



# Fabrication of a single sub-micron pore spanning a single crystal (100) diamond membrane and impact on particle translocation



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## ABSTRACT

The fabrication of sub-micron pores in single crystal diamond membranes, which span the entirety of the membrane, is described for the first time, and the translocation properties of polymeric particles through the pore investigated. The pores are produced using a combination of laser micromachining to form the membrane and electron beam induced etching to form the pore. Single crystal diamond as the membrane material, has the advantages of chemical stability and durability, does not hydrate and swell, has outstanding electrical properties that facilitate fast, low noise current-time measurements and is optically transparent for combined optical-conductance sensing. The resulting pores are characterized individually using both conductance measurements, employing a microcapillary electrochemical setup, and electron microscopy. Proof-of-concept experiments to sense charged polystyrene particles as they are electrophoretically driven through a single diamond pore are performed, and the impact of this new pore material on particle translocation is explored. These findings reveal the potential of diamond as a platform for pore-based sensing technologies and pave the way for the fabrication of single nanopores which span the entirety of a diamond membrane.

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## 1. Introduction

Detecting events at the single particle (and ultimately molecule) level on very short time scales is a fundamental challenge in the scientific community. One approach to the problem is the use of solid-state micropores, which span a membrane, i.e. thru-holes, as employed in traditional Coulter counters (sub-micron to millimeter sized pores) [1,2]. More recently, nanopores have been utilised [3].

Pore based sensors operate in real-time and rely on the measurement of changes in conduction current as the analyte (particle or molecule) passes through the pore. The amplitude, shape, duration and frequency of each translocation event can provide unique information about an individual analyte such as size, speed and relative population [4]. The dimension of the smallest

constriction of the pore controls the maximum size of molecules/particles that can pass through for detection. Highly sensitive electronics allows detection of very small changes in the conduction current, facilitating high-resolution size discrimination. The simplicity of the concept linked with the versatility of the method has led to the use of solid-state pores for a wide range of applications involving micro- and nano-sized particles [5–9], polymer chains [10] and proteins [11–14].

The capability of the technology to facilitate rapid and direct evaluation of individual DNA bases has made it particularly attractive for next-generation DNA sequencing [15–18]. However, a high noise level during high frequency, low current measurements continues to be a limitation of nanopore technology that still requires addressing. One potential approach, recently pioneered by Long and co-workers, is to simultaneously collect optical measurements, which do not suffer from flicker noise, with electrical measurements as analytes pass through a nanopore [19–21]. The choice of substrate material in which the pore is placed is critical for

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the stability and sensing capability of the device, including the noise level. In order to facilitate low noise and fast data acquisition experiments over the widest range of analytes the material should ideally have: (i) a high electrical resistivity and low dielectric constant; (ii) chemical stability in a wide range of solvents and; (iii) must be amenable to processing such that pores of a known geometry can be reproducibly fabricated at the single pore level.

To-date various materials have been employed to produce micro- and nano-pores, including silicon nitride [22,23], glass [24], aluminum oxide [25], graphene [26–28], and track etched polymer foils [29,30], using a range of fabrication methodologies, typically involving electron beam or focused ion beam (FIB) milling [31]. The length of the pore is often an important consideration, for example for sequencing of long chain molecules such as DNA, single-base discrimination requires high spatial resolution that can be provided by low aspect ratio pores [3], such as atomically thin graphene [26,27]. In contrast, investigation of pore-particle translocation dynamics is suited to pores where the length is greater than that of the analyte to facilitate enhanced time resolution and longer event signals [32,33]. Consideration of the platform material and fabrication methodology is therefore crucial to fabricate pores of appropriate dimensions for analyte detection.

One material that has received little attention to-date but has properties which make it ideal for micro- and nano-pore particle translocation measurements is diamond. Diamond is chemically stable and durable offering extremely high resistance to chemical attack in strong acid and alkali solutions [34], allowing treatments to be applied to clean the pore without changing the geometry or degrading the structure. This is highly advantageous because as the pores get smaller in size devices often fail due to analytes irreversibly blocking the pore [35].

Moreover, diamond surfaces are not prone to hydration “swelling” phenomenon, as found with silicate-based structures, e.g. glass and quartz [36], which change the geometrical properties of the pore. Diamond is also robust, amenable to microfabrication techniques, and can be easily modified between hydrophilic (O-terminated) and hydrophobic (H-terminated) surface functionalization for enhanced chemical selectivity [37,38]. Furthermore, the optical transparency of diamond offers the potential for dual optical-conductance sensing [39].

In single crystal form, diamond has a very high resistivity in the insulating state ( $10^{13}$ – $10^{16}$   $\Omega\text{cm}$ ), a very low dielectric constant (5.7) and a low dielectric loss tangent ( $<1 \times 10^{-5}$  at 30–150 GHz) [40,41], making it near ideal for fast, low noise current-time measurements compared to other materials. This means diamond should not require further surface modification to reduce overall dielectric noise, unlike materials such as silicon nitride, which often require coating with materials such as polydimethylsiloxane [42].

There are no reports in the literature for the formation of individual micro- or nano-pores which span a single crystal diamond membrane. Pores have been made in diamond by annealing nickel (or carbon soluble metal) nanoparticles on the surface to locally remove carbon and produce etch pits. However, the pores do not span the entirety of the diamond film and the pore density is often very high [43–46]. Masuda and coworkers reported a method for the fabrication of sub-micron thru-hole pores in polycrystalline diamond using oxygen plasma etching [47]. However, the dense array produced rendered the material microporous making it unsuitable for particle translocation studies. Furthermore, polycrystalline diamond is far from ideal, compared to single crystal diamond, due to its inferior electrical properties, reduced physical properties as a result of grain boundaries and impaired performance of optical defects [48]. Moreover, contamination from amorphous and  $\text{sp}^2$  carbon, often inherent in polycrystalline diamond unless growth conditions are

carefully controlled, will increase the capacitance of the diamond causing increased dielectric noise in particle transduction measurements [49].

In this paper, we demonstrate a new methodology for the fabrication of a single sub-micron thru-hole pore in a freestanding single crystal diamond membrane, and show how this structure can be employed to investigate polymeric particle translocation. Moreover, the resulting current-time traces can also be used to provide information on the internal properties of the pore.

## 2. Experimental

### 2.1. Solutions

All solutions were prepared using Milli-Q water (Millipore Corp., UK) with a resistivity of 18.2  $\text{M}\Omega$  at 25 °C that was filtered through a 0.22  $\mu\text{m}$  syringe filter (Millex<sup>®</sup> filter units, Millipore Corp). 0.1 M KCl (Sigma-Aldrich, USA) solutions were prepared for electrochemical characterization of the diamond pores. For the particle translocation experiments, polystyrene (PS) particles of mean 800 nm diameter (Sigma-Aldrich, USA) were dispersed in filtered 0.01 M KCl solution (pH 6.9) containing 0.1% Triton X-100 to prevent particle self-aggregation (Sigma-Aldrich, US) at a concentration of 107 particles  $\text{ml}^{-1}$ . The diamond was cleaned prior to use in boiling concentrated sulfuric acid (98%  $\text{H}_2\text{SO}_4$ ; Sigma Aldrich, US) supersaturated with  $\text{KNO}_3$  (Fischer Scientific, UK) [38]. Individual pores were cleaned *in situ* by cycling a potential across the pore between  $-2$  and  $+2$  V in 0.5 M  $\text{HClO}_4$  (Sigma-Aldrich, MO, USA).

### 2.2. Diamond pore fabrication

The starting substrate was a single crystal (100) diamond plate (Element Six, Harwell, UK), 4.38 mm  $\times$  4.48 mm and 50  $\mu\text{m} \pm 3$   $\mu\text{m}$  thick, grown using high pressure, high temperature conditions and polished to  $<5$  nm roughness on both sides (Element Six, Harwell, UK). Using a laser micromachiner (E-355H-3-ATHI-O, Oxford Lasers, UK, 532 nm laser wavelength, beam size  $\sim 3$   $\mu\text{m}$ ), the diamond was thinned down to  $\sim <5$   $\mu\text{m}$  thickness in sixteen evenly spaced  $\sim 180$   $\mu\text{m}$  diameter circular regions. Due to the high transparency of the insulating diamond surface, black glass pen was applied evenly to the upper diamond surface to ensure the laser pulse energy was maximally absorbed. This enabled the diamond to be ablated evenly rather than fracturing or being otherwise uncontrollably damaged. A higher laser power (15% attenuation) was required for the initial cut of the diamond surface, while a lower power (5% attenuation) was sufficient to cut a surface that had already been partially ablated. Hence, the laser power was reduced after the first pass and for all subsequent passes to maximize the z-resolution of the thinning technique.

To maximize the regularity of ablation, the pitch between pulses and lines of pulses were the same (3  $\mu\text{m}$  or  $\frac{1}{2}$  of the laser spot size) and the stage speed was kept slow enough (0.3  $\text{mm s}^{-1}$ ) so that no significant acceleration/deceleration artefacts were observed. A laser frequency of 100 Hz was employed to ensure that the pitch between pulses was 3  $\mu\text{m}$ . To keep the laser spot in focus, for ideal laser ablation, the focal position was moved downwards in line with the depth of material removed with each pass. This depth was monitored by white light interferometry (WLI; Contour GT, Bruker UK) profiling of the ablated structures after several passes. The final diamond membrane was imaged using a polarized optical microscope (Olympus BH2-HLSH).

Pores were fabricated using electron beam induced etching (EBIE) and the entrance side imaged using an FEI Nova NanoSEM variable pressure [51] field emission - scanning electron

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