Proposal for SNI sponsored PhD project in Nanoscience:

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Surface-Functionalization of diamond nano-magnetometers for applications in nano- and lifesciences

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1. BACKGROUND AND MOTIVATION

Magnetic field imaging and sensing are fundamental and widely used experimental methods, which are routinely applied in a variety of scientific disciplines from chemistry, biology to the physical sciences. While such use is well-established at the macro-scale (such as in clinical magnetic resonance imaging), promoting these imaging approaches to the nano-scale would open fascinating new avenues, ranging from the structural determination and dynamics of individual (bio)-molecules to the imaging of complex electronic systems at the single electron level. Currently, such applications are impossible, as existing approaches to magnetic imaging are hampered by poor spatial resolution and insensitivity to weak fields, which in combination do not allow for nanoscale magnetic field imaging. However, recent research results [1][2][3] give strong evidence that these limitations could be overcome by utilizing single electronic spins to enable a new generation of magnetometers, which operate deeply in the nanoscale. A particularly useful system sin this context are single electronic spins in the form of Nitrogen-Vacancy (NV) centers in ultrapure diamond [5]. The versatility of such NV magnetometers has been demonstrated in first proof-of-concept studies to yield single electron spin sensitivity [7] and imaging resolutions down to the nanoscale [4]. In order to fully exploit the potential of NV magnetometry in scientifically relevant settings and future application in sensing, stable and highly quantum-coherent NV centers have to be created in close proximity to the diamond surface [8], where they can positioned within few nanometers from an imaging target. However, such shallow NV centers are highly susceptible to and influenced by the chemistry of the nearby diamond surface. Indeed, recent studies have shown that such "shallow" NV centers exhibit significantly decreased spin coherence times as compared to their bulk counterparts [9] and as a result show reduced performance in magnetic sensing. This detrimental influence of the surface is caused by fluctuating fields generated by uncontrolled charges and spins (dangling bonds) present on the surface and could thus be avoided by proper termination of the diamond surface. To realize high-performance nanoscale NV magnetometers, it is therefore indispensable to gain a high degree of control of diamond's surface chemistry by a targeted even termination with different chemical funtionalities. Furthermore, such termination is an important prerequisite and starting point for further surface functionalization, which are key elements for future sensing applications. For example, a target for NV magnetometry, such as complex bio-molecules could be attached to the diamond surface and then be sensed and imaged by a close by, shallow NV center. The ultimate goal of this approach would be to provide atomically resolved, structural information of such molecules on the single-molecule level. This would provide deep insight into the structural behaviour of a broad range of molecules and will open up a new route to biosensing applications with ultimate sensitivity.

In order to achieve these challenging, scientifically highly interesting and demanding goals, we here propose the targeted engineering of the diamond surface by a defined chemical termination with a high degree of control with respect to uniformity and density of the terminating chemical entities. This will allow for deterministic preparation of highly quantum coherent NV centers in close proximity to the diamond surface for sensing. In the second phase of the proposed thesis project, diamond's surface chemistry will be further explored and expanded in first instance to the immobilization of small molecules exhibiting interesting magnetic properties like e.g. the spinlable TEMPO or various metal complexes and in a second phase more complex molecules like the haem-center or metalloproteins to point the direction towards first scientifically valuable applications of NV magnetometry in nano-physics and the life-sciences. In summary, the goals of our proposed project application are to obtain a well-defined, chemically terminated diamond surface, which protects the NV spin from surface-induced spin dephasing. Furthermore, we will demonstrate the functionalization of the as-prepared diamond surface with various molecules and molecular complexes with a particular focus towards future applications in the life-sciences. Finally we will combine our highly coherent, shallow NV spins with the functionalized diamond surfaces to study the physics and nano-chemistry of the attached molecules.

2. WORKPACKAGES AND METHODS

The following goals will be pursued during the proposed project (in approximate chronological order and increasing level of complexity):

2.1 Diamond surface termination:

We will perform chemical surface termination of diamond with the goal of decreasing spin-noise emanating from the diamond surface (to increase NV T_2 times) and to perform surface Fermi level pinning of diamond (to stabilize the charge-state of the NV center to NV^-). The effect of surface terminating chemical functional groups like e.g. OH, O, $-NH_2$ or F [11] on isolated NV centers will be explored. The diamond surfaces will be characterized by XPS, Auger spectroscopy and HR-EELS to verify successful termination, it's density and integrity. In an alternative approach to wet-chemical functionalization, the use of chemical vapor deposition and atomic-layer deposition for terminating the diamond surface with various stabilizing layers (DLC, SiO_2 Si_3N_4 and others) will be explored.

2.2 Characterization of shallow NV spins in functionalized diamonds:

The diamond samples obtained by surface termination and functionalization will be studied with respect to the spin-coherence of shallow NV centers. These centers will be created prior to chemical treatment either through ion-implantation or incorporation during growth [8]. Either method will yield Nitrogen atoms 2-10nm from the diamond surface, which will be converted to NV centers by vacuum annealing. The as-prepared diamonds will be subject to the surface termination steps developed in 2.1 and will then be studied on the single-spin level by optical spectroscopy and coherent microwave spin-manipulation.

2.3 Surface functionalization and conjugation of (bio)-molecules to the diamond surface:

Building on the successful surface termination (2.1), the well-defined chemically modified diamond surface will be subjected towards further functionalization with relevant and interesting molecules for applications in life-sciences and nano-physics. Primary target molecules include spin-labels such as TEMPO, metal complexes and complex bio-molecules such as hemoglobin and metalloproteins, which we will deposit in various densities and controlled patterns for imaging. The further functionalized surface will be investigated and characterized by all means of surface analytical techniques e.g. XPS, Auger spectroscopy, Tof SIMS and others.

2.4 Applications of functionalized diamond structures in life-sciences and surface physics:

In the final section of the proposed thesis project the successfully created, functionalized diamond sample structures containing highly coherent shallow NVs will be subjected to first nanomagnetic imaging and sensing tasks with a particular focus on life-science applications. As a specific proof of concept task, the study of the para- to diamagnetic switching of surface immobilized hemoglobin will be studied. The controlled creation of stable hemoglobin-layers on the diamond surface will enable a controlled chemical switching of hemoglobin between its two magnetic states upon oxygenation/deoxygenation and will bear clear magnetic signatures, to be detectable by the nearby NV centers. The ultimate goal is the detection of the different states on the single-molecule level and will thereby enable the study of this essential bio-molecule with unprecedented spatial and time resolution. Depending on the progress of the project further molecules like e.g. metalloproteins will be studied.

The sub-projects and milestones defined above will be conducted in close collaboration between the two partner institutions over the timespan of one Ph.D. thesis. The approximate time-line and distribution of tasks is as follows:

- Year 1: 2.1-2.2 (FHNW/UB)
- Year 2+3: 2.2-2.3 (UB/FHNW)
- Year 3+4: 2.4 (FHNW/UB)

3. COLLABORATIVE ASPECT OF THE PROJECT AND OUTLOOK

A special aspect of the proposed project is it's interdisciplinary approach, which ideally combines and complements the expertise in nanosciences, quantum physics, materials science and surface chemistry of the participating research institutions. The proposed PhD thesis project will be conducted in a close and unique collaboration between the groups of Prof. Dr. P. Maletinsky of the Department of Physics of the University of Basel and Prof. Dr. U. Pieles of the institute for Chemistry and Bio-analytics (ICB) of the School of Life Sciences (FHNW) respectively. Surface chemistry/functionalization and bio-conjugation of materials forms the basis of the approach and is one of the key competences of the Nanotechnology and Material Science group of the School of Life Sciences (FHNW-HLS) headed by Prof. Dr. U. Pieles. The strong background required in diamond nanofabrication and coherent spin manipulation of single NV spins on the other hand will be provided by the Quantum-Sensing lab of Prof. Dr. P. Maletinsky of the Department of Physics of the University of Basel. On the long run, this project will provide key steps in the field of nanoscale quantum sensing with single spins and will open up possible new routes to bio-sensing application with ultimate sensitivity on single molecule level. Furthermore potential extensions of the proposed PhD thesis project with far-reaching consequences include the application of the resulting shallow, highly coherent NV spins to the field of hybrid systems or quantum information processing.

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