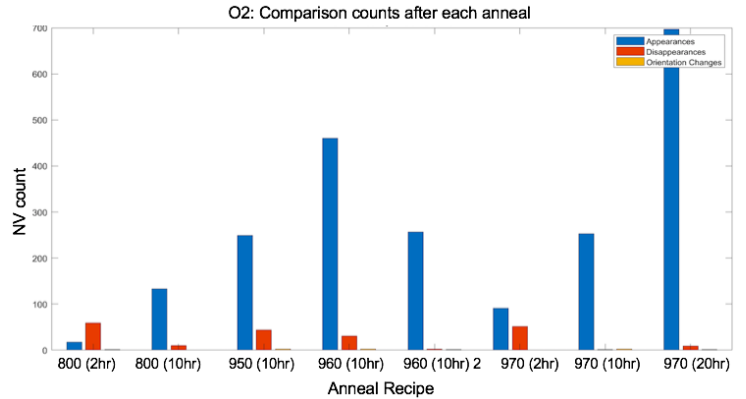


**FIGURE 5.** This is a graph showing the changes in the NVs with orientation two in a small area of the diamond after each anneal. These comparisons and counts were done by hand rather than with a code.

seemed to appear every time we increased the anneal temperature. This implies that the process responsible for the disappearances equilibrates relatively quickly ($<2$ hours). However, extrapolating from the data, we can expect the process responsible for appearances to take much longer to reach thermal equilibrium. This conclusion is supported by two data comparisons. We annealed at $960°$C twice for the same duration and noted that we still found appearances and disappearances after the second anneal but there were significantly fewer than the first cycle. This can be seen in Figures 4 and 5.

We annealed at $970°$C three times, increasing the duration of the anneal each time. The number of appearances continued to increase with each anneal cycle and the number of disappearances spiked a little at the beginning but stayed low in the following two $970°$C anneals. Again, this can be seen in Figures 4 and 5. We could have continued to anneal for longer
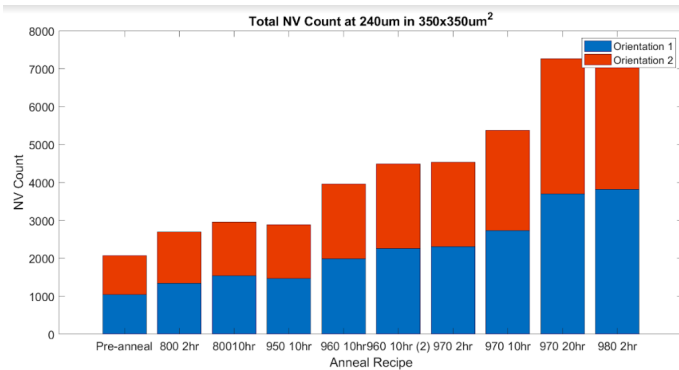
**FIGURE 6.** This is a graph showing the total number of NVs of each orientation after each anneal. These counts were done by a MATLAB code rather than by hand.
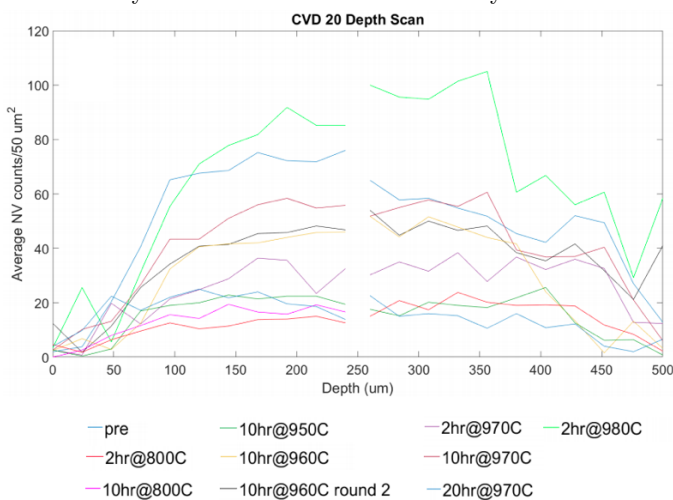


**FIGURE 7.** This graph shows the counts through the entire range of depths in our sample. Each point is the average of the counts in five regions at that depth.

durations until we possibly found a thermal equilibrium at 970°C but instead we decided to continue to increase the temperature for the subsequent anneal cycle.

## 4. DISCUSSION

### 4.1. Possible causes for Appearances and Disappearances

The most surprising and thus interesting thing about our data was the number of appearances. Based on understandings of diamond and NV centers, derived from theoretical analysis as well as experimental evidence, the observation of so many appearances after only annealing is unexpected. We expected to see the density of NV centers stay the same or, if anything, decrease slightly.

This is because there are multiple species of defects that can form in diamond at temperatures we have annealed at which are stable up to high temperatures that we have not annealed at . For example,

divacancies, $V_2$, are composed of two adjacent neutral vacancies and are stable up to 1100°C. Additionally, NVH is composed of an NV with a bonded hydrogen. Hydrogen can get into the diamond lattice without being irradiated or grown in because it is so small. These NVH defects are stable up to 1600°C. $N_2V$ is a defect with an extra nitrogen bonded to an NV and is stable up to 2200°C. NVs are stable up to 1700°C. If a defect is stable up to a certain temperature then we expect them to form and not break apart or move until they are exposed to that temperature. We would expect all of these defects to be forming . This means $NV^-$ could be forming but because of the very low concentration of vacancies to begin with and their limited diffusion range of only about 250 nm it seems unlikely that we would see so many new NVs continuing to appear. Their formation should be self-limiting as the number of single vacancies decreases. Our microscope setup is only sensitive to $NV^-$ so if any other species attaches to an NV, such as a hydrogen atom or another nitrogen atom then the NV will no longer be visible to us.

### 4.2. Error

The main source of possible errors in our data came from not being able to accurately compare sequential large scan images. Often small sections of the large scan image would not match up when we overlaid them. This was likely because some areas had not been stitched together properly or the red laser optimized to a slightly different depth in some areas. The overlay could also not match up because the diamond surface can change slightly during the clean and anneal process, causing the overlay images to be a few microns apart in the xy direction. There was also micro and piezo drift of less than 1 micron per hour. This meant that some sections of the scan would not be able to be compared and this affected the comparison counts. We also did the comparison counts by hand which likely caused some error.

The total counts, shown in Figure 6, were done with a MATLAB code. However, some of the images were slightly clearer or more contrasted than others which affected the code's ability to count accurately. To combat this we changed the sensitivity but there was still likely some error.

## 5. CONCLUSIONS

We showed that repeatedly annealing a sample of single crystal CVD diamond between 950°C and 980°C can result in an increase in the concentration of nitrogen-vacancy centers.

This is potentially useful for sensing applications because annealing does not cause damage to the diamond lattice. Previous work with nitrogen-vacancy centers has shown or suggested that increasing nitrogen-vacancy center concentration in a pre-existing diamond

sample is not possible without irradiation, which causes a significant amount of damage to the diamond lattice.

Increasing the concentration of NV centers by only annealing could be a useful shortcut to getting a lot of nitrogen-vacancy centers that are useful for sensing into a sturdy, minimally damaged diamond sample.

To determine whether or not repeated annealing is a viable way to increase NV concentration in diamond we would need a lot more data. Our findings could be sample dependent. Repeated annealing could have drastically different effects on another diamond sample.

To further this work it would be helpful to perform the same series of anneals on multiple diamond samples with similar initial conditions. It would also be useful to continue to anneal at higher temperatures. We suspect and other work shows that NVs will start disappearing but this would also be a surprising and interesting result. We would also like to do a scan for NV(0) because we suspect that if it is present it could be playing a role in the appearance trend we see. A GR1 scan for vacancies could also offer useful insight. Maybe we have more vacancies than we think we do.

It would be especially insightful to increase anneal duration as much as necessary to achieve saturation at each temperature. From this we would learn if we are observing an increase of NVs due to kinetics before a decrease or if we are really going to thermal equilibrium.

Essentially, future work would entail more data on more samples with different anneal recipes and progressions.

## 6. ACKNOWLEDGEMENTS

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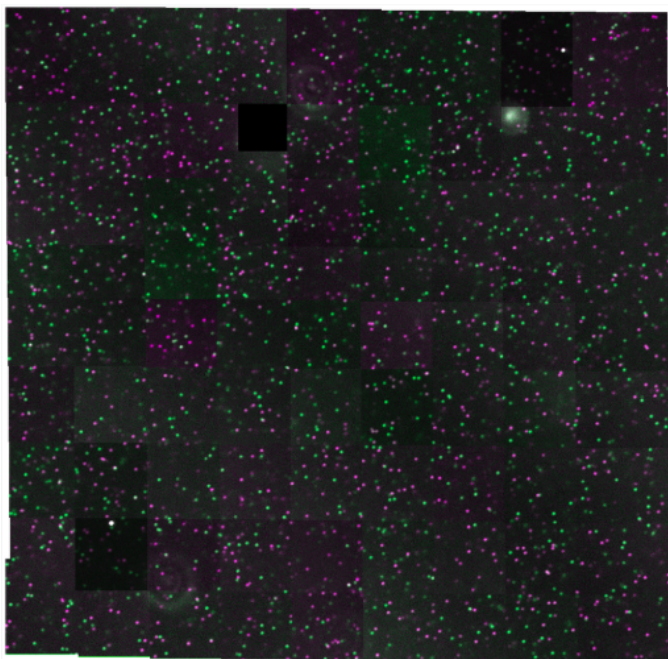
## APPENDIX A.



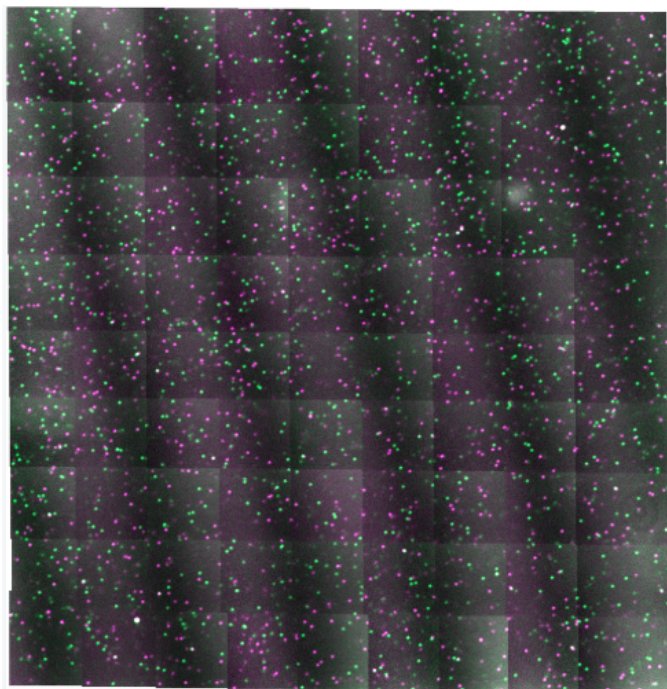**FIGURE A.1.** This is the large scan image performed before the sample was annealed.



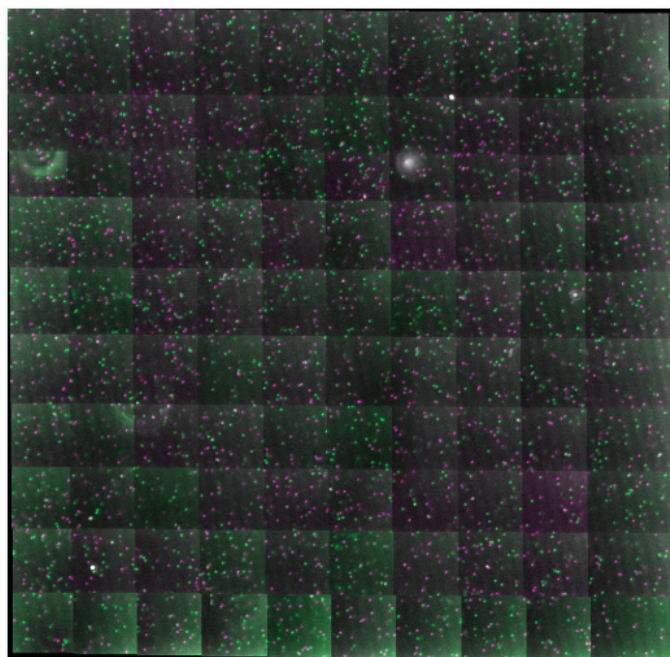**FIGURE A.2.** This is the large scan image performed after the sample was annealed at 800° for 2 hours.



**FIGURE A.3.** This is the large scan image performed after the sample was annealed at 800° for 10 hours.
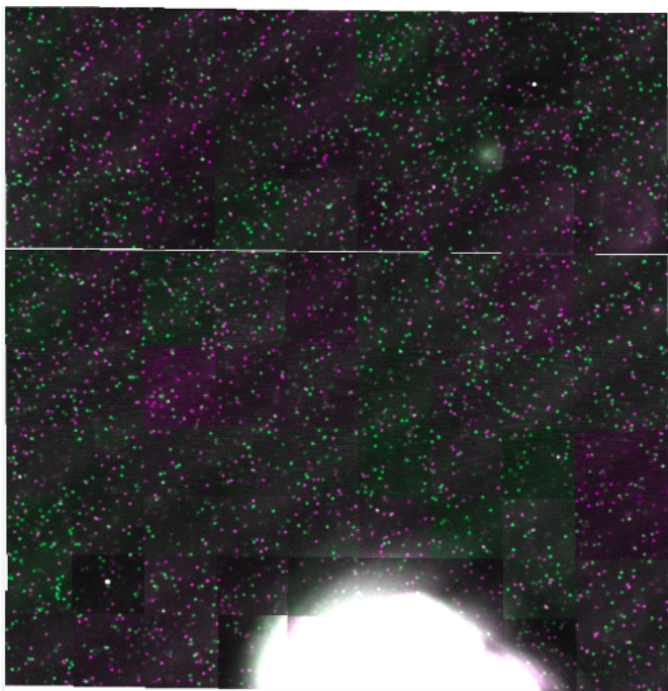
**FIGURE A.4.** This is the large scan image performed after the sample was annealed at 950° for 10 hours.
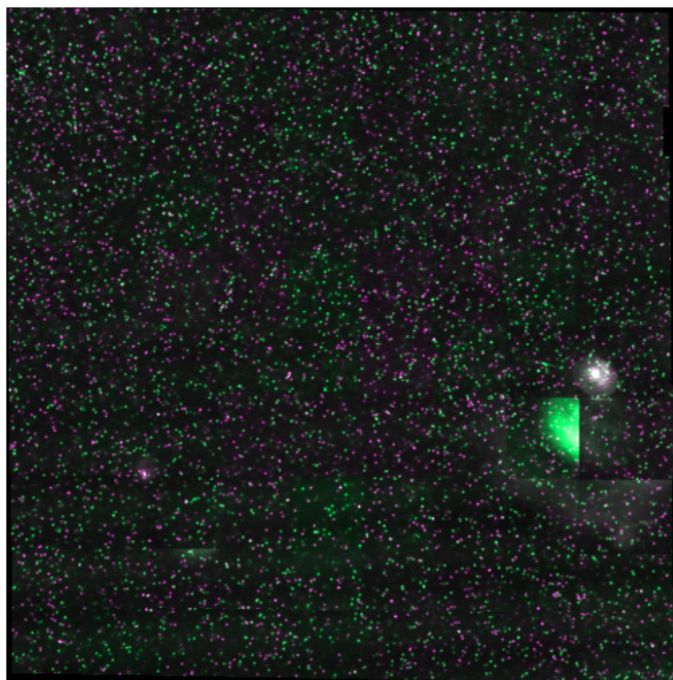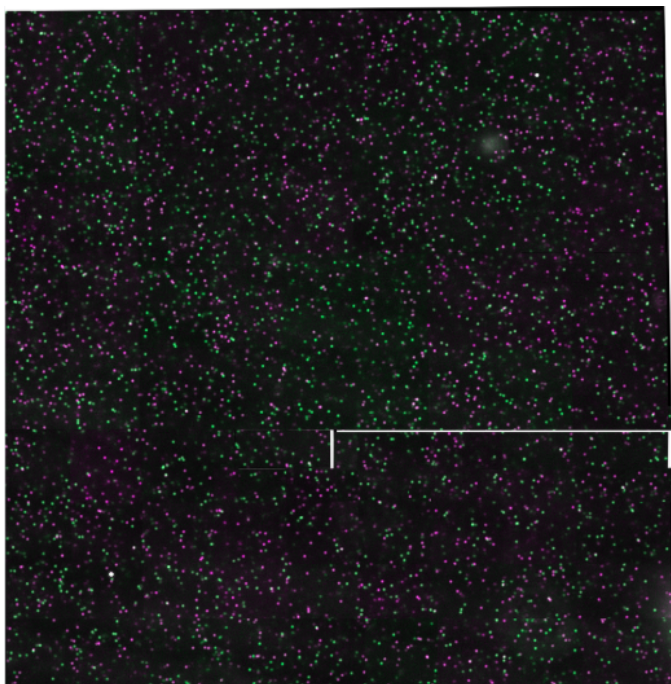


**FIGURE A.6.** This is the large scan image performed after the sample was annealed again at 960° for 10 hours.



**FIGURE A.5.** This is the large scan image performed after the sample was annealed at 960° for 10 hours.
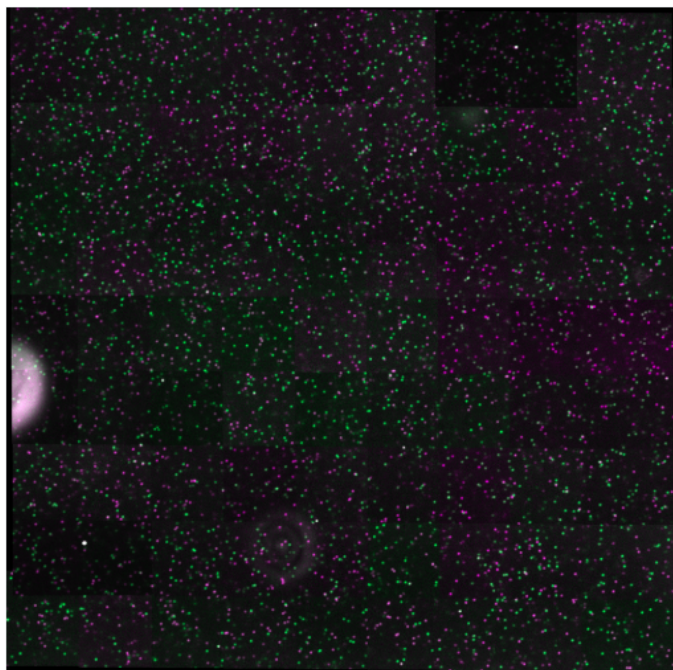


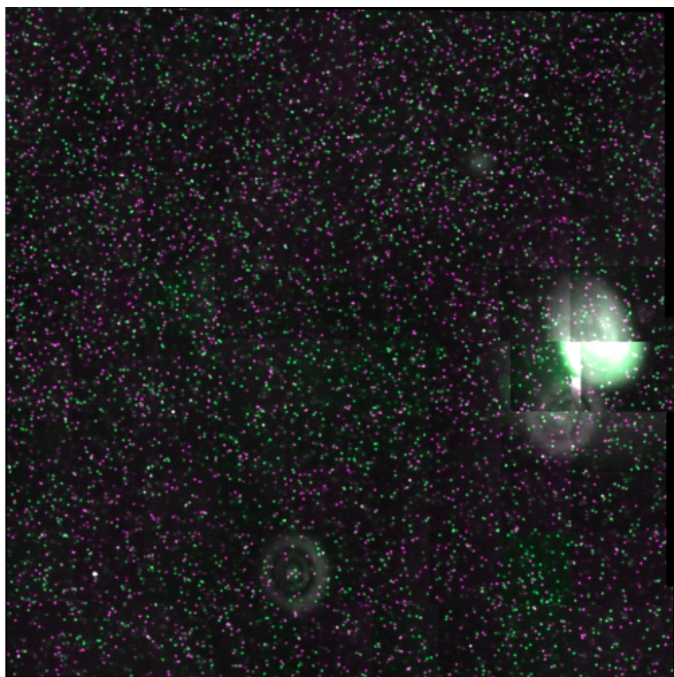**FIGURE A.7.** This is the large scan image performed after the sample was annealed at 970° for 2 hours.

**FIGURE A.8.** This is the large scan image performed after the sample was annealed at 970° for 10 hours.
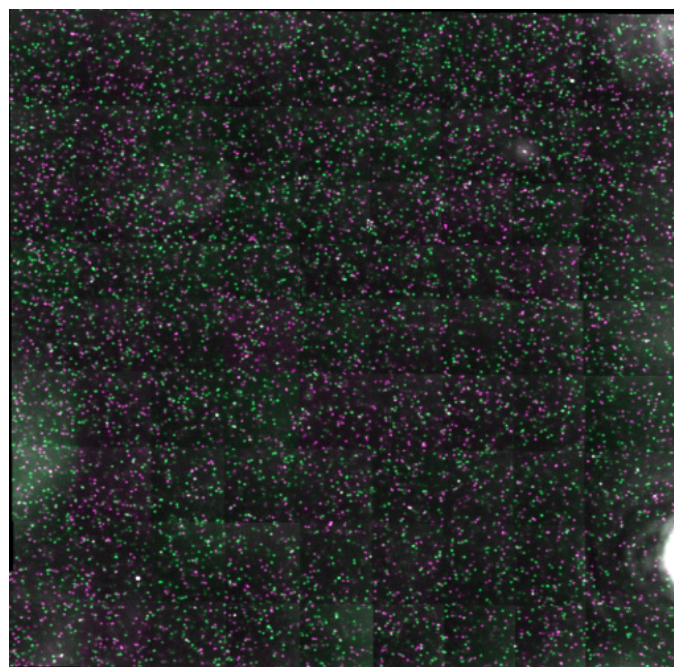


**FIGURE A.10.** This is the large scan image performed after the sample was annealed at 980° for 2 hours.
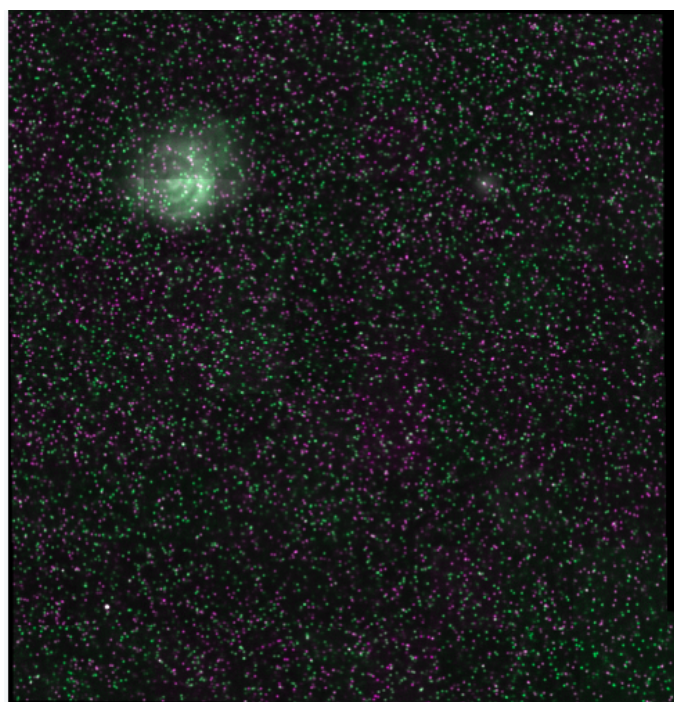


**FIGURE A.9.** This is the large scan image performed after the sample was annealed at 970° for 20 hours.