Abstract

Optically active spin defects in wide-bandgap materials have gained wide-spread attention as photonic systems for potential applications in quantum information and quantum sensing. Spin defects in two-dimensional van der Waals materials are just emerging to be investigated. Here we demonstrate that optically-addressable spin
Defects in hexagonal boron nitride (hBN) can be generated deterministically by femtosecond laser irradiation. We observe optically detected magnetic resonance (ODMR) of hBN spin defects created by laser irradiation. We show that the creation of spin defects in hBN is strongly affected by the pulse energy of the femtosecond laser. When the laser pulse number is less than a few thousand, the pulse number only affects the density of defects but not the type of defects. With proper laser parameters, spin defects can be generated with a high probability of success. Our work provides a convenient way to create spin defects in hBN by femtosecond laser writing, which shows promising prospects for quantum technologies.

Keywords: Spin defects, laser writing, hexagonal boron nitride, 2D materials

Main

Electron and nuclear spins in wide-bandgap materials offer promising platforms for studying quantum spintronics, and have many applications in quantum sensing and other quantum information technologies. The leading candidates such as nitrogen-vacancy (NV) centers in diamond exhibit room-temperature, spin-dependent photon emission that facilitates initialization and readout of spins. Inspired by the breakthrough in graphene and other two-dimensional (2D) van der Waals materials, a long-sought goal in the field had been to create similar spin qubits in 2D materials that can be initialized and read out optically.

In this context, hexagonal boron nitride (hBN) is important as it has a wide bandgap and can host high-quality emitters. Single-photon emissions above 800 K have been observed with quantum emitters in hBN. Due to their 2D geometry, hBN nanosheets can be readily integrated with other 2D materials, providing platforms for integrated nanophotonics. Spin qubits in hBN nanomechanical resonator will also be ideal for investigating spin optomechanics. Thanks to the low mass of a 2D hBN mechanical resonator, the coupling between an electron spin and the mechanical vibration can be very strong, which is good for quantum information transduction.
Figure 1: (a) Schematic of the laser writing process. A number of laser pulses are used to generate boron vacancies in hBN flakes. The laser has a center wavelength of 800 nm and a 1 kHz repetition rate. Each laser pulse has a duration of 50 fs. (b) Simplified $V_B^-$ energy-level structure and transitions between the ground state ($GS, \, ^3A_1$), the excited state ($GS, \, ^3B_1$), and the metastable state ($MS, \, ^1A_1$). The ground state has a zero-field splitting $D_{gs}$. (c) An optical image of an hBN flake after femtosecond laser writing. The scale bar is 30 µm. (d) Simplified schematic of the confocal system (BS: beam splitter; DM: dichroic mirror; SM: scanning mirror; LPF: long pass filter; FPC: fiberport collimator). A green laser ($\lambda = 532$ nm, green lines) is used to excite defects in hBN flakes on a glass slide. The emitted fluorescence (shown in red) is collected with an objective lens (NA = 0.9), and detected by a photon counter and a spectrometer. White light (blue line) from a LED is used to illuminate the sample. The reflected light is detected by a SCMOS camera for imaging the sample.

Recent discoveries of negatively charged boron vacancy ($V_B^-$) spin defects in hBN gained broad interest as they display spin-dependent photon emission at room temperature. The $V_B^-$ defect consists a missing boron atom and an extra electron in the hBN crystal. It has been created by high-dose neutron irradiation from a nuclear plant and ion implantation. While a few recent works have created defects with a femtosecond laser, no spin defects have been observed with laser irradiated hBN samples so far. Here we report the generation of $V_B^-$ defects in hBN using femtosecond laser writing. The creation process is controllable by tuning the laser parameters. With a proper energy of each femtosecond laser pulse and a wide-range of pulse number, we can create $V_B^-$ defects with the same emission spectrum as the ones created by neutron and ion implantation. Furthermore, the defects generated by laser irradiation exhibit good contrast in optically detected magnetic resonance (ODMR)
measurements. Compared with neutron and ion implantation methods,\textsuperscript{15,16} our laser irradiation approach is simpler and more flexible as it can be conducted at ambient environment with no vacuum requirement.\textsuperscript{20,22,33–34} Our work provides a new way to create controllable spin defects in hBN for spin-based quantum technologies.

Figure 1 shows the schematic diagrams of the laser writing process and our confocal system for characterizing samples. Laser writing is done using an 800 nm Ti: Sapphire femtosecond laser with a 50 fs pulse duration and a 1 kHz pulse repetition rate. The Ti: Sapphire femtosecond laser consists a Coherent Vitara Laser for seeding and a Coherent Elite Duo HE+ amplifier that can generate pulses with a maximum single-pulse energy of 13 mJ. The laser pulse is linearly polarized. It is focused on the hBN sample with an infinity-corrected 50x objective lens with NA = 0.8, which is used to simultaneously image the surface of the hBN sample. The number of pulses incident on the sample is controlled using an optical shutter. The hBN flakes are tape-exfoliated and transferred onto a glass coverslip for laser irradiation. The hBN sample is first placed in the laser focus within the Rayleigh range by monitoring the laser ablation of the hBN surface. The hBN surface is oriented normal to the direction of the laser beam to maintain its position along the laser propagation direction during scanning. For creating defects, the sample is moved 4 \( \mu \)m away from the focus, where the beam waist at the hBN surface is about 3 \( \mu \)m. The high-energy laser pulse breaks chemical bonds in hBN and creates defects.

After laser irradiation, the samples are moved to our home-built confocal system (Figure 1\textsuperscript{d}) for further characterization, which includes photoluminescence (PL) and ODMR measurements. To investigate the effects of laser parameters on defect generation, we pattern a group of spots. Each spot is irradiated by the femtosecond laser with a different combination of single-pulse energy and total pulse number. The high-energy pulses cause ablation at the center of the laser beam and leave a hole at each laser-written spot (Figure 1\textsuperscript{c}). Because the ablation process is highly nonlinear, the effect of the energy of each 50 fs pulse is very different from the effect of the total energy of many pulses separated by 1 ms.
Figure 2: Spin defects in hBN created by femtosecond laser irradiation. (a) A confocal image of a femtosecond-laser irradiated spot. This spot is irradiated by 20 pulses. Each femtosecond pulse has an energy of 1 µJ. The high energy pulses cause ablation of the hBN flake and leave a hole at the center. The spin emitters are observed at the edge of the hole. The emitters are excited by a weak 532 nm laser to obtain the PL image. Inset, a wide-field optical reflection image of the same spot under LED illumination. (b) An ODMR measurement of the spin defects generated by laser irradiation. The defects are excited by a 2.5 mW green laser. The data (blue dots) is fitted by double Lorentzian functions. (c) PL emission spectra of defects marked as E1, E2, E3 in (a). (d) Photostability of $V_{B}^{-}$ defects under 5 mW green laser excitation.

We carry out a series of measurements to characterize the irradiated spots. We find that within a certain range of pulse energies and pulse numbers of the laser, the spin defects can be generated with a very high probability of success. As shown in Figure 2, at the region irradiated by 20 repetitions of 1 µJ pulses, we observe bright and widely distributed $V_{B}^{-}$ defects at the edge of the ablated hole. The confocal image (Figure 2a) of this spot exhibits strong PL emission around the hole. All bright regions in the confocal image have similar emission spectra centered around 820 nm. Fig. 2c shows typical spectra at three different positions (E1, E2, E3) marked in Fig. 2a. The spectra agree with those of spin defects
generated by neutron and ion implantation, showing a high probability of creating $V_B^-$ defects. In addition, as shown in Fig. 2d, the emitters display good photostability under a 5 mW 532 nm laser excitation over a period of 1000 s. These hBN defects are stable for several months in storage at room temperature.

To further confirm that we have created $V_B^-$ spin defects in hBN by laser irradiation, we perform ODMR measurements of these defects (Fig. 2b). As reported in previous works, the resonant frequencies of the ODMR spectra of $V_B^-$ spin defects are given by $f_\pm = D_{gs} \pm \sqrt{E^2 + (g\mu_B B/h)^2}$, where $D_{gs} = 3.46$ GHz and $E = 50$ MHz are the zero-field splitting parameters of the triplet ground state of $V_B^-$ defects. $B$ is the external magnetic field, $g$ is the Landé factor, $\mu_B$ is the Bohr magneton, and $h$ is the Planck constant. To perform the continuous-wave (CW) ODMR measurement, we place a coplanar waveguide close to the laser-irradiated area to apply the microwave. Meanwhile, the sample is excited by a low-power CW 532 nm laser. The emitted photons are counted when the microwave frequency is swept from 3.15 GHz to 3.75 GHz. No external magnetic field is applied. The measured photon counts have two dips at 3.42 GHz and 3.52 GHz, consistent with former ODMR results of $V_B^-$ defects. It is noted that the contrast of our measured ODMR can exceed 1 % (Fig. 2b), which is higher than the reported ODMR results of $V_B^-$ defects in hBN so far. These show promising spin-optical properties of $V_B^-$ defects created by femtosecond laser writing.

To gain more insight on the formation of $V_b^-$ defects, we pattern a group of laser-writing spots with various pulse energies $E_s$ (Figure 3). The energy of each femtosecond pulse is varied from 200 nJ to 1.5 $\mu$J while the pulse number is fixed at 20. The beam waist of the femtosecond laser at the surface of the hBN nanosheet is about 3 $\mu$m. A confocal scan followed by the PL emission spectrum measurement is carried out for each spot. In Figure 3a, we show four typical confocal images of spots created with different pulse energies. In Figure 3b, we compare their PL emission spectra. With different irradiation pulse energies, the intensity and spectrum of PL emission from the resulting spots vary significantly. For
Figure 3: Effects of the pulse energy on defect generation. The pulse energy is varied from 200 nJ to 1.5 µJ in this study. The pulse number is fixed at 20. (a) PL intensity mapping of spots irradiated by lasers with pulse energies $E_s = 400 \text{ nJ}$, $600 \text{ nJ}$, $1.25 \text{ µJ}$, and $1.5 \text{ µJ}$. (b) PL emission spectra of emitters under green laser excitation. Spectra of emitters created by laser pulses with pulse energies $E_s < 800 \text{ nJ}$ show a big difference from the spectrum of $V_{B^{-}}$ defects. When $E_s \geq 800 \text{ nJ}$, the created defects have similar spectra. (c) ODMR measurements of emitters created by high-energy (1.5 µJ) and low-energy (600 nJ) pulses. The data are obtained from regions marked with white circles in (a). The signal of spin resonance is observed for emitters created by 1.5 µJ pulses while emitters created by 600 nJ pulses do not have spin signals.

Low pulse energies ($E_s \leq 400 \text{ nJ}$), the PL intensities are very low for most parts of confocal images, indicating the low densities of optically-active defects. Besides, the emission spectra of the bright spots, in this case, only show a tail at short wavelengths ($< 750 \text{ nm}$), implying that a different type of defect is created. As the pulse energy increases, the PL intensity increases while the emission spectrum changes as well. At 600 nJ, the emission spectrum varies dramatically at different positions, which means that various defects were created at this pulse energy. An example emission spectrum for $E_s = 600 \text{ nJ}$ is shown in Figure 3b. Such emitters generated by low-energy pulses have no spin signal in the ODMR measurement.
Figure 4: Effects of the pulse number \( N \) on defect generation. (a) PL intensity mapping of spots created with different pulse numbers (\( N = 50 \) or \( N = 1000 \)). (b) ODMR measurements of emitters created by 50 pulses or 1000 pulses of fs laser irradiation. Data are obtained from areas marked with white circles in (a). (c) Emission spectra of defects created by laser writing with different pulse numbers. The center wavelength does not change as a function of the pulse number, indicating that the pulse number (within 5000) will not affect the type of defects to be generated.

(Figure 3c). The origin of these different types of emitters is still unknown, but it is out of the scope of this work.

The \( V_B^- \) spin defects, which are our main focus, are observed from the sites exposed to pulses with \( E_s \geq 800 \) nJ. For defects created by the four different high-energy pulses (800 nJ, 1 \( \mu \)J, 1.25 \( \mu \)J and 1.5 \( \mu \)J), the emission spectra are centered around 820 nm (Fig. 3b) and the ODMR measurements have spin signals (Fig. 3c), which confirm the successful generation of \( V_B^- \) defects. Especially, at 1 \( \mu \)J and 1.25 \( \mu \)J, we have the highest probability of success to create \( V_B^- \) defects, while 800 nJ pulses only create some bright spots with the signature of \( V_B^- \) defects.

Next, we study the influence of pulse number on the formation of \( V_B^- \) defects. A number of laser pulses with 1 \( \mu \)J single-pulse energy are delivered to write defects at each spot. The pulse number \( N \) is varied from 20 to 5000 for different spots. As shown in Fig. 4, the center wavelength of PL spectrum is not sensitive to the pulse number within our experimental range. All these regions exhibit ODMR signals. So the type of defects to be generated is
insensitive to the number of pulses. In addition, the PL intensity has no significant change at small pulse numbers \( N \leq 200 \), while it decreases for very large pulse numbers \( N \geq 1000 \). We attribute this observation to the annealing effect of the large number of laser pulses, as it has been reported that annealing leads to a reduction of PL emission of \( V_b^- \) defects.\(^{10}\) In contrast, a pulsed laser has been used for annealing diamond to help create NV color centers.\(^{34}\) This is because the diffusion of vacancies and nitrogen atoms is required to form a nitrogen-vacancy pair in diamond. On the other hand, diffusion of boron vacancies in hBN will lead to combination of them to form more complex defects that do not have spin signals.

In conclusion, we have performed controllable laser writing of optically-addressable spin defects in hBN. We show that the single-pulse energy significantly affects the type of defects generated, while the pulse number only affects the density of the created defects. With proper pulse energy \( (E_s \sim 1 \mu J) \) and pulse number \( (N < 200) \), \( V_B^- \) defects can be generated with high probability of success. Furthermore, the \( V_b^- \) defects produced by laser irradiation show a good ODMR contrast at room temperature. This result shows promising spin-optical properties of \( V_B^- \) defects for quantum sensing and other quantum information applications. Further efforts are needed to non-destructively create \( V_B^- \) defects and isolate single emitters. Moreover, coherent control and dynamical decoupling of electron spins are important to explore for future applications of \( V_B^- \) defects. Our work provides a new tool for controllable engineering of spin defects in hBN. Such progress motivates more endeavors to explore spin-based quantum technologies, including sensing and quantum information processing in 2D materials.

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