Diamond nanocrystals with nitrogen-vacancy centers as new type temperature sensors

Nanokryształy diamentu z centrami barwnymi azot-wakancja jako czujniki temperatury nowego typu

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Nitrogen vacancy color centers in diamond (NVs) as a new type of temperature sensors were presented in the article. Recent progress in the field of NV thermometry and summarize the techniques of NVs manufacturing was briefly discussed. The use of NVs for characterization of thermoelectric materials was proposed.

KEYWORDS: nitrogen-vacancy, NV, thermometry, thermoelectrics, nanodiamonds

W artykule zaprezentowano centra barwne azot-wakancja (NV) w diamentach w roli czujnika temperatury nowego typu. Krótko omówiono ostatnie doniesienia naukowe oraz podsumowano techniki wytwarzania diamentów z centrami NV. Zaproponowano nowatorskie wykorzystanie centrów NV do badania materiałów termoelektrycznych

SŁOWA KLUCZOWE: azot-wakancja, NV, termometria, termoelektryki, nanodiamenty

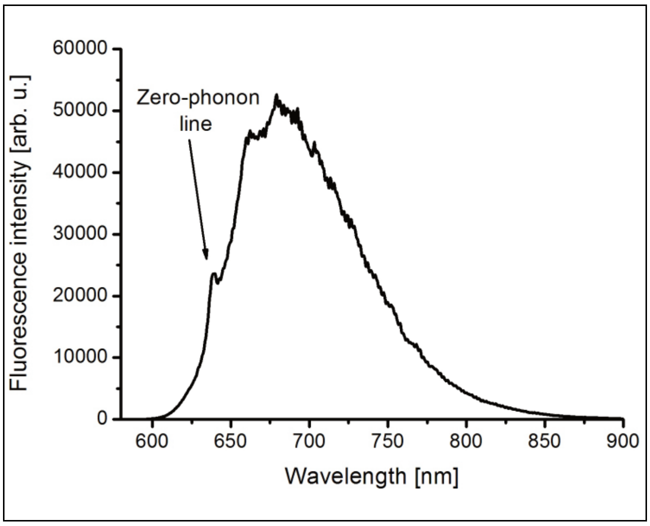
Modern thermometry

Many methods have been developed for measuring temperature. Among the most important challenges remaining in the thermometry field are high-sensitivity measurements with a sub-micrometer spatial resolution. The development of precise micro-/nanoscale temperature measurements is important in many research fields [1]. It might be very useful e.g. to track and control intracellular processes in biology/medicine [2], chemical reactions [1] and/or quality of the new materials (e.g. thermoelectrics or semiconductors). These issues motivate a demand for new sensors and drive the progress in the field. Examples of the new developments are scanning thermal microscopes [3], dispersed or scanned fluorescent nanoprobes [4, 5], and Raman spectroscopes [6]. Despite many novel techniques, precise nanoscale temperature measurements have not been realized so far. The nitrogen-vacancy (NV) center in diamond is a promising candidate to fill this gap.

Diamond with NV center as a temperature sensor

Diamond crystals are known for high hardness and chemical inertness. Thanks to the superb thermal conductivity, diamond is also an ideal material to host a temperature sensor. In this paper the nitrogen-vacancy color centers are introduced [7]. These extraordinary objects are used as sensors in different fields, like quantum information processing [8], magnetometry [9], optical tracking [2] and thermometry [1]. The NV center may be incorporated into nanodiamonds (NDs) and serve as a thermometric sensor, which might be localized with a nanometer resolution [1]. Moreover, nanodiamonds are biocompatible and might be introduced and tracked within living cells [2]. The sensing is performed optically in an non-contact and non-destructive way. The sensitivity of such sensors could potentially reach 1 mK [10]. They can be used for temperature measurements up to about 600 K.

The NV center consists of a substitutional-nitrogen atom and an adjacent lattice vacancy. The electronic structure of the center contains two triplet levels (spin equal to 1) split by 1.945 eV, which lie within the diamond electronic band gap. The optical excitation of the center with a green light results in a strong and stable red fluorescence [11] (see figure). In room-temperature the ground-state sublevels are equally populated. The green-light illumination causes the NVs to preferentially populate the $m_s = 0$ sublevel [12]. By the application of a microwave (MW) field one can then induce the magnetic resonance. Since the intensity of the red fluorescence depends on the population distribution within the ground state, the magnetic resonance can be observed optically as variations of the luminescence intensity. The technique is called optically detected magnetic resonance (ODMR).



Fluorescence spectrum of the NV$^-$ illuminated by green light (532 nm). Zero-phonon line indicates the optical transition at 637 nm, which does not induce phonons

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Close to the room temperature, the resonance frequency D_g depends on the temperature T of the crystal as [13]:

$$dD_g/dT = -74.3 \text{ kHz/K}$$

By monitoring the changes of D_g one can measure the temperature of the diamond crystal and its environment. The measurement sensitivity depends on the ODMR linewidth and the signal magnitude. These values are limited by the NV coherence time (T_2) and the number of centers used as sensors, respectively. The ideal diamond temperature sensor should contain close to 500 NVs with the T_2 not less than 1 ms [14] (the longer the better).

In the recent years several groups have presented temperature measurements using NV centers. Toyli et al*.* have shown in [15] that with special protocols preserving the NV's coherence, the sensitivity approaching 10 mK $Hz^{-1/2}$ is achievable for single centers. Neumann et al*.* recorded a temperature noise floor of 5 mK $Hz^{-1/2}$ for single NVs in a bulk, which results in the accuracy of about 1 mK [10]. In the same work 130 mK $Hz^{-1/2}$ was measured for few tens of nanometers diamond containing NV centers.

The measurements with microwaves require a way to deliver MW power to the crystal, not trivial in the case of intracellular measurements. Recently, Plakhotnik *et al.* proposed an all-optical thermometry using NV centers in nanodiamonds [14] which eliminates the MWs. The idea is to measure the ratio between the components of the optical spectra in the visible range. For an ideal diamond containing 500 NVs the noise floor is predicted at 100 mK $Hz^{-1/2}$ level. This value is higher than in an ideal case with the ODMR technique, but the fabrication of ideal nanodiamonds with still remains a challenge. The proposed technique is much simpler, does not require microwaves, and might be implemented readily using commercial spectral-resolving imaging systems.

The manufacturing of diamond containing NV centers

To create efficient sensors one has to optimize the technique of producing ideal nanodiamonds with NVs. The two main techniques of diamond manufacturing are typically used, the high pressure-high temperature (HPHT) and the chemical vapour deposition (CVD). The ideal sensor should contain about 500 NVs [14], hosted in a nanocrystal of ultrapure diamond below 100 nm size. Creation of fluorescent nanodiamonds (fNDs) presents several difficulties since the nanocrystals should be strain-less and defects-free but with high-NV concentration. In one of the first successful proposals [16] fNDs were produced from commercial microdiamonds (HPHT type), which were subsequently irradiated by e^- beam and annealed for 2 hours in 800 °C. Next, the crystallites were milled and washed in the HNO_3/HF. In that way, 15% of the original mass was transformed to the powder below 10 nm size. The more recent approach with irradiation in aqueous colloidal solution [17] increased the fNDs fraction but the ideal way of production of fNDs remains as a serious challenge.

Using nanodiamonds for a characterization of new materials

The fND might be used to study new thermoelectric materials e.g. by observing processes on the surface (e.g*.* on the grain boundaries). Coating a surface of a new material with a ND powder will enable a non-contact all-optical thermometry with high spatial resolution. It would be a new convenient method of characterization of novel materials.

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