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All-Optical Thermometry with NV and SiV Color Centers in Biocompatible Diamond Microneedles

Lena Golubewa, Yaraslau Padrez, Sergei Malykhin, Tatsiana Kulahava, Ekaterina Shamova, Igor Timoshchenko, Marius Franckevicius, Algirdas Selskis, Renata Karpicz, Alexander Obraztsov, Yuri Svirko, and Polina Kuzhir**

Monitoring of tiny intracell temperature variations is of high importance to understand the mechanisms of exothermic/endothermic processes inside the living cells. Small shifts in thermal balance may drastically influence cell functioning and induce pathological conditions. By using biocompatible diamond single-crystal microneedles enriched with nitrogen-vacancy (NV)/silicon-vacancy (SiV) color centers, this study demonstrates all-optical in vitro temperature monitoring in the physiologically significant range (25–55 °C). Zero-phonon line (ZPL) of SiV centers belonging to the "therapeutic window" is used to improve measurement precision via suppression of the tissue autofluorescence. The simultaneous detection of the NV and SiV fluorescence enables two-band visualization of the living cells combined with the temperature sensing. This study demonstrates experimentally that temperature can be measured by lifetime, full-width at half maximum, and peak position of SiV ZPL, while accuracy can be further improved by normalizing the photoluminescence (PL) ZPL peak intensity on the PL signal measured at the wavelength where it is temperature independent. According to performed numerical simulations diamond microneedles enable real-time temperature measurements because their characteristic heating time is less than 10 ns. The results open a way toward accurate, noninvasive, precise, and real-time monitoring of temperature variations accompanying intracellular biochemical reactions and processes on the single-cell level.

1. Introduction

Temperature is one of the most important characteristics of a living system functioning because the temperature range, in which intracellular biochemical reactions occur, is very narrow. It may vary from 0.5 to 1.5 K (e.g., physiological temperature gradient between nucleus and cytoplasm was measured to be 0.98 K,[1] intracellular Ca^{2+} currents are accompanied by temperature increase by around 1.5 K[2,3]) down to 10^{-5} K (gene expression, protein folding, ligand–receptor interaction[4,5]).

Color centers in diamonds are the most promising tools for precise temperature sensing at the nanoscale.[6] Neutral nitrogen-vacancy (NV^0), negatively charged nitrogen-vacancy (NV^-), and group IV (Si, Ge, Sn, and Pb) vacancies color centers are capable to outperform commonly used fluorescent labels and dyes in a super-resolved bioimaging.[7–9] This is because despite much less quantum yield of photoluminescence (PL) and lower absorption cross section,[10] the stable light emission of these color centers at no blinking can be accumulated[11,12] improving spatial resolution.

NV color centers[13] in diamonds have been proved to be an effective platform for temperature measurement with mK accuracy and nanometer spatial resolution.[6] However, exploring the temperature-dependent frequency shift of NV-centers spin resonance requires microwave irradiation control,[14] which may overheat and even damage cellular structures.

All-optical thermometry with silicon-vacancy (SiV) color centers[15] is free from this drawback due to their temperature-dependent intense and narrow zero-phonon line (ZPL) in the PL spectrum.[16] The SiV ZPL belongs to the first tissue transparency window, 700–950 nm[17] allowing one to suppress tissue autofluorescence and to improve sensitivity.

Both nanodiamonds (NDs)[18] and bulk diamonds[16] have been used for SiV color centers based thermal biosensing. Appropriate size and tailorable surface chemistry[19] make nanodiamonds most suitable for biovisualization[20] and nanothermometry.[16] However, controlling the concentration and spatial distribution of functional defects in nanodiamonds is difficult task because high degree of imperfection may suppress or

L. Golubewa, Y. Padrez, M. Franckevicius, A. Selskis, R. Karpicz
State Research Institute Center for Physical Sciences and Technology
Sauletekio Av. 3, Vilnius LT-10257, Lithuania
E-mail: lena.golubewa@ftmc.lt
S. Malykhin, A. Obraztsov, Y. Svirko, P. Kuzhir
University of Eastern Finland
Yliopistokatu 7, Joensuu 80101, Finland
E-mail: polina.kuzhir@uef.fi
T. Kulahava, E. Shamova, I. Timoshchenko
Belarusian State University
Nezavisimosti av. 4, Minsk 220030, Belarus
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