Graduate School of Pure and Applied Sciences

Study of nitrogen-vacancy centers in diamond Schottky barrier diode
（ダイヤモンドショットキーバリアダイオードの窒素空孔中心評価）

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Chapter 1 Introduction

In recent years, the nitrogen-vacancy (NV) centers in diamond have received great attention due to its wide application. For example, NV centers can be used as a high-sensitivity quantum sensor1-3) because of its sensitive response to temperature, electric field, magnetic field, and stress. It is even possible to use in biological imaging by implanting nanodiamonds containing NV center into cells4). At the same time, it can also become a single-photon source, which is widely used in quantum computing and quantum communication5). However, most of these applications require negatively charge state NV-, because only the spin state of negatively charge state NV- can be initialized and optically read3). For this reason, the charge state control of the NV centers is crucial, especially the fast switching. The charge state of NV centers is affected by many factors such as Fermi level position6), laser irradiation7), surface defects8), ion implantation conditions9) and followed annealing process. Compared to the fast single direction transition of the NV center charge state caused by electrical control, optical control includes the slow double direction

transition of the NV charge state. Obviously, electrical control is easier to achieve with devices. Therefore, we should master the charge state control of NV centers in diamond device, which will be better for their efficient use and integrate into circuit. And also it can provide new opportunities for integrating diamond devices based on NV centers into electronic control circuitry.

Optically detected magnetic resonance (ODMR) can provide detailed information on the microscopic structure of NV centers. However, its low sensitivity makes it difficult to apply this technique to study on the present devices. We should develop sensitive detection methods for devices. As we know, photocurrent and photocapacitance is sensitive to defects in diamond devices, which are good choices to combine them with ODMR and develop new sensitive methods to detect NV centers in device. For example, photocurrent detected magnetic resonance (PDMR) and capacitance detected magnetic resonance (CDMR).

In this work, we used transient photocurrent and photocapacitance to study in detail the electrical and optical control of the NV centers charge state in the diamond Schottky barrier diodes (SBDs) and the ionization dynamics during the illumination process and their dependence on the excitation wavelength, light intensity, and temperature, and confirmed the feasibility of the PDMR and CDMR.

This work is divided as follows: Chapter 2, entitle "Sample preparation", present the sample fabrication process. Chapter 3, entitle "Investigation of defects level and electrical control of NV centers " is discussed the transient photocapaictance spectroscopy and photoluminescence spectroscopy results. The photocurrent results and discussion are presented at Chapter 4 entitle "Investigation of optical control and transition process of NV centers". Chapter 5, entitle "Investigation of temperature-dependent transition process of NV centers", present the temperature dependence of the transient photocapaictance spectroscopy and photoluminescence spectroscopy results. Chapter 6 is the conclusion.

Chapter 2 Sample preparation

In this chapter, the sample fabrication process will be introduced. The sample preparation including the diamond Schottky barrier diode fabrication process and the NV center production process will be introduced in details. A lightly boron-doped homoepitaxial diamond layer was grown on the HTHP diamond substrate using microwave plasma chemical vapor deposition technique. After the deposition, half of the diamond epitaxial layer was nitrogen ion-implanted followed high temperature annealing to create NV centers. After that, we deposited sandwich structure contacts (Ti/Pt/Au for Ohmic contact and Mo for Schottky contacts) using a photolithography technique to fabrication the Schottky barrier diode. Due to the difference in the

number of electrons contained in NV0 and NV-, their mutual conversion will cause changes in capacitance and current of Schottky barrier diodes. The transient photocapacitance spectroscopy (TPC) and transient photocurrent (PI) are good choices as sensitive methods for investigation of NV centers in diamond Schottky barrier diode. Photoluminescence (PL) spectroscopy is used to detect the fluorescence of the NV center (voltage and temperature dependent).

Chapter 3 Investigation of defects level and electrical control of NV centers

This chapter has been published in [2]. This chapter is divided in 2 sections. In the section 3.1, in order to detect the defects position and origin of the diamond Schottky barrier diode, transient photocapacitance spectroscopy was measured in different sample area and under different biases. Section 3.2 discuss the photoluminescence spectroscopy results to investigate the charge state electrical control of NV centers.

3.1 Investigation of defects level by Transient photocapaictance spectroscopy

In this section, transient photocapacitance spectroscopy results in different sample area and under different biases are discussed. Figure 1 (a) shows the TPC signals (S_{TPC}) normalized by the photon flux as a function of the photon energy. The red and black curves are TPC signals of Schottky diodes fabricated in the areas with and without ion implantation, respectively. There are two thresholds in the red curve, which is probably because of the existence of excited defect energy levels. The spectra were fitted with a Lucovsky function for photoionization cross section[10, 11]:

$$\sigma_{hv} \propto \frac{(hv-E_t)^{\frac{3}{2}}}{hv^3} \qquad (1)$$

where hv is photon energy, Et is photoionization energy of the defect. The obvious increase from around 1.2 eV of photocapacitance in spectra should be resulting from the hole emission from traps in the depletion region. The threshold of 1.2 eV appears in both signals, where the intensity of the signal in the implantation area is higher than that in without implantation area. The 1.2 eV defect signal can be enhanced by nitrogen implantation and the possible chemical candidate may be assigned as vacancy or NV center. The 2.2 eV defect only exists in the implantation area, which probably is attributed to NV centers. To try electrical control of the NV center, TPC spectroscopy was measured under different quiescent biases (reverse bias), as shown in Figure 1 (b). From G. M. Matain's reports[12], the TPC is increasing with higher reverse bias. The experimental results below 2.2 eV are a good agreement to it. However, after 2.2 eV, the spectrum shape changed, the capacitance is not increasing with higher bias. It is assumed that the change is from the

variation of the charge state of NV centers. When applying reverse bias, the Fermi level may cross the NV+/0 level, some NV+ change to NV0.11) Another assumption is the distribution of NV centers at 100 nm. The ratio of NV distribution and depletion layer may affect the result.

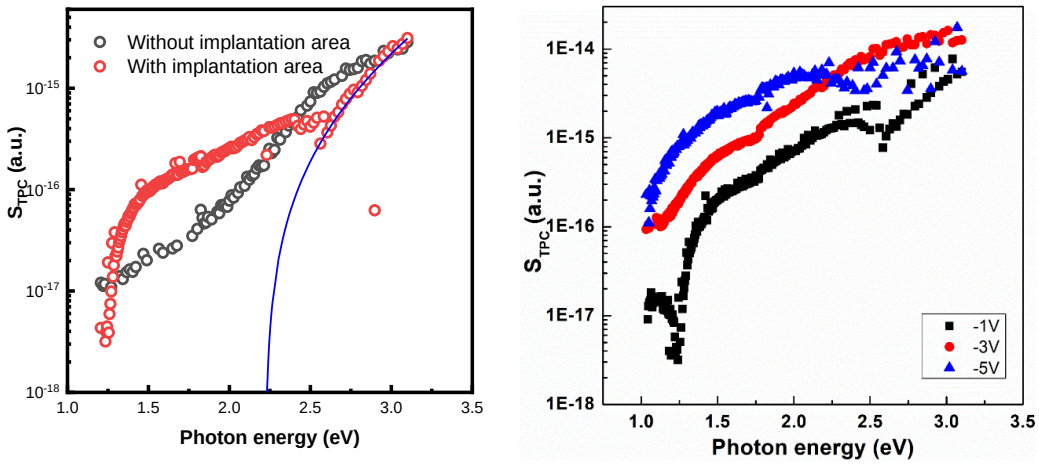

Fig. 1. (a) The transient photocapacitance (TPC) spectroscopy of both areas in the diamond Schottky barrier diodes with illumination wavelengths from 400 to 1200 nm. The results were normalized by the photon flux (S_{TPC}). The red and black curves are TPC signals of Schottky diodes fabricated in the areas with and without ion implantation, respectively. The blue lines are the fitting results of the spectra using Eq. (1). (b) The transient photocapacitance spectroscopy under different quiescent biases (reverse bias). The filling pulse is 0 bias.

3.2 Investigation of electrical control of NV centers charge state by photoluminescence spectroscopy

In this section, the photoluminescence spectroscopy results are discussed to identify the electrical control of the charge state of NV centers. The PL spectra were measured under different bias conditions as shown in Fig. 2. When increasing the reverse bias from 0 bias, the PL spectra show increasing NV- signals with the characteristic ZPL at 637 nm and its phonon sideband and the intensity of the NV0 signal drastically decrease. The variation of PL spectra with different applied voltages suggests that applying different bias voltages can control the charge state of NV centers due to their effect on the Fermi level in the depletion region of Schottky contact. The band diagram is shown in Fig. 3, for 0 bias, since the Fermi level is around the NV+/0 transition level, the NV centers are mainly NV0 and NV+. When applying reverse biases on Schottky contact, the Fermi level starts to cross the NV+/0 and then the NV0/-, so the NV centers become from NV+ to NV0 and then to NV-. Between 0 V and -10 V, there is only NV0 intensity change but not

spectrum shape changes, which is because NV- is not saturated at all. For this reason, it is assumed that the change of NV+ and NV0 concentration may influence the TPC result with different reverse biases.

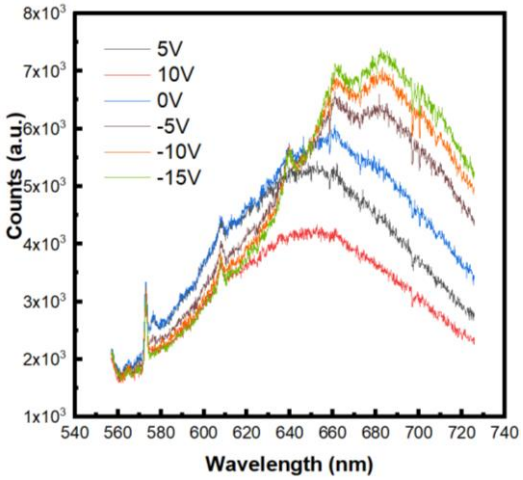

Fig. 2. The photoluminescence spectroscopy with different applied voltages using 532 nm green laser at room temperature.

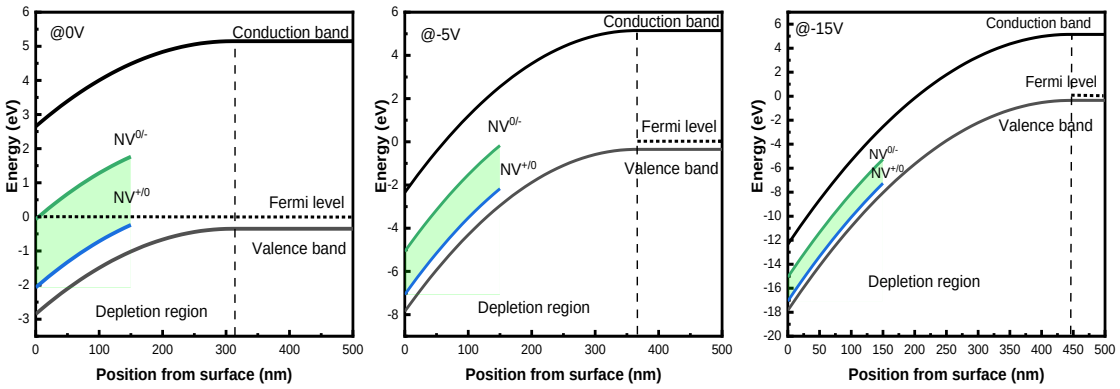

Fig. 3. Band diagram of the depletion region in diamond Schottky barrier diode (a) at 0 bias, (b) at -5 V and (c) -15 V. Fermi level (dot line) and the charge transition levels of nitrogen-vacancy centers (blue and green line) are shown.

Chapter 4 Investigation of optical control and transition process of NV centers

This chapter is preparing to be published recently. It is divided in 2 sections. In the section 4.1, in order to detect the optical control of NV centers charge state in the diamond Schottky barrier diode, transient photocurrent was measured in different sample area, with different light intensity and under different biases. Section 4.2 discuss the transient photocapacitance results to identify the optical transition process of NV center charge state.

4.1 Investigation of optical control of NV centers charge state at 0V by transient photocurrent and

photocapacitance

In this section, intensity dependent transient photocurrent results under different wavelengths are discussed. Under the irradiation of red light (700nm), the photocurrent increases linearly with the increase of light intensity. This is considered that an electron is excited from the valence band to a defect level after absorbing a photon, leaving a free hole in the valence band. That is the single photon process. Here the most likely candidate of the defect is the excited state of NV0 or a vacancy defect. The reason for the overshoot of the photocurrent is that the internal electric field changes instantaneously as the defect captures electrons quickly, and the depletion layer shrinks rapidly, which causes the photocurrent to increase instantaneously and decrease to steady state value as the defect state is gradually filled after a certain period of time. On the other hand, under the irradiation of green light (500nm), the photocurrent increases in a quadratic function with the increase of light intensity. Combined with the electrical structure of the NV center, this is considered that an electron is excited from the ground state of NV0 to an excited state after absorbing a photon, and then transitions from valence band to the NV0 after absorbing a second photon, leaving a free hole in the valence band. And NV0 becomes NV-. Vice versa, excited NV- becomes NV0 after losing an electron, leaving a free electron in the conduction band. That is the two-photon transition process.

The experimental results of the photocapacitance are also in good agreement with the above. In general, for a single deep level contributing to the photocapacitance transient, the change in capacitance can be written as

$$C(t) = \Delta C(1 - e^{-t/\tau}) \qquad (2)$$

where ΔC is the steady-state photocapacitance, and τ is the time constant for the transition process. Thus, by fitting Eq. (2) to the photocapacitance transient, the time constant of the photocapacitance transients could be obtained. The transient photocapacitance curve at 700 nm can be fitted with one time constant, while the transient photocapacitance curve at 500 nm must be well fitted with two time constants. And the photocapacitance changes much faster at 700 nm than at 500 nm, which can be used explain the photocurrent overshoot.

4.2 Investigation of optical control of NV centers charge state at reverse bias by transient photocurrent and photocapacitance

All measurements in Section 4.1 were performed at 0 bias, which is considered to be the NV0 dominated. In this section, the transition process of the charge state of the NV centers (NV- dominated) was

investigate.

Under the illumination of red light (700 nm), the photocurrent still increases linearly with increasing light intensity. It is thought that an electron in the 3E excited state of NV- centers transitions from the excited state to the conduction band after absorbing a photon, leaving a free electron in the conduction band. It is a single photon process. Under the illumination of green light (500 nm), the photocurrent increased as a quadratic function with increasing light intensity. As we mentioned in the introduction section, this is a two-photon process of transition between different charge states in the NV centers.

The results of transient photocapacitance at reverse bias under illumination at 700 nm and 500 nm are also proves. The same conclusions could be got as for the transient photocapacitance at 0 V.

Chapter 5 Investigation of temperature-dependent transition process of NV centers

This chapter will be published in this year. After investigation of transition process of different NV centers charge state in diamond SBDs at room temperature. In this chapter, we will introduce the temperature-dependent transition process of different NV centers charge state in diamond SBDs by photoluminescence and transient photocurrent. This chapter is divided in 2 sections. In the section 5.1, in order to detect the first step of two-photon transition process of NV centers in the diamond SBDs, photoluminescence at different temperature was measured. Section 5.2 discuss the transient photocurrent results at different temperature to investigate the transition process of NV centers charge state.

5.1 Investigation of temperature-dependent transition process of NV centers charge state by photoluminescence spectroscopy

In this section, temperature dependent photoluminescence results are discussed. At low temperature, because of the strengthening of fluorescence emission of NV centers, we can see high intensity of ZPL and appearance of phonon side band of NV centers. As the temperature increases, radiative recombination is gradually replaced by non-radiative recombination, and the intensity of the PL spectra decreases, and the change is significant at 340K. Therefore, we think that the NV center may be related to the activation energy of warm blood, which is about 30 meV.

The temperature-dependent photoluminescence results were fitted using the Arrhenius equation,

$$I(T) = \frac{1}{1+C\ exp\left(\frac{-E_A}{k_B T}\right)} \qquad (3)$$

where C is constant, k_B is Boltzmann constant, T is temperature and E_a is the thermal activation energy. By

fitting Eq. (3) to the photoluminescence results, the non-radiative recombination energy barrier of the neutral charge state NV0 is about 35 meV, and for negative charge state NV- is about 338 meV. However, since only intensity of NV centers ZPL is fitted, its phonon edges cannot be included, this fitting results is not accurate enough and needs further discussion and research.

5.2 Investigation of temperature-dependent transition process of NV centers charge state by transient photocurrent

In this section, the temperature-dependent photocurrent was measured. Two regions of photocurrent at different temperatures can be determined: region I (T <340 K) and region II (T> 340 K). In region I (T <340 K), the optical emission rate is much lagger than thermal capture rate, the number of photogenerated carriers is more than the number of traps. As a result, at a sufficiently low temperature, a constant photocurrent was also observed, indicating that a constant photocarrier density was achieved in the device. As the temperature rises, the thermal and optical emission increases, the thermal capture also increase, and the photocurrent decreases after reaching the critical value. The critical value is related to many factors such as material properties, light intensity, and defects. In our example, the critical value about NV0 or vacancy defect is approximately 340 K. The situation after the reverse bias is applied is quite different. Because the increased electric field limits the recombination of carriers, the photocurrent continues to rise, and the critical value will be reached at a higher temperature. The critical value about NV- is high and cannot be observed here.

Chapter 6 Conclusion

This chapter presents the final conclusions. In this work, we studied in detail the electrical and optical control of the NV centers charge state in the diamond SBDs and the ionization dynamics during the illumination process and its dependence on illumination wavelength, light intensity, and temperature. We demonstrated the photoionization of NV centers induced a change in SBDs current and capacitance, which it provides us with ideas for better and new spin detection technique such as capacitance detection magnetic resonance (CMDR).

Defect levels of 1.2 and 2.2 eV were found in nitrogen ion implanted diamond films by transient photocapacitance (TPC) spectroscopy. Defects located at 1.2 eV are assumed to be related with vacancies or NV centers, while 2.2 eV are associated with NV centers. By applying different bias voltages on the Schottky contacts, the NV centers can transport among the negative, neutral, and positive states. This is because of the

shift of the Fermi level near the transition level, which changes the charge state of the NV centers and its properties. The different charge state of NV centers transition to each other by one photon and two photon transition process. When applying a reverse bias, larger electric field enhances the process of hole (electron) emission and capture. The activation energy of the associated NV center comes from the temperature-dependent PL, which is about 30 meV (this value is very small and not accurate enough, it will be discussed in further studies), while the activation energy of the associated NV- is 338 meV. Temperature affects the first step (from ground state of NV centers to excited state) of the two-photon transition process for different charge states in the NV center more than the second step (from valence to NV0), but when it rises above 340 K, has a great impact on the whole process.

Publication lists

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