

Long-Lived Ensembles of Shallow NV⁻ Centers in Flat and Nanostructured Diamonds by Photoconversion

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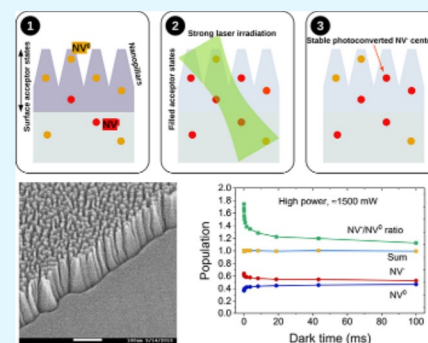
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ABSTRACT: Shallow, negatively charged nitrogen-vacancy centers (NV⁻) in diamond have been proposed for high-sensitivity magnetometry and spin-polarization transfer applications. However, surface effects tend to favor and stabilize the less useful neutral form, the NV⁰ centers. Here, we report the effects of green laser irradiation on ensembles of nanometer-shallow NV centers in flat and nanostructured diamond surfaces as a function of laser power in a range not previously explored (up to 150 mW/μm²). Fluorescence spectroscopy, optically detected magnetic resonance (ODMR), and charge-photoconversion detection are applied to characterize the properties and dynamics of NV⁻ and NV⁰ centers. We demonstrate that high laser power strongly promotes photoconversion of NV⁰ to NV⁻ centers. Surprisingly, the excess NV⁻ population is stable over a timescale of 100 ms after switching off the laser, resulting in long-lived enrichment of shallow NV⁻. The beneficial effect of photoconversion is less marked in nanostructured samples. Our results are important to inform the design of samples and experimental procedures for applications relying on ensembles of shallow NV⁻ centers in diamond.

KEYWORDS: diamond, nitrogen-vacancy centers, NV⁰, photoconversion, nanostructures, surface effects



INTRODUCTION

Negatively charged nitrogen-vacancy (NV⁻) centers are solid-state defects in the diamond lattice whose properties have been exploited to detect temperature gradients,^{1,2} magnetic^{3,4} and electric fields^{5,6} at the nanoscale, and interactions with magnetic molecules and nanoparticles.^{7–10} Due to their biocompatibility, NV⁻-enriched fluorescent nanodiamonds represent promising sensors to investigate the cellular microenvironment in living tissues and their use in high-sensitivity bioassays has been proposed.^{11–13} Furthermore, NV centers can be used in dynamic nuclear polarization (DNP) protocols where the polarization of the NV⁻s is transferred to ¹³C nuclei, leading to hyperpolarization of ¹³C nuclei in the diamond lattice.^{14–16} Substantial efforts are ongoing to promote polarization transfer from shallow NV centers to molecules adsorbed at the diamond surface,¹⁷ thus enabling hyperpolarization of high-sensitivity tracers for biomedical magnetic resonance imaging.

For all these applications, the proximity of NV⁻ centers to the diamond surface, where NVs can effectively interact with spins outside the diamond lattice, is of paramount importance, as the coupling strength between magnetic dipoles decreases with increasing distance. To this end, specially engineered layers of shallow NV⁻s^{18,19} as well as nanodiamonds²⁰ have been proposed.

Unfortunately, surface states and defects at and close to the diamond surface can affect the charge stability of NV centers, reducing the availability of magnetically active NV⁻ centers in favor of the neutral form (NV⁰ centers), which do not present the same detection features. The relative stability and interconversion between the neutral and negatively charged states of the NV centers have been the object of investigation in several studies,^{21–25} and various attempts have been made to increase the stability of NV⁻ centers, for instance, by surface termination,²⁶ by doping of the diamond lattice,²⁷ or by application of an electric field.²⁸

Here, we investigate the effects of laser power and surface structures on charge stability and attainable spin polarization of shallow NV⁻ centers in high-purity diamonds. Specifically, we aim to establish experimental conditions that maximize the availability of magnetically active NV⁻ at the diamond surface. To this end, we apply fluorescence spectroscopy, as well as optically detected magnetic resonance (ODMR), in electronic-

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