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Creation, Control, and Modeling of NV Centers in Nanodiamonds

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Sensing based on Nitrogen-Vacancy (NV) centers in nanodiamonds (NDs) represents a potentially groundbreaking technology with broad applications. Nevertheless, the optimization of their quantum-optical properties is still a challenging issue. The present work aims at enhancing and controlling NV centers optical properties in NDs by combining their surface chemistry tuning and proton beam irradiation. Systematic thermal oxidations are carried out to study the evolution of surface chemical groups (IR spectroscopy), as well as their influence on optical properties (photoluminescence spectroscopy, PL decay measurements). Proton irradiation is performed by exploring a wide range of fluences (10^{14} – 10^{17} cm^{-2}) in order to precisely control the amount of NV centers, thus defining the conditions that maximize their creation and emission intensity. In addition, NV centers charge state control is achieved by assessing NV^-/NV^0 ratio upon different surface termination tuning and NV centers amount. Finally, a novel predictive mathematical model is developed, allowing for the evaluation of the efficiencies of the formation of both NV^- and NV^0. Although the model is tested in the specific case study with proton irradiated NDs, it offers a broad applicability, thus representing a key landmark in the prediction of the outcome of ion-beam-based color centers generation in diamond.

1. Introduction

Nanodiamonds (NDs) present excellent chemical and physical properties exploitable for a wide variety of applications. One of their most appealing characteristics is provided by the presence of different classes of lattice defects called "color centers", especially the Nitrogen-Vacancy (NV) center. This defect is formed when a vacancy defect is coupled with a nitrogen impurity and presents two charge states: the negative NV^- center and the neutral NV° center. These defects provide a highly photostable and bleaching-resistant fluorescence with Zero Phonon Line (ZPL) at 638 nm and 575 nm,[1] respectively, and a wide phonon sideband associated with a stable emission ranging between 600 and 800 nm, with an excitation window at 500 – 600 nm.

The mentioned photoluminescence (PL) properties make NDs excellent candidates as fluorescent biomarkers for in vitro experiments.[2–7] Besides, the electronic structure of the NV^- center shows peculiar spin-dependent radiative transitions that can be exploited to perform sensing of weak electro-magnetic field or small temperature variations, by means of Optically Detected Magnetic Resonance (ODMR) technique. Previous works proved the effectiveness of this technique, with challenging perspectives in high-sensitivity and high-resolution sensing applications, also in the biomedical field.[6,8–11] In addition, owing to their biocompatibility, tunability of surface terminations, and the small sizes, nanodiamonds have been proposed as candidates for drug delivery systems in the last decade.[2,12,13]

Pristine NDs typically possess weak luminescence due to the quenching effect of a pronounced sp^2 component and of amorphous carbon defective phases on the outer surface. Treatments aimed at improving NDs optical characteristics by removing these phases are predominantly oxidative,[14–18] including both chemical etching in acid solution (e.g.,: H_2SO_4/HNO_3) and thermal processes in oxygen-containing environment. Due to their impact also on structural and surface chemical properties, a systematic exploration of the processing parameters is fundamental for optimizing or finely tuning the NDs properties according to the desired application.[19] Moreover, optical properties can be improved by controlling the density of NV centers by means of

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