

Formation of nitrogen-vacancy centres in diamond: tight-binding molecular dynamic simulation

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Abstract. Molecular dynamics simulation of the vacancy diffusion in diamond and its interaction and merging with substituted nitrogen atom at different temperatures is presented. The activation energy was calculated from temperature dependence of the diffusion and merging rates. Presented data provides optimal temperature and duration of annealing for efficient formation of NV-centres with desired spatial localization. Simulation results are also useful for creating of solid structures for realization of quantum memory registers.

1. Introduction

In the last decades, a quantum information systems is widely used in many scientific and technical fields that include quantum computers, quantum communication systems, quantum metrology, etc. Operation of such devices is based on the quantum mechanical approach and use of such phenomena as superposition and entanglement, which significantly increases the performance and security of information flows from unauthorized access and at the same time reduces the size of quantum devices by several orders of magnitude.

The main element of a quantum computer is the quantum memory register, which consists of orderly arranged unit cells of quantum memory (qubits). The construction of a full-scale matrix, consisting of many synchronously working qubits, is one of the most relevant and promising challenge at nowadays. A well-insulated system, the state of which can be initialized and controlled, is required for its creation. It is also important that the selected system can be scalable. It is supposed to use an NV-centers (substituting nitrogen atom coupled with vacancy) in diamond as such a system.

The nitrogen-vacancy center in diamond is one of the defects in the crystal lattice of diamond, consisting of a substituting nitrogen atom and a neighboring vacancy (see Figure 1). Its unique properties, such as long spin coherence times at room temperature, spin-dependent fluorescence (zero-phonon line (ZPL) with a wavelength of 637 nm for negatively charged NV-centers), the ability to initialize and read the state of the electron spin of the NV center by optical methods, and controlling the spin state using a microwave field with a frequency = 2.87 GHz forms the basis for the practical use of NV-centers as a qubit [1].



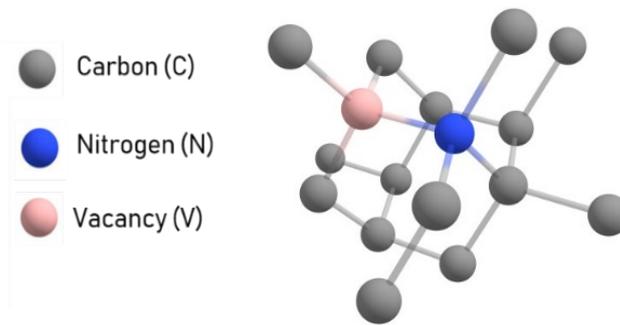


Figure 1. Schematic illustration of nitrogen-vacancy centre in diamond.

The formation of single NV-centers with a given position in space is a very difficult technological task, since the process of merging nitrogen impurities and vacancies was incidental. The most flexible tool for the formation of the NV-center is the use of the method of ion implantation of nitrogen atoms in the diamond crystal lattice. Because of effective ion braking into the bulk of the crystal, it is possible to control the concentration of defects and the depth of their occurrence; hence, the spatial distribution of NV-centers can be controlled. Next step, high-temperature annealing is carried out, that directly affects the number of formed NV-centers. The formation of centers is statistical and activates with increasing temperature and annealing time, as a result, vacancies diffuse over the crystal volume and interact with nitrogen impurities to form NV centers.

This study is aimed at simulation the merging of vacancy with impurity nitrogen at different temperatures. The obtained results will allow to select the optimal values of the temperature and annealing time, therefore, to debug the technological process of the formation of single NV centers in diamond.

2. Materials and Methods

The basis of the mathematical tools technique in computer simulation is the selection of the potential of interatomic interaction. Its selection significantly affects the accuracy and reliability of the results. The traditional method of analyzing such phenomena as migration and diffusion of vacancies or nitrogen defects in diamond under various external conditions (temperature and pressure) is molecular dynamics with classical interatomic interaction potentials [2]. At the same time, the use of molecular dynamics becomes impossible to study the electronic, energy and spin characteristics, since the quantum-mechanical contribution of the electronic system is not taken into account.

More rigorous first principles approaches are used to analyze these characteristics. Density functional theory (DFT) is the most common approach. However, performing calculations by *ab initio* method requires significant computing power and provide treating of the system evolution during the only relative short period of time (typically, up to 10 ps). When studying the merging of nitrogen and vacancy, it is important to take into account the quantum-mechanical nature of chemical bonds, therefore, it is necessary to select a method that describes such processes well and has high speed. In this paper, we apply non-orthogonal tight-binding model NTBM [3] with parametrization [4]. NTBM takes into account the quantum-mechanical contribution of the electronic subsystem to the total energy, which allows us to analyze large systems (up to 1000 atoms) during long periods of time (up to 1 μ m), also greatly facilitates the study of dynamic processes by means of molecular dynamics. It is worth noting that, the non-orthogonal tight-binding model provides better agreement with experimental data for various compounds among other semi-empirical using methods, for example, AM1 and PM3/PM7 [4]. Moreover, it provides accurate description of carbon-nitrogen systems [5-6], which are in well agreement with more rigorous *ab initio* data, and used for long-time molecular-dynamic simulation of carbon systems with both sp^2 and sp^3 types of hybridization [7-8].

3. Results and Discussions

To simulate the process of merging a vacancy with a nitrogen impurity, we regard a unit cell of diamond under periodic boundary conditions. Considered unit cell contains 62 carbon atoms, one nitrogen atom in the position of substitution and the vacancy (see Fig. 2). This number of atoms is assumed to be sufficient to describe the process under study.

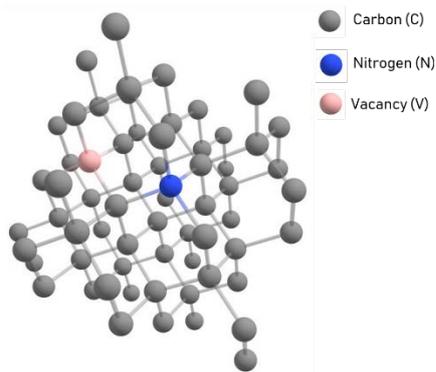


Figure 2. Unit cell of diamond contained substituting nitrogen atom and vacancy.

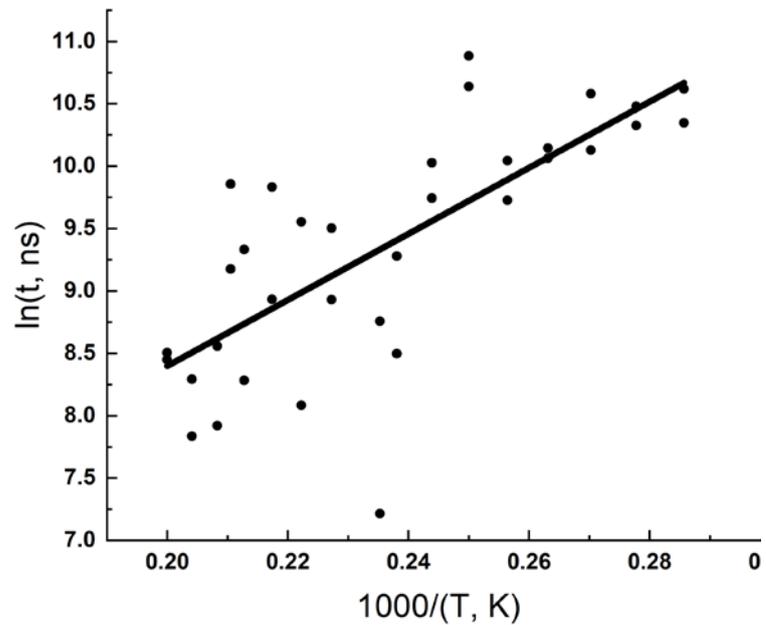


Figure 3. The emerging time of the vacancy with the nitrogen atom as a function of temperature. Circles are results of calculations, solid line is the approximation.

Molecular dynamics process was based on the classical equations of motion, which were integrated with a time step of 0.1 fs using the common velocity Verlet algorithm [9]. The merging of nitrogen and vacancy was simulated at various temperatures in the range from 3500 to 5000 K. To maintain a constant temperature until the formation of the NV center, an Andersen's thermostat was used [10]. For the simulation results the dependence of the emerging time on the temperature of the system was analyzed (see Fig. 3). These data were approximated by a linear function obtained by logarithm of the Arrhenius equation that has the following form:

$$\ln(t) = E_a \cdot \frac{1}{kT} + const,$$

where t is the emerging time, T is the temperature, E_a is the activation energy, k is the Boltzmann's constant. We derived the activation energy from the slope of the line (see Fig. 3). Accounting of statistical dispersions gives us a value of 2.28 ± 0.37 eV. Note that it is close to experimental value of activation energy 2.3 ± 0.2 eV [11].

4. Conclusions

In this study, the numerical simulation of the formation of a single NV center by merging a vacancy and a nitrogen impurity using the NTBM method was performed. As shown by studies of atomic dynamics using atomic displacement visualizers in the temperature range under consideration, nitrogen impurity and vacancy were formed an NV-center; their discrepancies were never observed. According to the

simulation results, the activation energy was determined that is in well agreement with the experimental value. Based on this, it can be said that the selected NTBM method for further calculations in more complex diamond structures will allow us to determine the optimal annealing parameters (duration, temperature), which are necessary for debugging the technological process of formation of a single NV center. In the future, we plan to dynamically simulate the migration of vacancies at different concentrations of nitrogen in the diamond in the presence of the additional defects.

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