Nanoscale mapping of the three-dimensional deformation field within commercial nanodiamonds

Muhammad Salman Maqbool
ARC Centre of Excellence for Advanced Molecular Imaging, Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Victoria, 3086, Australia
Email: S.Maqbool@latrobe.edu.au

David Hoxley
Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Victoria, 3086, Australia
Email: D.Hoxley@latrobe.edu.au

Nicholas W. Phillips, Hannah D. Coughlan and Connie Darmanin
ARC Centre of Excellence for Advanced Molecular Imaging, Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Victoria, 3086, Australia
Email: Nicholas.Phillips@latrobe.edu.au
Email: hdcoughlan@students.latrobe.edu.au
Email: C.Darmanin@latrobe.edu.au

Brett C. Johnson
ARC Centre of Excellence for Quantum Computing and Communication Technology, School of Physics, University of Melbourne, Victoria, 3010, Australia
Email: johnsonb@unimelb.edu.au
Abstract: The unique properties of nanodiamonds make them suitable for use in a wide range of applications, including as biomarkers for cellular tracking in vivo at the molecular level. The sustained fluorescence of nanodiamonds containing nitrogen-vacancy (N-V) centres is related to their internal structure and strain state. Theoretical studies predict that the location of the N-V centre
Nanoscale mapping of the three-dimensional deformation field and the nanodiamonds’ residual elastic strain state have a major influence on their photoluminescence properties. However, to date there have been no direct measurements made of their spatially resolved deformation fields owing to the challenges that such measurements present. Here we apply the recently developed technique of Bragg coherent diffractive imaging (BCDI) to map the three-dimensional deformation field within a single nanodiamond of approximately 0.5 µm diameter. The results indicate that there are high levels of residual elastic strain present in the nanodiamond which could have a critical influence on its optical and electronic properties.

**Keywords:** nanodiamonds; fluorescence; cellular tracking; 3D strain mapping; Bragg coherent diffractive imaging; BCDI; biomarkers.


**Biographical notes:** Muhammad Salman Maqbool studied Metallurgy and Materials from University of the Punjab, Lahore, Pakistan to obtain his BSc (Engineering) degree in 2010. He received his MS in Materials Science from the University of Science and Technology, South Korea in 2014. During that period, he has served as a Research Assistant at the Korea Institute of Science and Technology from September 2011 to February 2014, working on the development of catalysts for nitrogen-oxide reduction with ammonia. Currently, he is a PhD candidate at La Trobe University in Australia. His PhD thesis is focused on the optimisation of nanodiamonds for bioimaging applications.

David Hoxley has pursued research interests in wide band gap semiconductors, particularly the electronic properties of the diamond surface, since his PhD at the University of Melbourne, Australia and Postdoctoral work at the University of Surrey, England. He is presently a Faculty Member of the Department of Physics and Chemistry at La Trobe University in Melbourne, Australia.

Nicholas W. Phillips is a PhD student in the ARC Centre of Excellence for Advanced Molecular Imaging based at La Trobe University in Melbourne, Australia where he previously completed his undergraduate studies (BSc with honours majoring in Physics, Biochemistry and Nanotechnology and an MSc in Nanotechnology). His research interests revolve largely around coherent diffractive imaging, with a view to applying materials science approaches to the study of biological systems.

Hannah D. Coughlan received her BSc/MSc (Nanotechnology) from La Trobe University, Melbourne, Australia with a research thesis concentrating on Coherent Diffractive Imaging in the water window energy range. She is currently in the third year of her PhD with the ARC CoE in Advanced Molecular Imaging based at La Trobe University. Her research combines physics and biochemistry to apply Bragg Coherent Diffractive Imaging to study the strain of micron sized Lysozyme protein crystals and has included multiple synchrotron and X-ray free electron laser crystallography experiments.

Connie Darmanin has a PhD in Protein Crystallography from Monash University, she then continued in the field of structural biology during her Post-Doctoral career at CSIRO. She has spent the last nine years developing new techniques to help understand in meso crystallisation and novel approaches
for structure determination. Recently she has moved to La Trobe University, in Melbourne, Australia, and focused her career on nanocrystallography and X-ray free electron laser to solve structure of difficult proteins.

Brett C. Johnson received his PhD in Physics from the University of Melbourne, Australia in 2004. He has worked as a JSPS research fellow at the Japan Atomic Energy Agency and, from 2013, works at the Melbourne node of the CQC2T developing ion implanted materials for quantum computer related devices. His research interests are on the optical and electrical characterisation of irradiation-induced defects in semiconductors and also ion-implantation- and pressure-induced phase transformations.

Ross Harder received his BSc, MSc and PhD degrees from the University of Wisconsin – Milwaukee, USA in 1994, 1997 and 2002, respectively. He has worked as a Post-Doctoral Research Associate at the Department of Physics, University of Illinois – Urbana Champaign, USA (2003–2005), and at the Department of Physics, University College London, UK (2006–2007). He served as an Assistant Physicist from 2008 to 2013, and was promoted to his current position as Physicist at X-ray Science Division, Argonne National Laboratory, USA. His research interests include synchrotron radiation-based, nanometre scale imaging methods involving in-situ and in-operando applications to materials science.

Jesse N. Clark received his PhD in Coherent Diffraction Imaging from La Trobe University. He then moved to the London Centre for Nanotechnology (University College London) where he worked on developing coherent diffraction imaging techniques for imaging strain in nanocrystals. He is currently a Peter-Paul Ewald Fellow at the Stanford PULSE Institute (SLAC, USA) and the Center for Free Electron Laser Science (DESY, Germany) where he is developing ultrafast imaging techniques for use with free electron lasers.

Eugeniu Balaur holds a PhD in Materials Science and Engineering at Erlangen-Nueremberg University, Germany. He moved to Australia to continue his research and support the work in the field of nanotechnology and fabrication at CoE for Coherent X-ray Science. He worked part time as process engineer at Melbourne Centre for Nanotechnology before moving full time to the new CoE for Advanced Molecular Imaging. His current interests are in the field of plasmonics and developing microfluidic systems for sample delivery for XFELs.

Brian Abbey received his PhD in Chemistry from Cambridge University (UK) in 2007, he also holds Master’s degrees in Physics (2002) and Nanomaterials (2003) from UCL and Imperial College London (UK), respectively. From 2007–2008, he worked as a Research Fellow within the Centre of Excellence for Coherent X-ray Science in Melbourne. In 2008, he moved back to the UK to work within the engineering science department at the University of Oxford where he helped pioneer methods in X-ray microdiffraction to characterise sub-grain deformation structure. In 2010, he returned to Melbourne a year later took up a permanent position in condensed matter physics at La Trobe University where he is currently an Associate Professor. In 2012, he received the deans’ award for excellence in research and in 2014 began an ARC Future Fellowship.
1 Introduction

Diamond is an allotrope of carbon in which each atom of carbon is tetrahedrally bonded to four other carbon atoms with sp$^3$ hybridisation. Diamond possesses a wide range of useful characteristics, including high electrical resistivity and thermal conductivity, extreme hardness, chemical inertness, optical transparency, facile functionalisation, and low toxicity [1]. On the basis of this unique set of properties, diamonds have found a variety of applications ranging from electronic devices to filler materials in nanocomposites and from targeted therapy to biolabelling for biological applications [2]. Owing to their biocompatibility and fluorescence properties, nanodiamonds containing nitrogen-vacancy (N-V) centres have emerged as a promising candidate for tracking biological functions at the molecular level [3–5]. N-V centres are point defects in carbon which emit a bright red light when excited by visible light sources; the intensity and peak wavelength of this light can be modulated by elastic strain. Several simulation studies have been published that explore the relationship between the strain fields associated with N-V centres, the dimensions of the nanodiamonds and the resulting optoelectronic properties of the system [6,7]. However, obtaining direct experimental information about the spatially resolved deformation field inside the nanodiamonds for comparison and input into these models presents significant practical challenges.

The goal of the work presented here is to apply the technique of Bragg coherent diffractive imaging (BCDI) to the study of the spatially resolved elastic strain within a single nanodiamond. Previously BCDI has been restricted to materials composed of heavy elements (e.g., gold) where the signal-to-noise ratio for individual Bragg peaks is high. The recent availability of ultra-high sensitivity single photon detectors however has enabled the extension of this technique to a wider range of samples. Here we show that BCDI can be used to obtain information about the three-dimensional elastic strain state of nanodiamonds. The results show that the nanodiamonds as deposited from solution already contain significant levels of deformation which will in turn influence their photoluminescence properties. By measuring and then optimising the strain state of the nanodiamonds we hope to be able to produce nanodiamonds with more-stable fluorescence suitable for in-vivo studies. In the case of studies of molecular tracking the efficient production of fluorescent signal is essential for avoiding damage to the sample caused by prolonged exposure to the visible light probe.

Transmission electron microscopy (TEM) has been used extensively to study the structural characteristics of nanodiamonds [8–10]. However, obtaining three-dimensional strain information from nanoparticles using TEM is a difficult and laborious process often requiring special sample preparation which can itself induce additional strain to the sample. The sensitivity of TEM to lattice strain is also typically less than that of X-ray diffraction which is sensitive to strains on the order of $\Delta d/d \sim 10^{-6}$. Although, the real space resolution of X-ray microbeam diffraction measurements and direct imaging methods such as X-ray topography is normally on the order of microns, which is too low to resolve any internal features of nanocrystals [11–13]. The recently developed technique of BCDI however offers spatial resolutions on the order of 10 nm whilst retaining great strain sensitivity. In addition, with BCDI it is possible to obtain three-dimensional information about the lattice deformation very easily, without any sectioning of the sample.

The recent development of coherent diffractive imaging (CDI) at the nanoscale using hard X-ray sources has opened the door to imaging materials samples which may be
millimetres in size with spatial resolutions on the order of tens of nanometres or less [14].

BCDI is a type of diffractive imaging in which a two-dimensional image of a single Bragg peak diffracting from a small, isolated crystal is collected at each point on the X-ray rocking curve. Together the two-dimensional images are assembled to form a three-dimensional reciprocal space map of the reflection. Provided the continuous diffraction signal around the Bragg peak is sufficiently well-sampled in the detector plane, phase retrieval algorithms can be used to determine the phase component of the diffracted wave field. A 3D Fourier transform can then be used to propagate between real and reciprocal space to recover an image of the nanocrystal. The real-space phase information is directly related to the relative displacement of the atoms within the sample from their ideal positions. Further details of the BCDI analysis and the process of analysing the data are given in Section 2.

For over 10 years BCDI has been successfully applied to the high-resolution characterisation of a range of materials. In 2001, Robinson et al. [15] were the first to successfully demonstrate the phase retrieval of two-dimensional diffraction data measured from gold nanocrystals. Five years later, Pfeifer et al. [16] were able to further develop this work for in-situ, three-dimensional mapping of strain fields within lead nanocrystals. This technique for reconstructing crystal deformation in three-dimensions would later become known as BCDI [16]. By measuring multiple Bragg reflections such that lattice displacements along all three principal axis were measured Newton et al. [17] were able to reconstruct the full 3D strain tensor in micron-sized zinc oxide pillars. More recently we have shown that it is possible to map deformation fields within biocrystals composed of macromolecules [18]. An increasing number of groups are also using BCDI to map the elastic strain fields associated with individual defects [19].

Here, we report a proof-of-principle experiment where we apply BCDI to map the three-dimensional deformation within a single nanodiamond. To the authors knowledge this is the first successful mapping of the spatially resolved strain state within individual nanodiamonds. This study thus paves the way to understanding the effect of residual elastic strain on the optical properties of nanodiamonds which is a vital step in improving their performance as biomarkers.

2 Experimental

During illumination with a coherent X-ray beam and under Bragg conditions, a perfect crystal will generate a single Bragg peak on the detector (i.e., in reciprocal space). The centre of the Bragg spot contains information about the average properties of the crystal lattice, whereas regions away from the centre contain information about its detailed structure. If the crystal under observation contains a small amount of strain, the diffraction pattern obtained will be asymmetric. The intensity (I) of the diffraction pattern is given by:

\[
I(q) \propto \left| \int_{-\infty}^{\infty} \rho_L(r) s(r) e^{i qr} e^{i u(r)} dr \right|^2
\]  

(1)

where \( \rho_L(r) \) is the electron density of the sample, \( s(r) \) is its shape function which is dependent on the diffraction volume and the relative displacement of the atoms from their original lattice points, and \( u(r) \) is its strain state [20]. For reconstruction of the phase, the
intensity $I$ and a hypothetical 3D support are used as inputs to an iterative algorithm which updates the real- and reciprocal-space arrays at each cycle. Here, the number of pixels should be at least twice the number of unknown density values within the support, so as to acquire a unique dataset in two or more dimensions (oversampling) [21–23]. By iteratively updating the phase of the measured diffracted intensity distribution whilst refining the shape of the nanocrystal, a three-dimensional image of the sample and any deviations from perfect crystallinity for the lattice planes corresponding to the measured reflection can be obtained. Thus BCDI of oversampled RSM data can be effectively used for phase retrieval from a continuous diffraction pattern around a Bragg spot.

BCDI measurements were carried out at beamline 34-ID-C at the Advanced Photon Source (APS) at the Argonne National Laboratory (ANL) in Chicago, USA. A schematic of the experimental setup in the vicinity of the sample is shown in Figure 1. The source was composed of quasi-monochromatic 9 keV X-rays from a channel-cut Si(111) monochromator focused using Kirkpatrick-Baez mirrors to a focal spot in the sample plane of $2.0 \times 2.0 \mu m^2$. Nanocrystals were located using a confocal microscope mounted vertically above the sample. A kappa diffractometer, with a centre of rotation at the nominal beam position, combined with piezo stages was used to place the nanocrystal in the beam. The crystal was then rotated (in the $\theta$ direction) until the (111) reflection could be found. The (111) reflection was chosen for the BCDI measurements since it produced one of the strongest diffracted signals. Although only one reflection was measured here, each reflection is sensitive to atomic displacements from a different set of lattice planes. Hence, if one wishes to recover the full quantitative strain tensor a minimum of three independent reflections need to be measured. The detector was a medipix-2 photon-counting pixel area detector, consisting of $256 \times 256$ square pixels of $55 \mu m$ in each linear dimension and placed at $0.675 m$ from the sample.

Figure 1 (a) Experimental setup for BCDI measurements at beamline 34-ID-C at the APS. During the measurements the nanodiamond (reconstruction of the crystal shown in blue) is rocked in the $\theta$ direction to bring it in and out of the diffraction condition. Note the $\theta$ rotation was about the $z$-axis. (b) 3D rendering of the reciprocal space map data collected from the nanodiamond. This data was used to recover a real-space image of the crystal (see online version for colours)

To attain a complete 3D diffraction dataset, the crystal was rocked through a total $\theta$ angle of $0.6^\circ$ in increments of $0.005^\circ$. At each step the detector exposure time was 1 second. By assembling the two-dimensional series of images into a three-dimensional volume a complete, oversampled, reciprocal space map was obtained. The phase of the measured
intensity data was recovered using iterative phase retrieval algorithms [16,24–26]. During the image reconstructions a combination of error reduction (ER) and difference map (DM) methods were used. These two algorithms (ER and DM) can be applied to any coherent diffraction dataset and have generally been found to be robust provided there is sufficient signal-to-noise ratio in the measured data [27]. Owing to the electronic noise in the Medipix-2 detector being negligible and the use of a He filled flight tube between the sample and the detector, noise levels in the data used here were low. A small amount of extraneous air scatter consisting of very low numbers of photons was removed by setting a small threshold of $1.20 \times 10^{-3}$ on the data (less than 1% of the data range). The 3D support is defined as the volume which contains the complex density of the sample. The initial support used here was a cube whose dimensions were more than twice the maximum size (which can be determined from the diffraction fringe spacing) of the crystal. In the algorithm, the support was updated using ‘shrinkwrap’ after every five iterations. An acceptable reconstruction was reached when the error metric, defined as the difference between measured and reconstructed intensity, approached $10^{-3}$ [28]. The reconstruction approach used here was found to provide the best solution for the complex crystal density as judged by the error metric. Further details of the image reconstruction process can be found in Clark et al. [25].

The sample consisted of monocrystalline nanodiamonds supplied as a powder, purchased from Microdiamont, Switzerland (MSY-ND) and synthesised using high-pressure-high-temperature (HPHT) method. To create a sparse array of nanodiamonds they were suspended in 10 : 10 by volume solution of poly-diallyldimethylammonium chloride (20 wt.% in water; Sigma Aldrich, Australia) in deionised (DI) water, and deposited onto oxygen-plasma cleaned silicon substrates. Unfortunately owing to the lack of strong adhesion of the nanodiamonds on the substrate after dispersion, the number density of nanodiamonds on the substrate was extremely low (typically only a few nanodiamonds per 200 µm²). The low number density of nanodiamonds was the primary reason why it was only possible to collect one high-quality BCDI dataset in this proof-of-principle study. For the X-ray measurements the nanodiamonds were coated with an approximately 80 nm thick layer of SiO₂ using plasma-enhanced chemical vapour deposition (CVD) to immobilise them in the beam. For the Scanning electron microscopy (SEM) measurements, a Nova FEG-SEM (Melbourne Centre for Nanofabrication, VIC, Australia) was used at a working distance of 5.1 mm with a voltage of 18 kV. SEM characterisation required a very thin (maximum 10 nm) layer of gold to be deposited on the nanodiamonds to minimise charging effects. From the sparse field of nanodiamonds adhered to the substrate a single one was selected for the proof-of-principle BCDI measurements presented in this paper.

3 Results and discussion

3.1 Scanning electron microscopy (SEM)

Some representative SEM images of the sample are presented in Figure 2. The commercial nanodiamonds were found to possess a large range of sizes and shapes. The dimensions of the crystals varied in size from 0.1 to 1 µm whilst the geometry of the crystals varied from rhombus through tetrahedral to quite irregular shapes. The functional properties of nanomaterials often depend on their structural properties e.g., [29].
Similarly, the size and shape of nanodiamonds are known to influence their optical and electronic properties [2,6,30]. Therefore, a more controlled synthesis at the laboratory level has been suggested in order to attain nanodiamonds with predictable and reproducible morphologies in order to control their functional characteristics [31,32].

Figure 2  Representative SEM images of two of the nanodiamonds examined with BCDI (not the exact same one as measured here). Note the irregular shape and size of the nanodiamonds.

3.2 Bragg coherent diffractive imaging (BCDI)

Figure 3 represents slices of the nanodiamond, reconstructed using BCDI. In all the slices, the crystal was very highly strained. These results indicate that the HPHT nanodiamonds possesses a significant internal deformation, particularly towards the surface of the crystal. This may impact the effectiveness of this nanodiamond in a number of biological applications where it has been shown that the location of the defect of the nanodiamond dramatically affects the fluorescence quality [6].

Figure 3  2D slices showing the density (amplitude – black background) and projected lattice displacements for the (111) planes of the nanodiamond from BCDI for two different views (see online version for colours)
The 3D reconstruction of the whole nanodiamond crystal (whose slices are shown in Figure 3) is presented in Figure 4. The shape of the crystal appeared to be asymmetric with uneven surfaces and rough boundaries, this confirms the results from the SEM images; in both cases the crystal facets are not well-defined and there appear to be irregular terraces. This is an important observation since the crystal shape is known to have a strong influence on the strain distribution [2], though it should have little direct influence on the quality of the BCDI measurement (which is largely determined by the crystallinity). The dimensions of the crystal were calculated to be 0.231 µm × 0.472 µm × 0.035 µm. The slices cut at regular intervals through the crystal represent the atomic displacements corresponding to the (111) reflection. The internal deformation varied at different regions of the crystal.

**Figure 4** Three-dimensional reconstruction (shown in blue) of single-crystal nanodiamond using BCDI. Two-dimensional slices of the lattice displacements (shown above the 3D image) are taken from the front to the back of the crystal along x-axis (see online version for colours)

From a qualitative assessment of the two-dimensional slices in Figures 3 and 4 it appears that the middle of the nanodiamond may be more ordered (i.e., smaller displacement values) than the outer layers. To confirm this through quantitative analysis we used a 3D Euclidean distance transform to calculate the shortest distance from every point contained within the nanocrystal to the nanocrystals’ surface. By correlating this against the lattice displacement associated with each point we are able to determine the lattice displacement as a function of distance from the nanocrystal surface. The results are presented in Figure 5. There are three features from this analysis to note. One is that the displacements seem to peak at zero and at around \(d/4\) lattice displacement. The second point is that, the rate of change for the positive lattice displacement is smaller than for the negative lattice displacement, which we believe is due largely to the irregular shape of the nanodiamond.
Finally, as shown by the 2D slices, the distribution of displacements is higher at the surface spanning the full range (equivalent to one whole lattice spacing). In the interior of the sample, however, the distribution of displacements is significantly narrower. The interpretation of this could be that there is a differing surface reconstruction inducing a resulting elastic strain profile or that the interior is inherently more ordered owing to defects present at the surface of the nanodiamond.

**Figure 5** Scatter plot showing the distribution of lattice displacements as a function of the minimum distance from the surface of the crystal for every point inside the nanodiamond. Each red dot represents (111) lattice plane displacement from a different sample voxel within the 3D nanocrystal volume. The left side of the plot shows the displacements measured closer to the surface whilst the right side of the plot shows the displacements that were recorded nearer to the core of the nanocrystal. The purple and cyan lines trace the approximate upper and lower boundaries for the positive and negative lattice displacements respectively (see online version for colours).

Previous modelling work of the influence of strain on the optoelectronic properties of nanodiamonds has ignored any effect of residual strain within the crystal [6,7]. On the basis of the preliminary study presented here the effect of residual strain on the optoelectronic behaviour of nanodiamonds may be significant. To accurately incorporate these effects into modelling of the fluorescence properties of N-V centre nanodiamonds, the source of the strains must first be confirmed. This is likely to involve a range of complementary techniques e.g., density functional theory (DFT) modelling and TEM to study the nanodiamond surface which can then be used in combination with BCDI to simulate the residual elastic strains within the nanodiamonds. From the point of view of readily predicting the functional behaviour of nanodiamonds ideally there would be zero residual elastic strain present. However, if the results of this study are confirmed and there is an unavoidable residual strain profile present in commercial nanodiamonds, incorporating this information into any future simulations will be essential. In this case it may be possible to not only accurately predict the functional behaviour of nanodiamonds but actually to exploit the residual strain which is present in order to tune their optical properties.
4 Conclusions

The current work describes a proof-of-principle study characterising three-dimensional deformation in nanodiamond using BCDI. Our results illustrate that BCDI shows strong potential for mapping directly the spatially resolved internal strain distribution of low-Z materials such as nanodiamond. The information from the BCDI experiment indicates that the three-dimensional shape of the commercially supplied nanodiamond crystal was asymmetric, which was consistent with the images obtained from scanning electron microscopy. Pre-existing deformation fields were found within the as-received crystals without any implantation, which might affect their optical properties. In particular we note that the level of lattice disorder increases steadily as one moves from the centre of the crystal outwards. Further experiments are needed to study a larger number of nanodiamonds in order to validate our findings. In addition work is being carried out to determine the implications of this type of structure on the resultant optical properties of nanodiamonds which will impact upon their application as biomarkers. We also plan to investigate the effect of shape on the resultant strain distribution in future BCDI experiments. Finally, we are currently developing methods for pre-patterning of the substrate to tailor the number density of nanodiamonds, allowing a much larger systematic study to be performed.

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References


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