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Nanometer-scale isotope analysis of bulk diamond by atom probe tomography

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ABSTRACT

Atom-probe tomography (APT) combines field emission of atoms with mass spectrometry to reconstruct three-dimensional tomograms of materials with atomic resolution and isotope specificity. Despite significant recent progress in APT technology, application to wide-bandgap materials with strong covalent bonds has remained challenging or low yielding. Here we report APT measurements on bulk diamond grown by chemical vapor deposition. Using a conductive substrate in combination with laser-pulsing, carbon atoms could be controllably field evaporated and tomograms containing up to 6 million atoms could be reconstructed. We have subsequently applied the technique to iage the depth distribution of a sub-surface nitrogen δ-layer with nanometer spatial resolution. With future development, the technique may enable detailed characterization of dopants in diamond at an atomic level, which would be of great interest to the many scientific and industrial applications exploiting the unique properties of the material.

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1. Introduction

Doping of diamond is important for many emerging technologies that attempt to exploit the materials' remarkable properties in high-end electronic devices and sensors. For example, doping of diamond by phosphorus or boron introduces donors or acceptors that can turn insulating into semiconducting diamond [1], with potential applications in high-power diodes or transistors. Boron-doped diamond is also a candidate electrode material for next generation, highly stable and accurate pH sensors [2] and a range of other electrochemical applications [3]. Optically bright defects, such as the silicon vacancy (SiV) or the nitrogen vacancy (NV) color centers, hold promise as single photon emitters in photonic networks [4]. NV centers are moreover beginning to be utilized as nanoscale probes for magnetic and electric fields, or temperature, with potential uses in sensor arrays or high-resolution magnetic imaging [5]. In most of these applications, it is crucial that defects or dopants can be precisely positioned within tens of nanometers, and sometimes within a few nanometers from a diamond surface.

Controlled vertical placement of foreign atoms is possible both by ion implantation and by *in-situ* growth using chemical vapor deposition (CVD). For ion implantation, the penetration depth can be approximately chosen by adjusting the ion acceleration voltage, and surface proximities of a few nm have been realized for low (<10 keV) implantation energies [6,7]. The placement of defects, however, is stochastic and the peak depth and distribution can only be predicted by Monte Carlo or molecular dynamics simulations [8]. Although these simulations are extremely useful, they usually neglect effects like channeling, tilt of crystallographic planes, or surface potential build up, and thus are approximate at best. *In-situ* growth by CVD overcomes these issues by temporarily adding the dopant precursor to the feed gas, and surface layers or interlayers as thin as 5 nm have been reported [9,10,11]. Achieving precise thicknesses and absolute placement of such δ-layers of high foreign atom concentration, however, remains challenging because growth rates for thin layers are difficult to control and calibrate [12].

An important obstacle to controlled shallow defect generation is the lack of suitable analytical tools that can experimentally verify defect depths or lateral placement. Secondary ion mass spectrometry (SIMS) has been used to study diamond [12,13] and to investigate nitrogen contents [14,15], but depth resolutions are typically >10 nm and large, homogeneous surface areas are required. SIMS is especially problematic for obtaining information on insulating materials, like diamond, due to charge build-up and other artifacts [14]. For nitrogen, which is the target dopant in this study, SIMS is additionally hampered because the species does not form stable negative ions in isolation, such that ionization efficiencies and yields are low. Other techniques include non-Rutherford

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backscattering spectroscopy or elastic recoil detection analysis [16], but also these require large sample areas. For the specific case of NV color centers, depth measurements have also been reported using fluorescence quenching [17] and spin relaxometry [18,19,11]. In this study, we explore whether atom probe tomography [20] could serve as a method for analyzing atomic defects in bulk diamond with nanometer spatial resolution.

Atom probe tomography (APT) combines field evaporation of ions with time-of-flight (TOF) mass spectrometry to obtain three-dimensional tomograms of materials with sub-nanometer resolution and isotope specificity. In APT, the material under investigation is sculpted into a nanoscale tip and ions are evaporated by voltage pulses that create extremely high local electric fields (typically 10s of V/nm). Since ion emission is directional, a three-dimensional tomogram can be reconstructed (see Fig. 1A). The method thus avoids limitations imposed by SIMS, including the requirement of a large, uniform surface area, and it has inherently higher spatial resolution. The main challenges with APT of ceramics and dielectrics, like diamond, are the presence of strong covalent bonds and the fact that these are electrical insulators. Although successful APT has been reported for, *e.g.*, alumina [21], silicon carbide [22], and zinc oxide [23] the precise mechanistics of atom emission in these materials is only partially understood [23,24]. Diamond is especially challenging because carbon has the highest evaporation field (>100 V/nm) of any element [25] and because the material has a large bandgap (E_{Gap} = 5.5 eV) that remains unaffected even at the sub-nanometer scale [26]. Pioneering work with diamond-like materials has been carried out by Nishikawa and coworkers in the late 1990s using a scanning atom probe [27,28]. More recently, APT has been applied to meteoritic nanodiamonds embedded in a platinum matrix [29], and initial measurements on thin diamond films grown by chemical vapor deposition (CVD) have been reported [30].

In this work, we discuss APT measurements of bulk single crystal diamond. We find that the adverse material properties of diamond can be overcome by the use of a conductive diamond substrate in combination with high-energy laser pulsing. APT runs with up to 6 million atoms could be reconstructed, eventually limited by tip rupture, and the associated mass spectra consistently reproduced the correct ^{12}C-to-^{13}C ratio of naturally occurring carbon isotopes. Although rather high laser-pulsing energies of typically 500 pJ were required to achieve stable and sufficiently high ion count rates, we found carbon to evaporate smoothly and controllably in the diamond phase. We have subsequently applied APT to image the depth distribution of a ~6 nm nitrogen δ-layer created by ion implantation, in reasonable agreement with Monte Carlo simulations. The AP tomogram further showed indications of local clustering of nitrogen and displayed no signs of ion channeling.

2. Materials and methods

The substrate used in this study was a bulk piece of boron-doped (~100 ppm) diamond grown by chemical vapor deposition. The as-grown polycrystalline diamond had a predominately (111) orientated surface. The surface was subsequently mechanically polished to a surface roughness of about 1 nm-rms as measured by atomic force microscopy. The crystallite size was 10–50 μm at the investigated surface. Since this was much larger than finished APT probe tip diameters (~50 nm), the defect-rich grain boundaries were avoided and single-crystal behavior could be assumed. The boron doping served to enhance the electrical conductivity of the diamond.

Tips were prepared by focused ion beam (FIB) milling and subsequent transfer to a sample post [31]. For some of the tips, the diamond surface was coated by 3 nm of titanium and ~50 nm of platinum before FIB milling. The Ti was deposited by e-beam evaporation and served as a fiducial layer referencing the diamond surface, while the Pt was accumulated by gas-assisted FIB deposition and served to minimize unwanted Ga ion implantation and substrate damage. We found during APT analysis that the Pt/Ti protection was efficient, and only very little Ga penetrated into the diamond. Moreover, no indications of tip damage by the Ga were seen even in unprotected diamond tips. In order to form sharp tips suitable for field emission, a triangular wedge was carved out of the diamond surface using a focused ion beam (FIB) and then transferred by a micromanipulator to a sample post. The triangular subunits of the wedge were then sculpted by FIB, using annular mill patterns, into needle-like geometries of ~50 nm apex diameter. A scanning electron micrograph of a finished tip is shown in Fig. 1B and a sketch of the layered tip structure is shown in Fig. 1C. Additional details on tip preparation by FIB are given as Supplementary Information.

The samples were analyzed in a Cameca LEAP 4000X-HR instrument in pulsed laser mode at 100 K specimen temperature. The laser pulses (λ = 355 nm, focused to a < 3 μm spot size) were applied at a rate of 160 kHz to the specimen apex in order to obtain a C^{++}/C^{+} charge state ratio of 0.85. The energy per pulse was not accessible with this instrument; we estimate it at around 500 pJ distributed over a Gaussian spot of ~3 μm diameter. We have initially tried lower pulse energies, but found that high pulse powers were essential for achieving stable evaporation at sufficiently high rates. The high pulse energy led to an increased background noise and possibly surface diffusion of Ti and Pt in metal-capped tips (see Results and discussion). Detection rates were ~0.5 ions per 100 laser pulses at a ratio of about 80% single detector hits and 20% multiples. Of about 50 tips fabricated, 15 yielded mass spectra and all of them were reconstructed. Not all analyses produced meaningful results, either because of early tip rupture or because tip diameters were too large.

The data were reconstructed using IVAS 3.6.8 software by correlating to the best known pre-run tip geometries and concentration gradients in the reference layer. (Post-run geometries were not available as an APT run was typically continued until a tip spontaneously ruptured). Reconstruction of the vertical *z* position was based on the temporal sequence of detection events. Due to the significant number of multiplicity events and cluster emissions especially in the sacrificial Pt layer, the overall vertical scaling was difficult to establish. We have

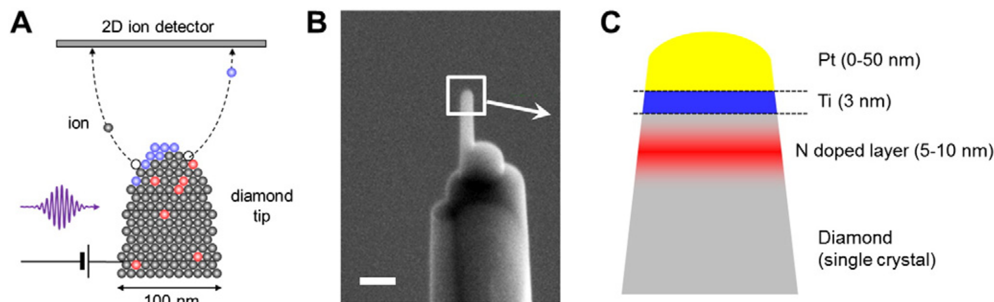

Fig. 1. (A) Principle of atom probe tomography (APT). The material under investigation, here surface-doped bulk diamond grown by chemical vapor deposition (CVD), is structured into a nanoscale tip. A combination of high voltage and UV laser pulses is used to evaporate atoms one-by-one and to record their original position using a two-dimensional ion detector. The temporal sequence of detection events then allows for reconstructing the three-dimensional position. Ion detection is coupled to a time-of-flight (TOF) mass spectrometer for isotope identification. (B) Scanning electron micrograph of a finished single-crystal diamond tip. Scale bar is 200 nm. (C) Sketch of the layered structure of a diamond tip with nitrogen δ-doping.

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