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Efficient generation of nitrogen vacancy centers by laser writing close to the diamond surface with a layer of silicon nanoballs

Youying Rong[1], Zhiping Ju[1], Qiang Ma[1], Shikang Liu[1], Chengda Pan[1], Botao Wu[1], Si Shen[1] and E Wu[1,2,3]

[1] State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, People's Republic of China
[2] Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China
[3] Joint Institute of Advanced Science and Technology, East China Normal University, Shanghai 200062, People's Republic of China

E-mail: ewu@phy.ecnu.edu.cn

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Abstract

We proposed a method to effectively fabricate negatively charged nitrogen vacancy (NV^-) centers close to the diamond surface by applying femtosecond laser writing technique. With a thick layer of silicon (Si) nanoballs coated, diamond surface was irradiated by high-fluence femtosecond laser pulses. A large number of NV^- centers were created around the laser ablation crater area without thermal annealing. The distribution of the NV^- centers was expanded to about 50 μm away from the crater center. To demonstrate the function of Si nanoballs, we performed the exactly same laser illumination process on the bare region of the sample surface. In this case, only a few NV^- centers were generated around ablation crater. At distance of 32 μm away from crater centers, the NV^- density for the case with nanoballs was up to 15.5 times higher compared to the case without nanoballs. Furthermore, we also investigated the influence of laser fluence and pulse number on the NV^- density for the case with Si-nanoball layer. Finally, the formation mechanism of NV^- centers and the role of Si nanoballs were explained via Coulomb explosion model. The method is demonstrated to be a promising approach to efficiently and rapidly fabricate NV^- centers close to the surface of the diamond, which are significant in quantum sensing. Furthermore, the results provide deep insights into complex light-matter interactions.

1. Introduction

Wide-bandgap diamond crystal hosting optically active color centers attracts researchers' attention as an exceptional quantum platform. The material also holds features of bio-compatibility and robustness in chemical environment [1, 2]. There are more than 500 luminescent centers in diamond [3, 4]. Among these color centers, NV^- center is the most extensively investigated photon emitter, which consists of a substitutional nitrogen and an adjacent lattice vacancy [5]. NV^- centers are one of the most promising candidates for applications in elementary quantum optics [6], quantum information processing [7] and biomarker [8] due to their stably bright photoemission under ambient environment. Especially, remarkable electron spin properties of NV^- centers make them prominent in quantum metrologies for sensing variation of magnetic fields, electric fields, and temperature [9–11].

An intense effort has been made for the efficient fabrication of NV^- centers. Usually, NV^- centers are generated by doping nitrogen impurities during diamond growth applying chemical vapor deposition (CVD) technique, implanting ionized nitrogen into diamond or electron irradiation [12–15]. By these methods, highly pure or precisely positioned NV^- centers could be obtained. In recent years, femtosecond laser technique is exploited as a newly promising tool to conveniently produce single emitters in diamond [16–22]. The femtosecond laser is used to write vacancies through high-speed electron beam in air filament resulted by high-intensity laser pulses [16] or multi-photon ionization [17, 18]. Vacancies move to native nitrogen impurities in diamond under thermal annealing [16, 18, 20–22] or driving of laser pulses [17, 19] to form single or ensemble

NV^- centers. Especially, combined with aberration correction, femtosecond laser could write high-quality NV^- centers effectively at desire positions [18–20].

In this paper, we put forward another scheme to rapidly and efficiently fabricate NV^- centers by illuminating femtosecond laser on diamond surface, on which a layer of Si nanoballs was coated. For comparison, the same operation was performed in a bare region on diamond surface without Si nanoballs. We show that NV^- centers in the case with nanoballs were produced more efficiently. While high-energy femtosecond laser irradiated on Si nanoballs, on the one hand, extra vacancies could be created in diamond as Si elements were implanted into diamond via Coulomb explosion. On the other hand, local high temperature ensuing from the Coulomb explosion made the vacancies move to nitrogen impurities. Therefore, more NV^- centers would be formed compared to the case without nanoballs.

2. Methods

The sample used here was a high purity CVD bulk diamond (Element Six Ltd) with nitrogen concentration [N] $<$ 5 ppb. Before femtosecond laser irradiation, fluorescence images near the diamond surface were scanned under excitation of 532 nm laser at pre-written regions, where fluorescent emitters were scarcely observed. Subsequently, the diamond was cleaned in a mixture of sulfuric acid and 30% hydrogen peroxide (3:1) for 10 min. Si nanoballs with average diameter of 46 nm were dispersed uniformly as much as possible in ultrapure water after >30 min sonication. The nanoball solution was firstly spin-coated on the cleaned diamond surface at a low speed of ~1200 r m^{-1} to make the solution expand to the whole diamond surface. The coated sample was then kept in the ambient environment to vaporize the water naturally. A thick layer (>1 μm) of silicon nanoballs was finally coated on the diamond surface.

After nanoballs coating, 800 nm laser pulses with 50 fs pulse duration and 1 kHz repetition rate were focused by an air objective ($\times$100, NA $=$ 0.9) on the coated diamond surface. With a concave lens ($f = -150$ mm) above the objective, the diameter of the focal spot was ~28 μm. At the focus point, the average power of femtosecond laser was tuned from 5 to 20 mW. Correspondingly, the peak intensity and the fluence varied from 1.6×10^{13} to 6.5×10^{13} W cm^{-2} and 0.8 J cm^{-2} to 3.2 J cm^{-2}, respectively. The laser pulses near the focus point were intense enough to cause the multi-photon ionization and tunneling ionization of molecules in air [23] and the Coulomb explosion of Si [24]. The latter is a fundamental process leading to the fast ejection of positive ions. The created ions will be implanted into diamond. For each laser fluence, three craters were created with laser pulse numbers of 10, 30 and 50, respectively. For comparison, the laser illumination was repeated on a bare region after erasing away the Si-nanoball layer with optical cleaning tissues soaked with ethanol. After the illuminations, the diamond sample was cleaned in the ultrasonic bath of acetone to remove surface contaminants.

After the treatments, a copper wire with 20 μm diameter was soldered on the diamond surface to provide microwave radiation for optically detected magnetic resonance (ODMR) measurements. A confocal microscopy was built to characterize photoluminescence (PL) of bright spots near the laser-created craters [25, 26]. The diamond sample was mounted on a three-dimensional *XYZ* translation stage. A continuous-wave laser at 532 nm was used to excite the emitters in the diamond through an oil immersion objective ($\times$100, NA $=$ 1.4), which was also used to collect the fluorescence emitted from the emitters. After filtering spatially and spectrally, the fluorescence was either guided into a spectrometer (Acton Research Corporation, SpectraPro-300i), or split into two beams by a polarization beam splitter (PBS) and detected by two avalanche photodiodes (APDs, Perkin Elmer, SPCM-AQR-14) on each side. These two APDs were then connected to a time-correlated single photon counting module, i.e. to form a Hanbury Brown and Twiss (HBT) interferometer, to measure second-order autocorrelation function of fluorescence from the bright emitters.

3. Results and discussion

Right after the femtosecond laser processing, fluorescence images around the irradiated areas were scanned by the APD at the transmitted port of the PBS to detect the generation of NV^- centers. The power of the excitation laser at 532 nm was about 160 μW. Under the interaction of high-intensity femtosecond laser, ablation craters were created. No NV^- centers were observed inside the craters. Figures 1(a) and (b) show two 50 $\times$ 50 μm^2 images around the ablation craters irradiated when the Si-nanoball layer was on and off the diamond surface, respectively, at femtosecond laser fluence of 3.2 J cm^{-2} and pulse number of 50. For both cases, bright emitters were formed in the vicinity of the craters. Almost all (>90%) of the stable emitters were identified to be NV^- centers by spectral measurements and as the distance away from the crater centers increases, the density of the NV^- centers decrease. Apparently, NV^- centers in figure 1(a) were created more efficiently with the interaction of Si nanoballs. Figure 1(c) presents characteristic PL spectrum of NV^- centers around the craters.

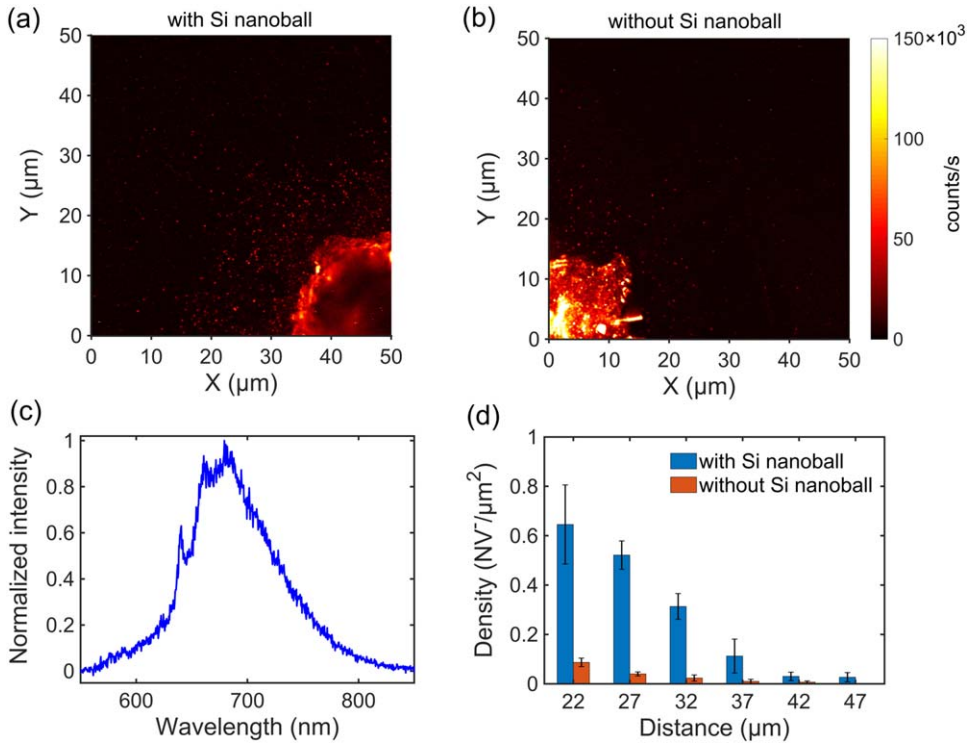

Figure 1. *X*–*Y* surface scanning fluorescence images of 50 × 50 μm^2 area around the craters irradiated (a) with and (b) without Si-nanoball layer. For both cases, laser fluence and pulse number of femtosecond laser were 3.2 J cm^{-2} and 50, respectively. Excitation power of green laser was ~160 μW. (c) Typical spectrum of NV^- centers in vicinity of the two ablation craters. (d) Histograms of NV^- density for increasing distances away from crater centers compared with the results for the craters in (a) and (b).

To quantitatively illustrate the difference between the two cases in figures 1(a) and (b), we statistically measured three individual sets of number of created NV^- centers in a 5 × 5 μm^2 area around each crater, as a function of distance d away from the crater centers. Here, we defined NV^- density as the number of NV^- centers divided by the scanning area in two-dimensions. Figure 1(d) presents the relationship of the average NV^- densities and the distance for the two cases. In the case with Si nanoballs, the distribution range of NV^- centers is extended up to 47 μm, while the range is about 42 μm in the case without Si nanoballs. At $d = 32$ μm, the average NV^- density in the case with Si nanoballs (0.31 μm^{-2}) is 15.5 times higher than that in the case without Si nanoballs (0.02 μm^{-2}). These results indicate that more NV^- centers were produced due to the existence of the Si nanoballs. Because of the Coulomb explosion caused by intense laser pulses, Si^+ ions ejected from nanoballs were implanted into the diamond creating extra vacancies. Then these vacancies moved to immobile nitrogen elements to form more NV^- centers under the high temperature arising from Coulomb explosion of Si.

To investigate the effect of femtosecond laser fluence and pulse number on the generation of NV^- centers with the Si-nanoball layer, we estimated the average NV^- density at different pulse number for four different laser fluences at $d = 22$ μm, and found that the average NV^- density decreases with pulse number and fluence decreasing as shown in figure 2. However, the density is almost zero at 0.8 J cm^{-2} fluence and 1.6 J cm^{-2} fluence with 10 pulse number, which can still trigger the Coulomb explosion of Si theoretically. We attribute it to that less nitrogen and silicon ions were generated with lower kinetic energy under the lower laser fluence or pulses number. The ions could not manage to penetrate the thick layer of nanoballs into diamond. Therefore, NV^- centers could not be formed due to the absence of vacancies.

To demonstrate the ability to write single NV^- centers in diamond by femtosecond laser, we scanned a 5 × 5 μm^2 area about 27 μm away from the center of crater irradiated with 50 laser pulses of 3.2 J cm^{-2} fluence with Si-nanoball layer. Figure 3(a) shows scanning fluorescence image of the area with ~160 μW excitation power. The number of NV^- center was confirmed to be about 13. In addition to PL spectrum characterization, the generated NV^- centers could also be identified through ODMR measurement at zero magnetic field. Figure 3(b) plots the fluorescence from the emitter (S) marked in figure 3(a) as a function of the scanning microwave frequency under excitation of the green laser. By a Lorentzian fitting, the single dip at 2.877 GHz demonstrates it is a NV^- center. Photon correlation function of the NV^- center (S) is displayed in figure 3(c) with the excitation power of 345 μW. Fluorescence intensities of the NV^- center from each APD in the HBT interferometer were 64.6 × 10^3 and 66.7 × 10^3 counts s^{-1} with background of 1.6 × 10^3 and 4.2 × 10^3 counts s^{-1}, respectively. The dip value at zero delay in the autocorrelation curve approaches zero, revealing its

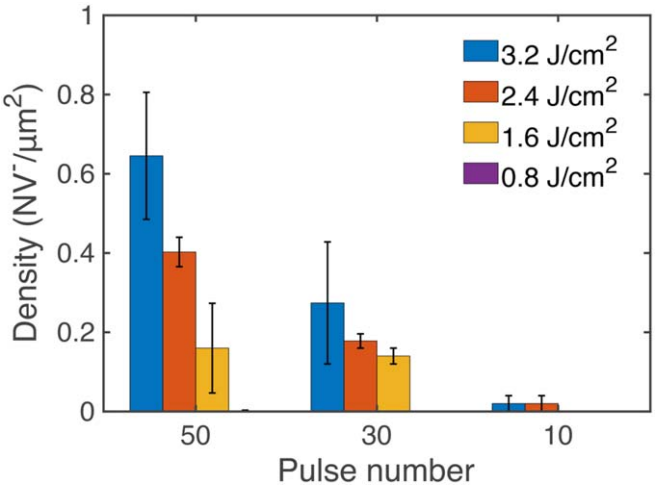

Figure 2. NV^- density versus fluence and pulse number of femtosecond laser at $d = 22$ μm in the case with Si-nanoball layer.

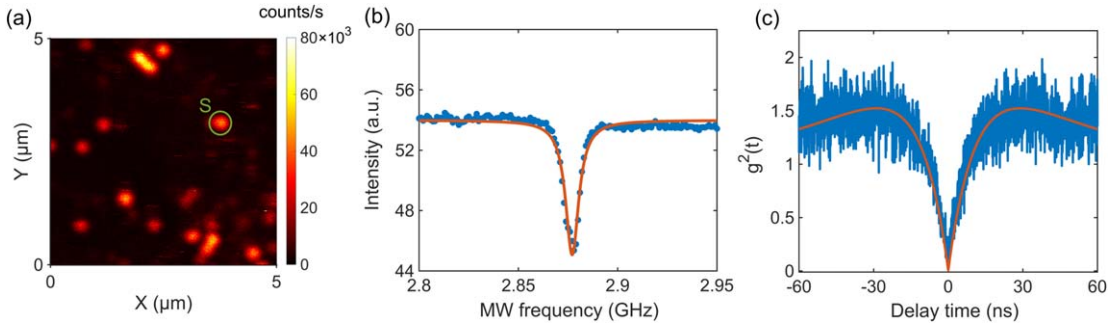

Figure 3. Single NV^- center in diamond generated by femtosecond laser illumination. (a) *X*–*Y* surface scanning fluorescence image of the area 27 μm away from crater center for diamond surface coated with Si-nanoball layer. The crater was ablated at 3.2 J cm^{-2} fluence and 50 laser pulses. (b) ODMR spectrum of emitter (S) marked with green circle in (a) at zero magnetic field. The characteristic single dip at 2.877 GHz reveals NV^- center. (c) Second-order autocorrelation curve of fluorescence from the NV^- (S) with excitation power of ~345 μW. The deep dip at zero delay shows single photon emission. Integration time for the measurement was 250 s and time bin of TCSPC electronics was 64 ps.

quantum emission property. The measured data are fitted by the autocorrelation function

$$g^2(t) = 1 - (1 + a)e^{\left(-\frac{t}{\tau_1}\right)} + ae^{\left(-\frac{t}{\tau_2}\right)}, \quad (1)$$

where t is delay time, τ_1 is fluorescence lifetime, and a, τ_2 are related to the interlevel rate constants. We obtained that the fluorescence lifetime of NV^- center 'S' was about 11.8 ns, in agreement with the typical fluorescence lifetime of NV^- centers in bulk diamond. The NV^- center was stable during the whole measurements. Single NV^- centers could also be observed in the vicinity of crater written without Si nanoballs.

Considering that the Si nanoballs were coated on the surface of the diamond and fs laser was also focused only on the surface, we expected the created NV^- centers might locate near the sample surface. Here, we applied an optical method proposed in [27] to evaluate the depth of the single NV^- center 'S' marked in figure 3(a). One of the two APD in the confocal microscope was used to detect the reflected excitation laser from the diamond surface. Meanwhile, the other APD was to monitor the fluorescence from the NV^- center 'S'. Then we performed depth scans along the *Z* axis by these two APDs at a range of 2.5 μm. Figure 4 presents signals from the reflected laser and the fluorescence in a single scan. The depth could be evaluated by the difference between the two maximum positions of Gaussian-shape curves of the reflected laser and the fluorescence. By Gaussian fitting, the maximum positions were located at 1.046 μm and 1.171 μm for the reflected laser and fluorescence, respectively. So the depth of the NV^- center 'S' was evaluated to be about 125 nm. By the same way, we measured the depths of another six laser-created single NV^- centers, which were evaluated to be 9 nm, 38 nm, 57 nm, 95 nm, 118 nm and 133 nm, respectively.

To get the coherence time of laser-writing color centers, Hahn echo measurements were performed on three different single NV^- centers in the vicinity of the crater irradiated by 50 laser pulses with 3.2 J cm^{-2} for the case

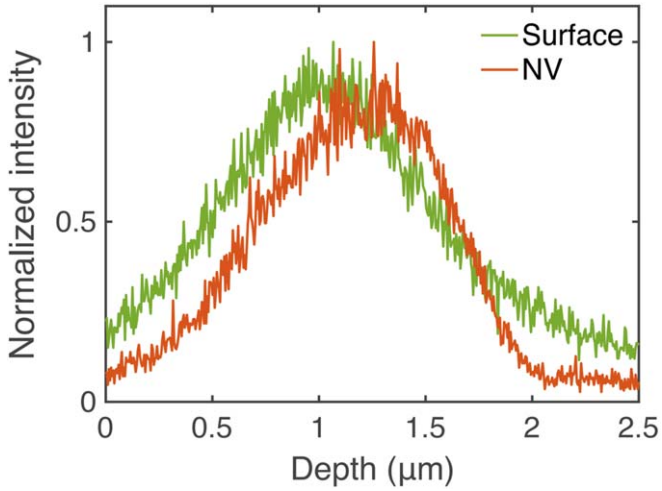

Figure 4. Signals of the excitation laser reflected by diamond surface (green) and fluorescent light emitted from single NV^- center 'S' (red) in a single scan along Z axis.

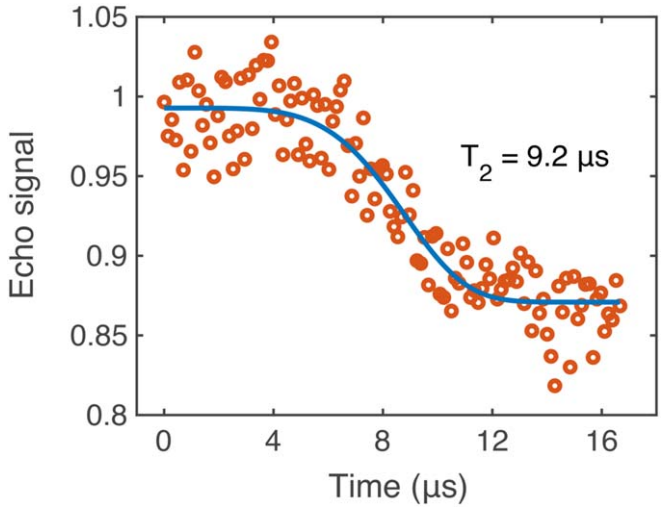

Figure 5. Electron spin coherence time of laser-writing NV^- center.

with Si nanoballs before annealing. An external magnetic field of 2.3 mT was applied and adjusted along the NV axis. The echo signals were fitted with the function

$$I(\tau) = y_0 e^{[-(\tau/T_2)^n]} + y_1, \quad (2)$$

where y_0, y_1 and T_2 are fitting parameters and n is a free parameter. The electron spin coherence times (T_2) were obtained to be 1.23 μs, 1.32 μs and 9.2 μs, respectively. Figure 5 shows the T_2 of one of the three single NV^- centers with $T_2 = 9.2$ μs.

To figure out the formation mechanism of NV centers and the role of the Si nanoballs playing in the generation of NV^- centers, the diamond sample was annealed at 850 °C in vacuum for 1 h. Figures 6(a) and (b) show the X–Y scanning fluorescence images of the same area before and after annealing, respectively. The area was about 24.5 μm away from the crater center irradiated by 50 laser pulses of 3.2 J cm^{-2} fluence with Si nanoballs coated. After annealing, the number and the PL intensity of NV centers increased dramatically. Figure 6(c) displays a X–Z depth scanning fluorescence image at a Y position denoted by a green dashed line in figure 6(b) after annealing. In figure 6(c), the Z axis presents the focal position of focused excitation laser and the green dashed line indicates the diamond surface. All the laser-created NV^- centers are located near the diamond surface.

To shed light on the formation of the NV^- centers, the diamond was excited by continuous laser at 662 nm to suppress fluorescence emission of NV^- centers. Negatively charged silicon vacancy (SiV^-) centers were observed around the craters after annealing [28], demonstrating that Si atoms were implanted into diamond via

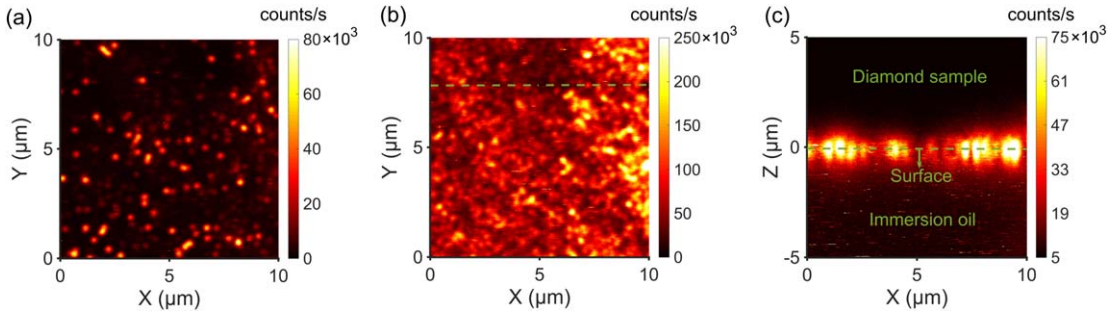

Figure 6. *X*–*Y* surface scanning fluorescence images of the same area 25 μm away from the center of crater irradiated by 50 laser pulses of 3.2 J cm^{-2} fluence (a) before and (b) after thermal annealing. (c) *X*–*Z* depth scanning fluorescence image at a position marked by the green dashed line in (b). The diamond surface is indicated by the green dashed line.

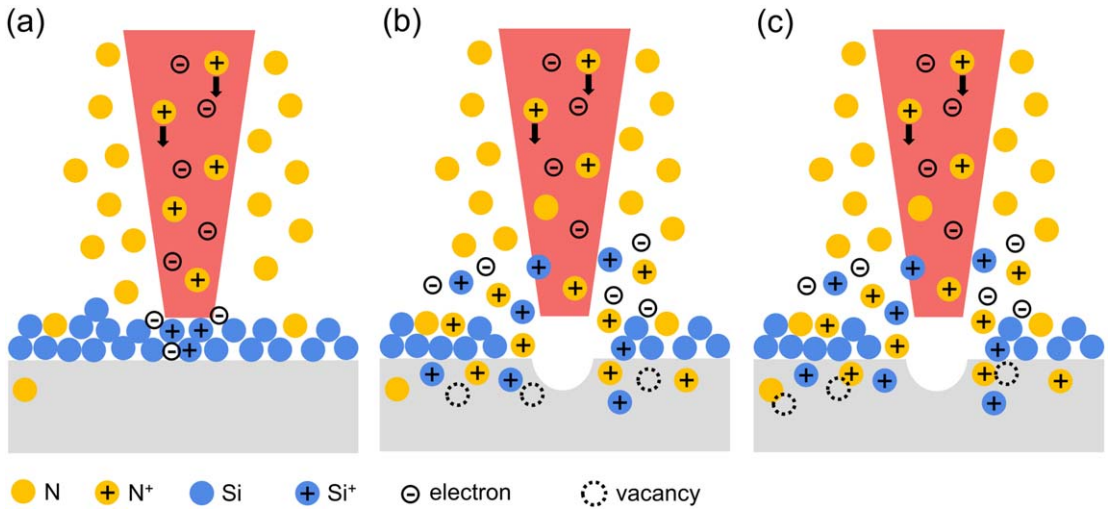

Figure 7. Femtosecond laser irradiation on diamond coated with a layer of Si nanoballs. (a) High-fluence laser ionized nitrogen atoms in air and made electrons eject fast from Si nanoballs. (b) Coulomb explosion of Si was triggered with Si^+ ions accumulating until bonds among ions were broken, resulting in ejection of Si^+ ions out of nanoballs in random directions. A part of N^+ and Si^+ ions with high kinetic energy impinged into diamond accompanied with creation of vacancies. (c) Vacancies diffused under high temperature ensuing from the Coulomb explosion to combine with nitrogen impurity, forming NV^- centers.

Coulomb explosion. Before the thermal annealing, no SiV^- centers were observed under excitation of 662 nm laser, because their unique atomic structure with Si atom in the middle of two adjacent lattice vacancies made them harder to form than NV^- centers. The formation mechanism of NV^- centers written by femtosecond laser is depicted in figure 7. It could be described as follows. Firstly, when the high-fluence ultrafast laser pulses was delivered to the Si nanoballs on diamond surface, electrons were ejected fast from the irradiated region at the initial period. And nitrogen atoms in air were also ionized and accelerated along laser propagation direction as shown in figure 7(a). Then, as Si^+ ions accumulated in the irradiated area, the Coulomb repulsive force became more and more intense until it broke bonds among Si^+ ions, triggering Coulomb explosion of Si and leading to fast ejection of Si^+ ions out of the nanoballs with high kinetic energy in all directions as shown in figure 7(b). Some of the N^+ ions would change their propagation direction due to collision with the ejected Si^+ ions. A part of N^+ and Si^+ ions with high velocity impinged into the diamond and knocked off carbon atoms at lattice sites to create vacancies like conventional ion implantation technique. In the end, the local high temperature ensuing from the Coulomb explosion [29] around the ablation craters diffused the created vacancies to combine with nitrogen elements forming NV^- centers as shown in figure 7(c). It is believed that nitrogen atoms in NV^- centers came from the native nitrogen impurity in diamond and nitrogen atoms in air. In contrast to the case with Si-nanoball layer, much less vacancies were created in the region irradiated without Si nanoballs due to the lack of Si^+ ions implantation, thus reducing greatly the generation of NV^- centers. All of the generated NV^- centers were observed near the diamond surface, which was crucial for their applications in quantum metrology due to the sensibility to changes in external environment.

4. Conclusion

In summary, we have shown that by applying femtosecond laser writing technique, NV^- centers could be efficiently and conveniently produced on an ultrapure diamond surface coated with a layer of Si nanoballs without annealing. Under the interaction of the high-intensity laser pulses, the Coulomb explosion of Si was triggered, resulting in fast ejection of Si^+ ions in random directions. A part of Si^+ ions with high kinetic energy impinged into diamond and knocked off carbon atoms in lattice sites to create vacancies. Compared to the region without nanoballs, more vacancies were created in the area with nanoballs. Moreover, high temperature induced by the Coulomb explosion made the vacancies move to form more NV^- centers. The results demonstrate the femtosecond laser writing introducing nanoballs is an alternative option to generate NV^- centers effectively and fast near the surface of the diamond sample. It may be adapted to fabrication of color centers in other materials like silicon carbide.

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