

# ***NV center Nanoscopy and Magnetometry***

## ***Start from diamond***

Diamond is a wideband semiconductor, 5.5 eV at room temperature, see Figure 1. This band-gap is about five times the band-gap of silicon and twice the energy of photon in visible region. Its refractive index is around 2.4, and is transparent from the deep-ultraviolet to the infrared. Diamond also has excellent thermal properties, with high thermal conductivity ( $2 \times 10^3 \text{ W m}^{-1} \text{ K}^{-1}$ ), low thermal expansion ( $1.1 \times 10^{-6} \text{ K}^{-1}$ ), and low thermal-optics coefficient ( $dn/dT = 15 \times 10^{-6} \text{ K}^{-1}$ ) [3]. With proper engineering and optimization, diamond will offer a promising platform for a new generation of technological devices.

## ***Nitrogen-vacancy color center***

The nitrogen-vacancy (NV) center is a point defect in the diamond. It consists of a substitutional nitrogen atom associated with a vacancy in a negative charged state (see Figure 2). NV center can be found in nature diamond or produced by irradiation followed by annealing or by high-pressure, high-temperature annealing. The luminescence spectrum of NV center is from 640 to 720 nm (see Figure 3). The absorption line is about 637nm (1.945eV). The spontaneous emission lifetime in bulk is about 12 ns.

The vacancy in the NV center results in broken bonds in the system. Three C atoms and one N atom do not have enough neighbor atoms to form a covalent bond for each of their valence electrons. These unpaired electrons are called ‘dangling bonds’. In the case of the NV center, we consider a simple model consisting of four  $sp^3$  dangling bonds, where three of them are centered on each of the three carbon atoms around the vacancy and the fourth dangling bond is associated with the nitrogen atom. [7]

Nitrogen atom has seven electrons, two of the electrons are in 1S orbit, three of the electrons form three covalent bonds with neighbor C atoms, and two remaining electrons are contributed to the vacancy. Similarly, three neighbor Carbon atoms each has six electron and contributes one electron to the vacancy. Since NV center is negative charged, there are totally six electrons in the vacancy. These six electrons will be distributed in the four dangling bond, and results in two unpaired electrons.

The two unpaired electrons give out the spin and energy level of NV center. Ground and excited states are both electron spin triplets (see Figure 4). There is also singlet

state  $^1A$ . There are optical transitions between ground state and excited state, and also non-irradiation transition between triplet states and singlet state. Non-irradiation transition will lead to optical spin polarization, which we will talk later.

NV center is a promising candidate for many applications, ranging from high spatial resolution imaging to quantum computation. A detailed understanding of the properties of NV center is very important. Although people have investigated in it both experimentally and theoretically, some details of the NV center are still not understood <sup>[7]</sup>.

### **STED Nanoscopy**

For many decades, the resolution of far-field optical imaging is limited by diffraction. Because of diffraction, it's almost impossible to achieve resolution better than half the wavelength of light. This limit has been overcome by STED microscopy, which is a lens-based fluorescence microscope with a resolution conceptually no longer limited by diffraction <sup>[12]</sup>. In brief, a STED microscope separates two or more adjacent objects by ensuring that only one of them fluoresces at a time. Sequential object signaling is accomplished by transiently switching the objects off by stimulated emission <sup>[13]</sup>.

The main idea of STED is forcing the emitters to drop back to ground state by stimulated emission with a circle laser (STED beam). So only the emitters at the center part can have spontaneous emission. By observing the fluorescence of these emitters, super-resolution can be achieved. The red shifted STED beam has a zero intensity point in the middle and depletes the molecular fluorescent state everywhere within the focal region, except at the zero intensity point and its proximity, thereby confining the spatial extent of effective molecular excitation and hence of fluorescence. <sup>[12]</sup>

Because of phonon process, in NV color center, the absorption spectrum have shorter wavelength than zero-phonon-line (ZPL), while fluorescence spectrum have longer wavelength than ZPL (see Figure 5). So, excitation photon, STED photon, and fluorescent photon can be distinguished by wavelength. Comparing to fluorescent photon, excitation beam is blue shifted and STED beam is red shifted (see Figure 6).

$$D = \frac{\lambda}{2n \sin(\alpha)} \quad (1)$$

$$D = \frac{\lambda}{2n \sin(\alpha)} \cdot \frac{1}{\sqrt{1 + I / I_{sat}}} \quad (2)$$

For normal confocal microscopy, the resolution is limited by Abbe's equation (1), and is impossible to achieve resolution higher than half wavelength. In STED nanoscopy, resolution is limited by modified Abbe's equation (2). ' $I$ ' is the intensity of STED beam. It is obvious that when we have a STED beam with high intensity, people can achieve a resolution of a resolution of 16–80 nm or even better (see Figure 7).

Since the STED beam often have very high energy intensity (several  $\text{Gw}/\text{cm}^2$ ), many common emitter will bleach. Diamond NV centers don't have this problem. According to repeated experiments, there is no blinking. The experiments demonstrate far-field optical nanoscopy recording without photobleaching <sup>[13]</sup>. NV center is an ideal emitter for STED nanoscopy.

### ***Magnetometry***

Magnetometry is another application of NV centers. Because of non-irradiation transition, the spin sublevel with magnetic quantum number  $m_s=0$  (bright state) scatters about 30% more photons than  $m_s=\pm 1$  states. By optical excitation, NV centers can be pumped into  $m_s=0$  state, and form an optically induced spin polarization. When NV center is polarized into  $m_s=0$  state, we can observe a strong fluorescence. According to Rabi rotation, a resonant microwave field with certain frequency can induce transitions between these spin sublevels. These transitions will destroy the optically induced spin polarization and result in a significant decrease in NV center fluorescence. The frequency of microwave field should be equal to energy difference between  $m_s=0$  and  $m_s=\pm 1$  degenerated state.

When an external magnet field is added to the NV center, things will be changed. Under external magnet field,  $m_s=\pm 1$  degenerated state will split into two different sublevels:  $m_s=+1$  and  $m_s=-1$ . These two sublevels have an energy difference in proportion to the magnitude of external magnet field. Then, there will be two Rabi frequencies, and we can observe fluorescence decrease in two different frequencies (see Figure 8). Their frequency difference is equal to the energy difference between  $m_s=+1$  and  $m_s=-1$  sublevels. By measuring the frequency of Rabi microwave, we can calculate the magnet field at the NV center (see Figure 9).

Although nitrogen 14 has a +1 nuclear spin, the unpaired electrons in NV center ground state are more close to neighbor carbon atoms (Carbon 12 has 0 spin) and far from nitrogen atom. So the  $m_s=\pm 1$  sublevels are hardly effected by the nuclear spin. This enables NV center magnetometer to be extremely precise.

In practical, people attach a NV center to the probe of AFM and use it to measure the magnet field. The measurement resolution can be 0.5mT. The limiting factor here is oscillatory motion of the nanodiamond attached to the AFM tip<sup>[9]</sup>.

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## Appendix

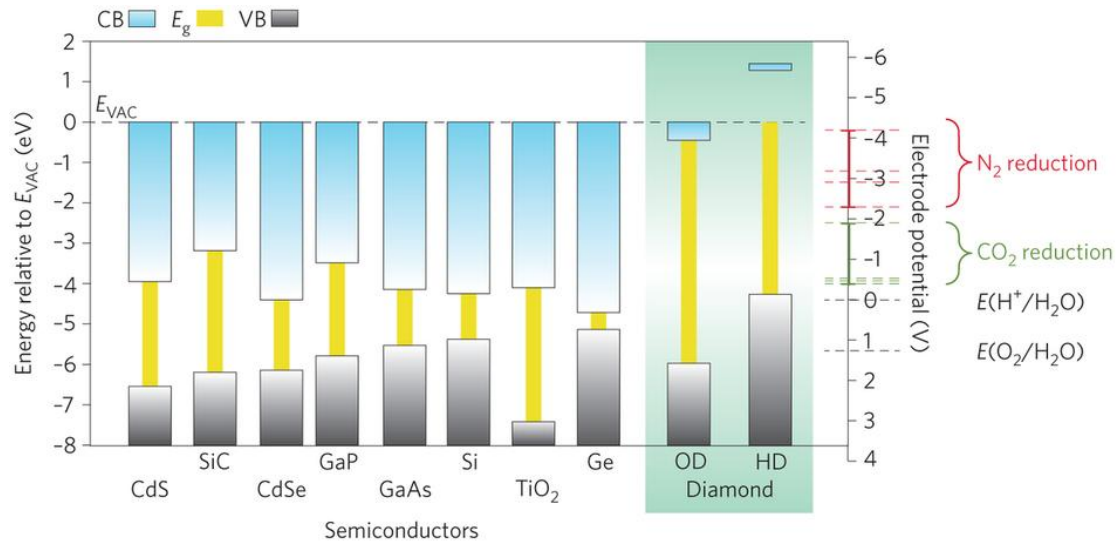


Figure 1: Valence-band maxima, bandgaps and conduction bands related to the vacuum energy for a variety of semiconductors shown as function of energy (left) with relation to  $E_{VAC}$  and as function of the electrode potential scale (right) relative to the standard hydrogen electrode. Diamond (OD = oxygen-terminated, HD = hydrogen-terminated) shows a large bandgap (5.47 eV) with the conduction band close to the vacuum energy. In the case of H-termination, the CB minimum is even above the vacuum energy, which is described as negative electron affinity. On the right axis, the water-splitting energies  $E(H^+/H_2O)$  and  $E(O_2/H_2O)$  (black lines), as well as the  $N_2$  (red lines) and  $CO_2$  (green lines) reduction potentials are shown.<sup>[2]</sup>

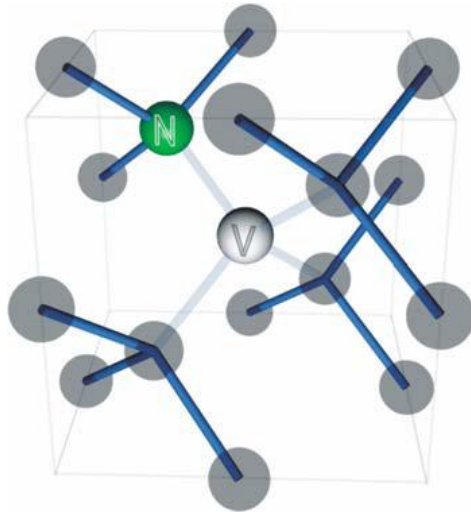


Figure 2: Schematic representation of the nitrogen vacancy (NV) center structure<sup>[8]</sup>

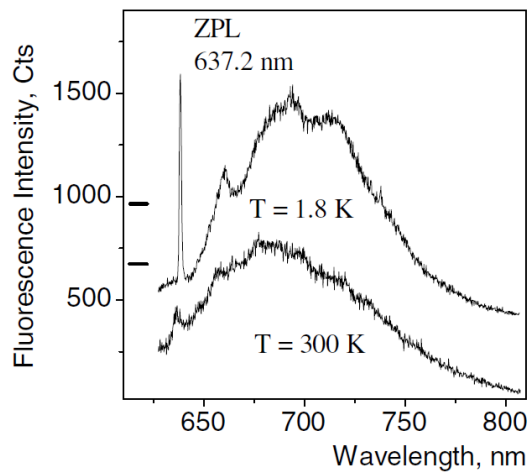


Figure 3: Fluorescence emission spectra of single NV centers at room temperature and LHe temperatures. Excitation wavelength was 514 nm<sup>[8]</sup>

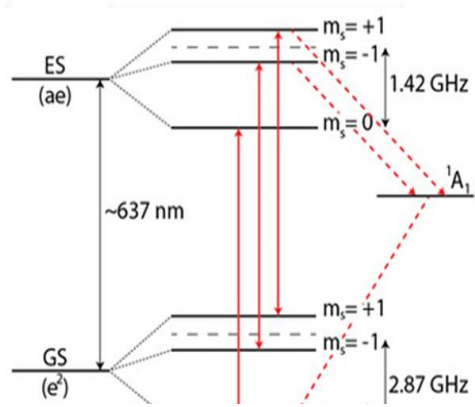


Figure 4: Energy level of NV center  
<http://pettagroup.princeton.edu/>

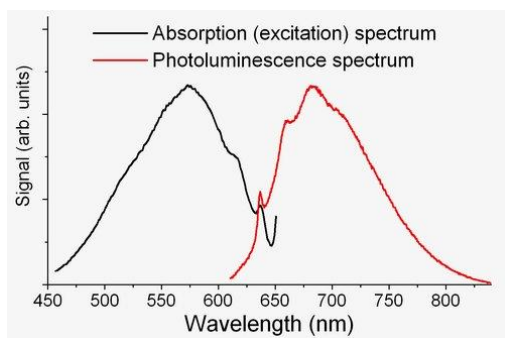


Figure 5: Optical absorption and emission of the NV center at room temperature

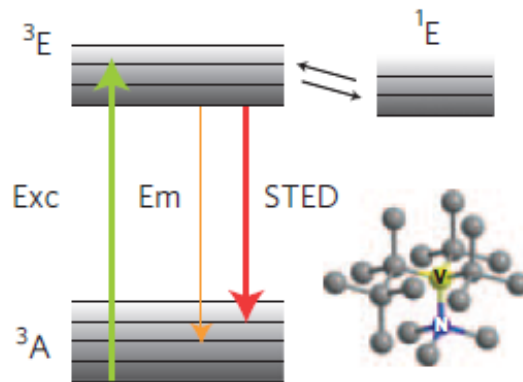


Figure 6: Energy diagram sketching the ground ( $^3A$ ), fluorescent ( $^3E$ ) and the dark singlet state ( $^1E$ ) along with excitation (Exc), emission (Em) and stimulated emission (STED) transitions in NV centers <sup>[13]</sup>

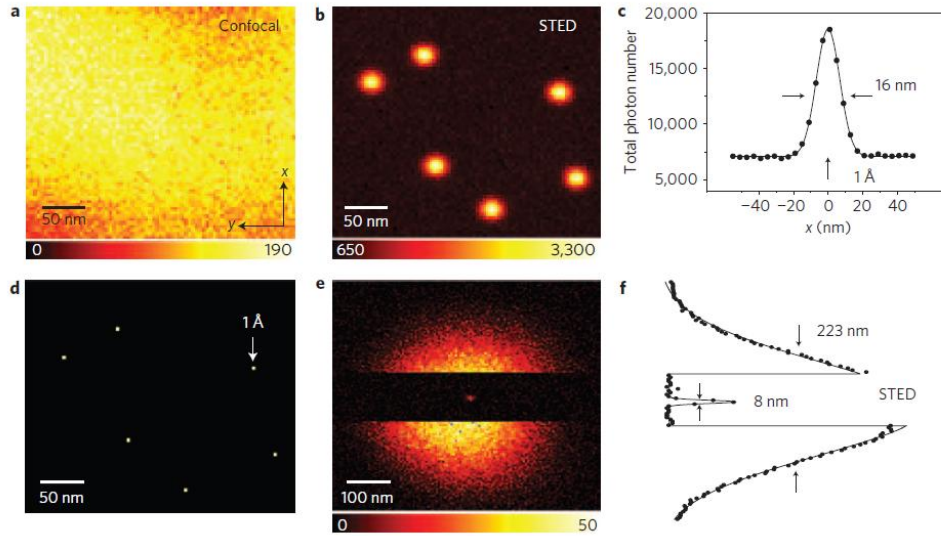


Figure 7: **Stimulated emission depletion microscopy reveals densely packed NV center in diamond.** **a,b**, Confocal (**a**) and STED (**b**) images from the same crystal region. **c**, The individual centers resolved in **b** automatically yield the effective PSF of the STED recording whose y-profile exhibits a FWHM of  $\Delta y = 16.0$  nm. **d**, The coordinate of each center can be calculated with 0.14 nm precision. Comparing **a** with **d** highlights the dramatic gain in information resulting from the unique increase in resolution. **e,f**, Applying  $I_{\text{STED}}^{\text{max}} = 3.7$  GW/cm<sup>2</sup> shrinks a confocal spot of 223 nm diameter (FWHM) down to 8 nm. Note that the increase in resolution is a purely physical phenomenon.

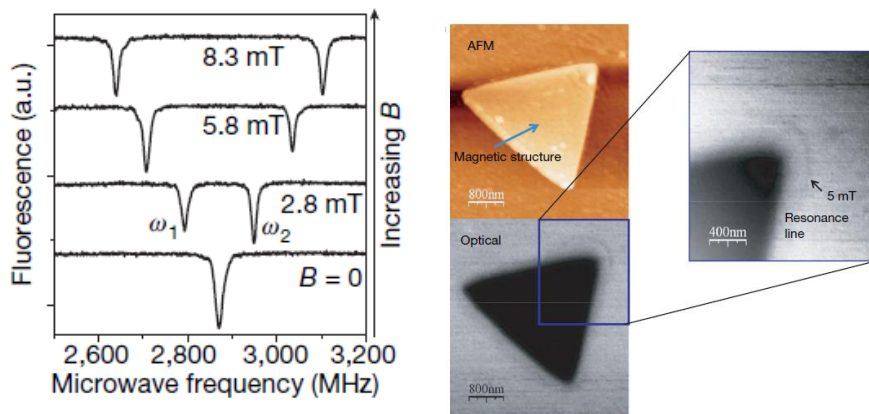


Figure 8: Optically detected magnetic resonance spectra for a single NV defect at increasing magnetic field [9].

Figure 9: Field reconstruction using the scanning probe single spin magnetometer.