Microscopic Imaging of the Stress Tensor in Diamond Using in Situ Quantum Sensors

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Supporting Information

ABSTRACT: The precise measurement of mechanical stress at the nanoscale is of fundamental and technological importance. In principle, all six independent variables of the stress tensor, which describe the direction and magnitude of compression/tension and shear stress in a solid, can be exploited to tune or enhance the properties of materials and devices. However, existing techniques to probe the local stress are generally incapable



of measuring the entire stress tensor. Here, we make use of an ensemble of atomic-sized in situ strain sensors in diamond (nitrogen-vacancy defects) to achieve spatial mapping of the full stress tensor, with a submicrometer spatial resolution and a sensitivity of the order of 1 MPa (10 MPa) for the shear (axial) stress components. To illustrate the effectiveness and versatility of the technique, we apply it to a broad range of experimental situations, including mapping the stress induced by localized implantation damage, nanoindents, and scratches. In addition, we observe surprisingly large stress contributions from functional electronic devices fabricated on the diamond and also demonstrate sensitivity to deformations of materials in contact with the diamond. Our technique could enable in situ measurements of the mechanical response of diamond nanostructures under various stimuli, with potential applications in strain engineering for diamond-based quantum technologies and in nanomechanical sensing for on-chip mass spectroscopy.

KEYWORDS: diamond, nitrogen-vacancy center, quantum sensor, strain, stress, implantation

P ressure is a powerful thermodynamic variable often used to modify a material's properties.¹ Most notably, strain enhances the charge carrier mobility in modern electronics.^{2–4} It allows the tuning of the optical properties of materials,^{5–7} can confer them with a ferroelectric nature,^{8,9} or even make them better superconductors.¹⁰ Despite these successes, strain engineering is still a largely unexplored field considering the huge parameter space available; indeed, stress is characterized by six parameters (three axial components and three shear components, defining the stress tensor), which, in principle, can be continuously and independently varied over many orders of magnitude to optimize the functional properties of materials.¹

Key to further innovations is the ability to characterize stress at the nanoscale, and in particular to quantitatively determine the six components of the stress tensor. Existing methods to probe stress in solids typically rely on the interaction between a beam of probe particles (usually electrons or photons) with the stressed material.^{11–19} However, these techniques are generally sensitive to only one or a convolution of the stress components. Exceptions include off-axis electron holography,²⁰ but at the cost of sample destruction to produce suitably thin lamellae (under 200 nm thickness, which may cause strain release), and off-axis Raman spectroscopy,^{21,22} which is not typically compatible with high-resolution imaging. In this work, we describe a radically different approach, which relies on atomic-sized strain sensors embedded into the material to characterize the local strain. In recent years, several materials have been found to host such in situ quantum sensors, in the form of optically addressable point defects that exhibit strain-

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Figure 1. Stress-tensor mapping with nitrogen-vacancy centers. (a) Diagram of the experimental setup, depicting a diamond sensing chip mounted on a glass coverslip with a microwave (MW) resonator. The layer of nitrogen-vacancy (NV) centers in the diamond is illuminated by a green laser, and imaging of the red NV photoluminescence (PL) is captured with a sCMOS camera. (b) Fine structure of the NV electronic ground state showing the two spin transitions with frequencies ω_{\pm} that can be probed experimentally by virtue of spin-dependent PL (symbolized by light bulbs of different brightness). (c) Schematic of the unit cell of the diamond crystal under different stress conditions: no stress (blue), axial stress (orange), and shear stress (green). (d) Unit cell with the four NV orientations depicted as different vacancy locations V_i (i = 1,2,3,4). The stress tensor is expressed in the natural coordinate system of the cubic lattice, (*xyz*). (e) Schematic cross-section of the diamond illustrating how the NV layer (green band) is used to probe the stress produced by local features. (f) Defect structure of the NV and its native coordinate system ($X_iY_iZ_i$). (g) Optically detected magnetic resonance spectra under an external magnetic field of strength $B \approx 50$ G, recorded from NV centers at three different locations in a scratched diamond indicated by circles in (h): away from scratch damage (blue), underneath a scratch (orange), and adjacent to a scratch (green). Each resonance is labeled according to its corresponding NV orientation. (h) Atomic force microscopy (AFM) image of the diamond surface showing scratches created with a diamond scribe.

dependent energy levels. These include diamond,^{23–25} silicon carbide,²⁶ and silicon.⁹ To date, however, real-space imaging of the full stress tensor using in situ sensors has remained elusive, in part due to the difficulty of addressing a sufficiently dense ensemble of sensors while retaining the capability to extract all the tensor components.

The in situ quantum sensor employed in this work is the nitrogen-vacancy (NV) defect in diamond.²⁷ It is a point defect with a spin-1 electronic ground state and a spin-dependent photoluminescence (PL), allowing optically detected magnetic resonance (ODMR) spectra to be recorded at room temperature.²⁸ By carefully analyzing the ODMR response of a dense layer of randomly oriented NV defects in a single crystal diamond, we are able to reconstruct the entire stress tensor and demonstrate wide-field two-dimensional (2D) mapping with submicrometer spatial resolution. Previous works have achieved 2D imaging of a single strain component^{29,30} (using a single NV orientation) and outlined a method to extract the entire tensor²³ (using several well resolved single NV centers with different orientations). Single NV defects have also been proposed for nanomechanical sensing, including vector force sensing and mass spectroscopy.²⁵ We apply the technique to spatially nonuniform strain features induced by scratches, implantation damage, nanoindents, and devices fabricated on diamond. These results establish NV-based wide-field stress mapping as a powerful technique for nanoscale mechanical studies of diamond, which is an interesting material for nanomechanical applications with extreme mechanical properties and sometimes unexpected strain-stress relationships.³¹ The technique may also facilitate strain engineering for diamond-based quantum applications³²⁻³⁸ and find applications in multiplexed nanomechanical sensing for mass spectroscopy and microfluidics.³⁹⁻⁴²

The experimental setup is depicted in Figure 1a. It consists of a wide-field fluorescence microscope equipped with microwave excitation to allow the spin transition frequencies of the NV centers (ω_+ , Figure 1b) to be probed via ODMR spectroscopy.²⁸ These frequencies depend on the spatial distribution of the unpaired spin density and so are sensitive to the local strain in the lattice, or equivalently²⁵ to the local stress, which can have axial and shear components (Figure 1c). As we will see, the use of multiple NV orientations (Figure 1d) enables the full reconstruction of the local stress tensor. By using a thin layer of NV centers near the diamond surface, we can then spatially map the stress tensor in two dimensions and study the effect of localized strain-inducing features (Figure 1e). We note that the presence of the NV centers and other unavoidable defects such as substitutional nitrogen may also contribute to the net measured stress.⁴

The fine structure of the NV electronic ground state (Figure 1b) is governed by the simplified spin Hamiltonian⁴⁴⁻⁴⁶

$$H_{i} = (D + \mathcal{M}_{Z_{i}})S_{Z_{i}}^{2} + \gamma_{NV}\vec{B}\cdot\vec{S}_{i} - \mathcal{M}_{X_{i}}(S_{X_{i}}^{2} - S_{Y_{i}}^{2}) + \mathcal{M}_{Y_{i}}(S_{X_{i}}S_{Y_{i}} + S_{Y_{i}}S_{X_{i}})$$
(1)

where $D \approx 2.87$ GHz is the temperature-dependent zero-field splitting parameter, $\gamma_{\rm NV} = 28.035(3)$ GHz T⁻¹ is the NV gyromagnetic ratio,²⁷ $\vec{S}_i = (S_{X_i}, S_{Y_i}, S_{Z_i})$ are the spin-1 operators, \vec{B} is the applied magnetic field, and $\vec{\mathcal{M}}_i = (\mathcal{M}_{X_i}, \mathcal{M}_{Y_i}, \mathcal{M}_{Z_i})$ is the effective electric field associated with mechanical stress, where we neglect any residual true electric field caused by charge effects^{47,48} (Supporting Information, Section IV). Here $(X_iY_iZ_i)$ is the coordinate system of the NV defect structure (Figure 1f), and the index *i* = 1,2,3,4 denotes the NV orientation with respect to the

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Figure 2. Stress induced by implantation damage. (a) Schematic of the stress induced by locally implanting C_3 molecules in the diamond. (b) NV PL image of an annulus-shaped implanted region. (c) AFM image of a segment of the annulus (dashed box in (b)). (d) AFM profile across the implanted region (dashed line in (c)). (e) Spatial maps of the six stress tensor components measured with the NV sensors in the same region as in (b). The amplitude of the σ_{xz} and σ_{yz} components has been multiplied by a factor of 5.

diamond unit cell (Figure 1d). The relation between $\dot{\mathcal{M}}_i$ and the local stress is most conveniently expressed by defining the stress tensor, $\vec{\sigma}$, with respect to the diamond unit cell coordinate system (*xyz*) defined in Figure 1d.^{25,46} This gives

$$\mathcal{M}_{X_i} = b\Sigma_X^{\text{axial}} + c\Sigma_{X_i}^{\text{shear}}$$
$$\mathcal{M}_{Y_i} = \sqrt{3} b\Sigma_Y^{\text{axial}} + \sqrt{3} c\Sigma_{Y_i}^{\text{shear}}$$
$$\mathcal{M}_{Z_i} = a_1 \Sigma_Z^{\text{axial}} + 2a_2 \Sigma_{Z_i}^{\text{shear}}$$
(2)

where the stress susceptibility parameters are $a_1 = 4.86(2)$, $a_2 = -3.7(2)$, 2b = -2.3(3), and 2c = 3.5(3) in units of MHz GPa^{-1,25} and we introduced the quantities

$$\Sigma_X^{\text{axial}} = -\sigma_{xx} - \sigma_{yy} + 2\sigma_{zz}$$

$$\Sigma_Y^{\text{axial}} = \sigma_{xx} - \sigma_{yy}$$

$$\Sigma_Z^{\text{axial}} = \sigma_{xx} + \sigma_{yy} + \sigma_{zz},$$
(3)

which capture the contribution of the axial stress components and are independent of the NV orientation,⁴⁹ and

$$\Sigma_{X_i}^{\text{shear}} = 2f_i \sigma_{xy} + g_i \sigma_{xz} + f_i g_i \sigma_{yz}$$

$$\Sigma_{Y_i}^{\text{shear}} = g_i \sigma_{xz} - f_i g_i \sigma_{yz}$$

$$\Sigma_{Z_i}^{\text{shear}} = f_i \sigma_{xy} - g_i \sigma_{xz} - f_i g_i \sigma_{yz},$$
(4)

which describe the effect of the shear stress components. In equation 4, the functions f_i and g_i evaluate to ± 1 depending on the NV orientation. Namely, using the vacancy positions i = 1,2,3,4 as defined in Figure 1d, we have $(f_{1i}f_{2i}f_{3i}f_4) = (+1, -1, -1, +1)$ and $(g_1, g_2, g_3, g_4) = (-1, +1, -1, +1)$. We note that the spin-mechanical interaction of the NV is invariant under inversion of the nitrogen and the vacancy; therefore, there are

only four orientations to consider in contrast to true electric fields. 50

Because the stress tensor is described by six independent parameters, a measurement relying on a single NV center is not sufficient to infer the full stress tensor even if the effective field $\vec{\mathcal{M}}_i$ is completely determined.²³ However, by using a small ensemble of NV centers with multiple orientations, it is possible to determine all six stress components in the corresponding volume, assuming a uniform stress within this volume. To see that, we consider the limit of small magnetic fields $|\vec{B}| \ll D$, for which the spin transition frequencies are given by^{25,47}

$$(\omega_{\pm})_i = D + M_{Z_i} \pm \sqrt{(\gamma_{\rm NV} B_{Z_i})^2 + (M_{X_i})^2 + (M_{Y_i})^2}$$
(5)

By using eqs 2–4, we find that the sum frequencies $(\omega_+ + \omega_-)_i = D + M_{Zi}$ of the four possible orientations can be used to uniquely determine the three shear stress components $(\sigma_{xyn}\sigma_{xzr}\sigma_{yz})$ as well as the sum of the axial components, $(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. The axial components are then determined individually by using the difference frequencies $(\omega_+ - \omega_-)_i = 2\sqrt{(\gamma_{NV}B_{Z_i})^2 + (M_{X_i})^2 + (M_{Y_i})^2}$, which in general is an overdetermined problem when the magnetic field \vec{B} is known. This is the basis of our method to determine the full stress tensor (see further details in Supporting Information, Sections I and II).

Experimentally, we measured the frequencies $(\omega_{\pm})_i$ for the four possible NV orientations by recording ODMR spectra under a small applied magnetic field \vec{B} aligned so that all eight transitions can be resolved simultaneously,^{48,51} as shown in Figure 1g. The magnetic field \vec{B} as well as the parameter D were estimated using the ODMR data from a region far from any obvious stress-inducing feature, where the stress was assumed to be zero, and then extrapolated to the whole field of view (via a linear fit) so that there are only six unknown

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Figure 3. Stress induced by a nanoindent. (a) AFM image of a representative nanoindent in the diamond surface. (b) AFM profile across the indent (dashed line in (a)). (c) NV PL image of a region containing a nanoindent. (d) Spatial maps of the six stress tensor components in the same region as in (b). The black shapes represent the contour of the nanoindent as determined from the PL image. The amplitude of the σ_{xz} and σ_{yz} (σ_{xy}) components has been multiplied by a factor of 10 (2). (e) Map of the body force deduced from the stress tensor using eq 6. The color denotes the magnitude \vec{J} , while the overlaid arrows indicate the projected force in the *xy* plane.

parameters for eight measurements at each pixel (Supporting Information, Section II). As a preliminary test, we investigated the stress induced from scratching the diamond with a diamond tipped scribe,⁵² generating cuts that are less than a micron wide and range from 5 to 20 nm in depth (Figure 1h), with the NV layer extending from about 5 to 30 nm below the surface.⁵³ A reference ODMR spectrum (i.e., away from any scratch) is shown in blue in Figure 1g, which is used to infer the magnetic field, here $(B_x, B_y, B_z) \approx (22, -13, -40)$ G. An ODMR spectrum taken from underneath the scratch is shown in orange and exhibits a shift of about 10 MHz that is relatively uniform across all the resonances, suggesting a stress field in the GPa range that is dominated by axial stress components. An ODMR spectrum taken from a region adjacent to the scratch is shown in green and exhibits shifts that are markedly different for different NV orientations. This is the signature of a large contribution from shear stress.

To test our method for reconstructing the full stress tensor, we first implanted C₃ molecules at 15 keV into the diamond through a Cr mask to create localized regions of damage extending 5–10 nm below the diamond surface. Implantation is commonly used in diamond to introduce dopants for electrical devices⁵⁴ or produce buried graphitic electrical wires.⁵⁵ The resultant confined amorphous carbon has a different density to diamond thus introducing an embedded force that pushes in all directions (Figure 2a). It also causes a reduction in PL from the NV defects by about 25%, as seen in Figure 2b. Here, the implant pattern is a circular ring of 1.5 μ m width and 50 μ m diameter. The embedded force from the damage is sufficient to cause a bulging of the diamond surface,⁵⁶ which was measured by atomic force microscopy (AFM) to be on the order of 2 nm in this case (Figure 2c,d).

The spatial maps of the six stress tensor components near this circular ring are shown in Figure 2e, revealing ring-shaped patterns with stress values of up to about 30 MPa (corresponding to ODMR frequency shifts in the 100 kHz range), much smaller than for the scratches discussed above. The pixel-to-pixel noise is about 1 MPa (standard deviation) for the three shear stress components, against 10 MPa for the axial stress components, with a total acquisition time of about 10 h. This difference originates from the presence of the magnetic field projection B_{Z_i} in the last term of eq 5 used to separate the individual axial components, which results in a reduced sensitivity when $(\gamma_{NV}B_{Z_i})^2 \gg (M_{X_i})^2 + (M_{Y_i})^2$ (Supporting Information, Section III). This loss of sensitivity could be mitigated by performing sequential measurements minimizing B_{Z_i} for each NV orientation. Moreover, because the individual axial stress components are determined based on the knowledge of $B_{Z,i}$ they are sensitive to the presence of background stress (assumed to be zero in order to determine the magnetic field), which limits the measurement accuracy (Supporting Information, Section V). This source of inaccuracy could be removed by using a calibrated source of magnetic field, which would then enable absolute measurements of the background stress in the diamond. Nevertheless, all stress components in Figure 2e exhibit resolvable features, and the different symmetries indicate they have been sensibly separated. In particular, the σ_{xx} (σ_{yy}) component is maximum where the ring is tangential to the y (x) axis, whereas σ_{zz} is relatively uniform along the ring, as expected from a body force pushing in the normal direction to the line of damage as depicted in Figure 2a. Likewise, the shear stress components exhibit the expected symmetries with respect to the x and yaxes. All the axial components have a positive value near the damaged region indicating a compressive stress, consistent with an expansion of the lattice caused by the implantation.⁵⁶ The smallest spatial features in Figure 2e have a size of the order of 1 μ m. Moreover, in the Supporting Information (Figure S2), we show that implanted regions separated by less than 1 μ m can be resolved in the stress maps, indicating a sub- μ m spatial resolution close to the optical diffraction limit (~400 nm⁵⁷).

The values of stress measured here are consistent with Raman spectroscopy⁵⁶ performed on a similar sample (Supporting Information, Figure S4), which indicates an axial stress of 7 ± 2 MPa in the damaged region. This validates the NV technique as a sensitive and quantitative tool to characterize the stress in diamond, with the added benefit of access to the complete tensor information.

As a second test structure, we performed a series of nanoindents in the diamond surface using a Berkovich tip with a tip radius of 200 nm to a load of 1 N, resulting in pyramidal impressions typically with a maximum depth of 30 nm (see AFM image of a representative indent in Figure 3a, and line cut in Figure 3b). Slight swelling around the perimeter of the impression but no major structural fractures are observed. Likewise, no discontinuities indicative of fracture formation were observed in the load-unload curve (Supporting Information, Figure S6). This suggests that the diamond has been plastically deformed under these indentation conditions similar to previous reports.58,59 It is likely that the indented region contains pressure induced graphitic material as observed recently.⁶⁰ Figure 3c reveals some quenching of the NV PL within the impression (by about 10%) due to this reduction in crystal quality. Beyond the perimeter of the indent, the impact on the strain can be quantified. We note that NV centers that were initially present in the plastically deformed material are not expected to contribute to the ODMR signal and hence the measurements quantify the stress in regions of elastically deformed diamond. The stress maps are presented in Figure 3d and reveal stress values up to 0.2 GPa for the in-plane components (σ_{xx} , σ_{yy} , σ_{xy}), the other components being much weaker indicate that the deformed material pushes predominantly in the directions parallel to the surface of the undeformed diamond.

To facilitate the interpretation of the stress maps, it is convenient to plot the body force instead, where the Cartesian components are derived from the stress tensor via

$$f_j = -\sum_i \partial_i \sigma_{ji} \tag{6}$$

with i,j = x,y,z (∂_i denotes the partial derivative with respect to Cartesian coordinate *i*). The *x* and *y* derivatives can be readily computed from the stress maps, while the *z* derivatives can be estimated through a suitable approximation (Supporting Information, Section VI). The body force near the indent is shown in Figure 3e, revealing a complicated pattern. This pattern indicates that the tips of the impression push mostly outward while there is an inward force at its flat edges. This illustrates that Berkovich indentation results in a significant shear stress component, which is known to aid phase transformation.⁵⁹

We now return to scratches made with a diamond scribe to map the full stress tensor. Scratching the diamond surface can result in plastic deformation.⁵⁹ Similar to the indent case, there is no sign of fracture of the diamond. A PL image of a scratched region is shown in Figure 4a, where the scratch appears as a dark streak due to the reduction in crystal quality. The body force derived from the measured stress tensor (Supporting Information, Figure S7) is plotted in Figure 4b.



Figure 4. Stress induced by a superficial scratch. (a) PL image of a region containing a scratch. (b) Map of the body force magnitude for the region imaged in (a), with the overlaid arrows indicating the force projected in the *xy* plane. (c) Line cuts of the PL (black) and AFM profile (orange) taken along the red dashed line shown in (a,b). The left inset is a zoom-in; the right inset is an AFM image of the angled section of the scratch. (d) Corresponding line cuts of the three body force components (in and out of plane). (e) Schematic of the diamond cross-section (not to scale), with the overlaid arrows indicating the body force projected in the *xz* plane as derived from (d).

For this shallow scratch (5 nm deep at most, see AFM profile in Figure 4c and image in inset), the magnitude of the body force reaches about 40 N μ m⁻³, corresponding to a stress of up to 0.2 GPa. Deeper scratches like those depicted in Figure 1g,h can produce in excess of 1 GPa of stress (Supporting Information, Figure S7). The body force decays from the **Nano Letters**



Figure 5. Stress induced by device fabrication. (a) Schematic cross-section of a device consisting of an evaporated metallic wire (Ti/Au). (b) PL image of a typical device. (c,d) Corresponding maps of the total axial stress $\Sigma_Z^{axial} = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$ (c) and of the shear stress component σ_{xy} (d). (e-h) Same as (a-d) but for an embedded TiC/Pt/Au contact. (i-l) Same as (a-d) but for a transistor device where the conductive channel is formed by a hydrogen-terminated (H-term.) region of the diamond surface (delimited by red dashed lines in (j) but giving no PL contrast), insulated via a Al₂O₃ oxide layer and controlled by a top Al gate (appears dark in the PL). A defect formed in the oxide layer above the conductive channel while operating the device, visible through a fringe pattern in the PL. (l) σ_{xz} map. All the stress maps share the same color bar ranging from -25 to +25 MPa, except (g) where the stress values have been divided by a factor of 4 (i.e., ranging from -100 to +100 MPa).

center of the cut over distances of several micrometers, much larger than the width of the physical cut (~300 nm fwhm, see orange line in Figure 4c) and the width of the PL quenching feature (~1 μ m fwhm, black line in Figure 4c). This illustrates that even a very shallow cut can elastically deform the diamond over distances significantly larger than the size of the cut itself. To gain more insight into the direction of the force, we plot the three force components across the scratch in Figure 4d, represented as arrows overlaid on the diamond cross-section in Figure 4e. Interestingly, the force remains mostly perpendicular to the diamond surface over several micrometers about the cut even though the NV sensors are located at a distance of ~15 nm from the surface. This behavior suggests a highly anisotropic propagation of the stress along the diamond surface.

As a final illustration of the technique, we mapped the stress resulting from the fabrication of electronic devices on diamond, which is of interest for high-power and high-frequency electronics applications⁶¹ and for studies of charge transport using NV-based magnetometry.^{51,62} First, we fabricated a strip of Ti/Au (thickness 10/100 nm) on the bare diamond surface by thermal evaporation and lift-off (Figure 5a,b) and found that the strip induces a small but measurable compressive stress in the diamond (Figure 5c,d) especially near the edges of the strip (~10 MPa). Here, we plot the sum of the axial stress components, $\Sigma_Z^{axial} = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$, as this gives a significantly improved signal-to-noise ratio over the individual components (Supporting Information, Section III), as well as one of the shear stress

components, σ_{xy} . We note that the weight of the deposited metal amounts to a pressure of about 0.02 Pa and, as such, cannot account for the measured stress. Also visible in Figure 5c are some polishing marks on the bare diamond surface, producing an axial stress of up to $\Sigma_Z^{axial} \approx 40$ MPa.

Next, we fabricated TiC/Pt/Au contacts that extend about 15 nm into the diamond, through evaporation of a Ti/Pt/Au stack (thickness 10/10/70 nm) and subsequent annealing⁴⁸ (Figure 5e,f). Such embedded contacts are typically used to form low-resistance ohmic contacts with the two-dimensional hole gas (2DHG) present on a hydrogen-terminated diamond surface^{48,63} as well as in high-power electronics.⁶⁴ As seen in the stress maps (Figure 5g,h), there is a large compressive stress in the diamond below the TiC contact ($\Sigma_Z^{axial} \approx 100$ MPa). This is expected because TiC has a lower atomic density than diamond. It is relatively uniform across the contact except for some small spots (a few μ m in size) where there is no stress, indicative of imperfections in the formed TiC layer.

We then fabricated a transistor device based on the 2DHG at the diamond surface, ^{63,65} by first patterning the surface termination to form a conductive (hydrogen-terminated) channel on an otherwise insulating (oxygen-terminated) surface, covering the whole surface with a 50 nm insulating layer of Al₂O₃, and evaporating a metallic top gate (Al, 50 nm thick). While operating the device, we observed the formation of a defect in the Al₂O₃ layer above the conductive channel next to the gate, as illustrated in Figure 5i and seen in the PL image (Figure 5j). The stress maps (Σ_{z}^{axial} in Figure 5k and σ_{xz} in Figure 5l) reveal a compressive stress under the oxide defect

 $(\Sigma_Z^{axial} \approx 20 \text{ MPa})$ and a tensile stress just outside the defect. The presence of the metallic gate on top of the oxide induces a stress of similar magnitude in the diamond, although the odd parity of Σ_Z^{axial} is in contrast with the fully compressive stress observed in Figure 5c, suggesting a nontrivial mediation by the oxide layer, possibly through permanent deformation of the oxide under the gate while operating the device. These experiments illustrate that the technique can be applied to monitor mechanical deformations in materials and devices outside the diamond, through the elastic stress applied to the diamond substrate as a result, which could find applications as a diagnostic tool for device variability or failure analysis.

In summary, we presented a method to quantitatively image the full stress tensor below the surface of a diamond, at room temperature, using a layer of NV strain sensors. We illustrated the versatility of the technique by experimentally imaging the stress under a number of scenarios, from localized implantation damage to nanoindents to devices fabricated on the diamond surface. With our current experimental setup, the spatial resolution is limited by the diffraction limit (~400 nm) but could be improved by implementing super-resolution techniques.^{66,67} The measurement sensitivity is of the order of 1 MPa per $1 \times 1 \ \mu m^2$ pixel for typical acquisition times (~10 h), corresponding to a strain of less than $10^{-6,25}$ and could be improved by an order of magnitude through further optimization of the NV-diamond samples.⁶⁸

The technique could be directly applied to characterize the residual stress in various types of diamond nanostructures commonly used for quantum sensing and quantum information science, such as solid-immersion lenses,⁶⁹ nanopillars,^{70,71} nanobeams,^{38,72} and photonic waveguides and cavities, which could help improve the sensing accuracy or optimize the fabrication processes. Moreover, the technique is compatible with stroboscopic measurements, capable, for instance, of imaging the time evolution of stress in mechanically driven diamond cantilevers,^{34,35,77} which are a testbed for hybrid spinmechanical quantum systems. More generally, the ability to measure the complete stress tensor at the nanoscale opens up the field of multiplexed nanomechanical sensing, where structures with multiple mechanical degrees of freedom could be designed and measured (consider, for example, a cantilever with a paddle on the end), with possible applications in on-chip mass spectroscopy and microfluidics.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.9b01402.

Details on the experimental methods, analysis of the ODMR data, uniqueness of the solution, sensitivity and accuracy of the method, body force approximations, diamond samples, and supplementary data related to the implantation damage, indentation, and scratches (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Li, J.; Shan, Z.; Ma, E. MRS Bull. 2014, 39, 108-114.
- (2) Chu, M.; Sun, Y.; Aghoram, U.; Thompson, S. E. Annu. Rev. Mater. Res. 2009, 39, 203–229.
- (3) Shin, B. G.; Han, G. H.; Yun, S. J.; Oh, H. M.; Bae, J. J.; Song, Y. J.; Park, C.-Y.; Lee, Y. H. *Adv. Mater.* **2016**, *28*, 9378–9384.
- (4) Adams, A. R. IEEE J. Sel. Top. Quantum Electron. 2011, 17, 1364–1373.
- (5) Smith, A. M.; Mohs, A. M.; Nie, S. Nat. Nanotechnol. 2009, 4, 56.
 (6) Ni, G.-X.; Yang, H.-Z.; Ji, W.; Baeck, S.-J.; Toh, C.-T.; Ahn, J.-
- H.; Pereira, V. M.; Ozyilmaz, B. Adv. Mater. 2014, 26, 1081-1086.

(7) Jacobsen, R. S.; Andersen, K. N.; Borel, P. I.; Fage-Pedersen, J.; Frandsen, L. H.; Hansen, O.; Kristensen, M.; Lavrinenko, A. V.; Moulin, G.; Ou, H.; Peucheret, C.; Zsigri, B.; Bjarklev, A. *Nature* **2006**, 441, 199.

- (8) Tang, Y. L.; Zhu, Y. L.; Eliseev, E. A.; Wang, W. Y.; Wang, Y. J.;
 Xu, Y. B.; Zhang, Z. D.; Pennycook, S. J. Science 2015, 348, 547–551.
 (9) Zhang, L.; et al. Science 2018, 361, 494–497.
- (10) Locquet, J.-P.; Perret, J.; Fompeyrine, J.; Mächler, E.; Seo, J.
 W.; Van Tendeloo, G. *Nature* 1998, 394, 453.
- (11) Vanhellemont, J.; Wolf, I. D.; Janssens, K.; Frabboni, S.; Balboni, R.; Armigliato, A. Appl. Surf. Sci. **1993**, 63, 119–125.
- (12) Jain, S. C.; Maes, H. E.; Pinardi, K.; De Wolf, I. J. Appl. Phys. 1996, 79, 8145-8165.
- (13) Voloshin, A. S.; Burger, C. P. Exp. Mech. 1983, 23, 304-313.
- (14) Tang, Y.; Rich, D. H.; Lingunis, E. H.; Haegel, N. M. J. Appl. Phys. **1994**, *76*, 3032–3040.
- (15) Wright, S. I.; Nowell, M. M.; Field, D. P. Microsc. Microanal. 2011, 17, 316-329.
- (16) Kato, Y.; Umezawa, H.; Shikata, S.-i.; Teraji, T. Diamond Relat. Mater. **2012**, 23, 109–111.
- (17) Holt, M.; Harder, R.; Winarski, R.; Rose, V. Annu. Rev. Mater. Res. 2013, 43, 183–211.
- (18) Hytch, M. J.; Minor, A. M. MRS Bull. 2014, 39, 138-146.
- (19) Whiteley, S. J.; Heremans, F. J.; Wolfowicz, G.; Awschalom, D. D.; Holt, M. V. ArXiv e-prints 1808.04920, 2018.
- (20) Hÿtch, M.; Houdellier, F.; Hüe, F.; Snoeck, E. Nature 2008, 453, 1086.
- (21) Loechelt, G. H.; Cave, N. G.; Menndez, J. J. Appl. Phys. 1999, 86, 6164-6180.

(22) Ossikovski, R.; Nguyen, Q.; Picardi, G.; Schreiber, J.; Morin, P. J. Raman Spectrosc. 39, 661–672.

- (23) Grazioso, F.; Patton, B. R.; Delaney, P.; Markham, M. L.; Twitchen, D. J.; Smith, J. M. Appl. Phys. Lett. **2013**, 103, 101905.
- (24) Doherty, M. W.; Struzhkin, V. V.; Simpson, D. a.; McGuinness,
- L. P.; Meng, Y.; Stacey, A.; Karle, T. J.; Hemley, R. J.; Manson, N. B.; Hollenberg, L. C. L.; Prawer, S. *Phys. Rev. Lett.* **2014**, *112*, 047601.

(25) Barson, M. S. J.; et al. Nano Lett. 2017, 17, 1496-1503.

- (26) Falk, A. L.; Klimov, P. V.; Buckley, B. B.; Ivády, V.; Abrikosov, I. a.; Calusine, G.; Koehl, W. F.; Gali, Á.; Awschalom, D. D. *Phys. Rev. Lett.* **2014**, *112*, 187601.
- (27) Doherty, M. W.; Manson, N. B.; Delaney, P.; Jelezko, F.; Wrachtrup, J.; Hollenberg, L. C. L. *Phys. Rep.* **2013**, *528*, 1–45.
- (28) Rondin, L.; Tetienne, J. P.; Hingant, T.; Roch, J. F.; Maletinsky, P.; Jacques, V. *Rep. Prog. Phys.* **2014**, *77*, 056503.
- (29) Trusheim, M. E.; Englund, D. New J. Phys. **2016**, *18*, 123023. (30) Bauch, E.; Hart, C. A.; Schloss, J. M.; Turner, M. J.; Barry, J. F.;

Kehayias, P.; Singh, S.; Walsworth, R. L. *Phys. Rev. X* **2018**, *8*, 031025. (31) Banerjee, A.; Bernoulli, D.; Zhang, H.; Yuen, M.-F.; Liu, J.;

- Dong, J.; Ding, F.; Lu, J.; Dao, M.; Zhang, W.; Lu, Y.; Suresh, S. Science **2018**, 360, 300–302.
- (32) Macquarrie, E. R.; Gosavi, T. A.; Jungwirth, N. R.; Bhave, S. A.; Fuchs, G. D. *Phys. Rev. Lett.* **2013**, *111*, 227602.
- (33) Teissier, J.; Barfuss, A.; Appel, P.; Neu, E.; Maletinsky, P. Phys. Rev. Lett. 2014, 113, 020603.
- (34) Ovartchaiyapong, P.; Lee, K. W.; Myers, B. A.; Jayich, A. C. B. *Nat. Commun.* **2014**, *5*, 4429.
- (35) Barfuss, A.; Teissier, J.; Neu, E.; Nunnenkamp, A.; Maletinsky, P. *Nat. Phys.* **2015**, *11*, 820.
- (36) Chen, H. Y.; MacQuarrie, E. R.; Fuchs, G. D. Phys. Rev. Lett. 2018, 120, 167401.
- (37) Macquarrie, E. R.; Gosavi, T. A.; Bhave, S. A.; Fuchs, G. D. Phys. Rev. B: Condens. Matter Mater. Phys. **2015**, 92, 224419.
- (38) Sohn, Y. I.; et al. Nat. Commun. 2018, 9, 2012.
- (39) Gil-Santos, E.; Ramos, D.; Martínez, J.; Ferníndez-Regúlez, M.; García, R.; San Paulo, Á.; Calleja, M.; Tamayo, J. *Nat. Nanotechnol.*
- **2010**, *5*, 641–645. (40) Arlett, J. L.; Myers, E. B.; Roukes, M. L. Nat. Nanotechnol.
- **2011**, *6*, 203–215. (41) Calleja, M.; Kosaka, P. M.; San Paulo, I.; Tamayo, J. Nanoscale
- **2012**, *4*, 4925–4938.
- (42) Hanay, M. S.; Kelber, S. I.; O'Connell, C. D.; Mulvaney, P.; Sader, J. E.; Roukes, M. L. Nat. Nanotechnol. **2015**, *10*, 339–344.
- (43) Biktagirov, T. B.; Smirnov, A. N.; Davydov, V. Y.; Doherty, M. W.; Alkauskas, A.; Gibson, B. C.; Soltamov, V. A. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96*, 075205.
- (44) Doherty, M. W.; Dolde, F.; Fedder, H.; Jelezko, F.; Wrachtrup, J.; Manson, N. B.; Hollenberg, L. C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 205203.
- (45) Udvarhelyi, P.; Shkolnikov, V. O.; Gali, A.; Burkard, G.; Pályi, A. Phys. Rev. B: Condens. Matter Mater. Phys. 2018, 98, 075201.
- (46) Barfuss, A.; Kasperczyk, M.; Kölbl, J.; Maletinsky, P. Phys. Rev. B: Condens. Matter Mater. Phys. 2019, 99, 174102.
- (47) Dolde, F.; Fedder, H.; Doherty, M. W.; Nöbauer, T.; Rempp, F.; Balasubramanian, G.; Wolf, T.; Reinhard, F.; Hollenberg, L. C. L.; Jelezko, F.; Wrachtrup, J. *Nat. Phys.* **2011**, *7*, 459–463.
- (48) Broadway, D. A.; Dontschuk, N.; Tsai, A.; Lillie, S. E.; Lew, C. T.-K.; McCallum, J. C.; Johnson, B. C.; Doherty, M. W.; Stacey, A.; Hollenberg, L. C. L.; Tetienne, J.-P. *Nature Electronics* **2018**, *1*, 502–507.
- (49) Ali Momenzadeh, S.; de Oliveira, F. F.; Neumann, P.; Bhaktavatsala Rao, D.; Denisenko, A.; Amjadi, M.; Chu, Z.; Yang, S.; Manson, N. B.; Doherty, M. W.; Wrachtrup, J. *Phys. Rev. Appl.* **2016**, *6*, 024026.
- (50) Doherty, M. W.; Michl, J.; Dolde, F.; Jakobi, I.; Neumann, P.; Manson, N. B.; Wrachtrup, J. *New J. Phys.* **2014**, *16*, 063067.
- (51) Tetienne, J.-P.; Dontschuk, N.; Broadway, D. A.; Stacey, A.; Simpson, D. A.; Hollenberg, L. C. L. Sci. Adv. **2017**, *3*, No. e1602429.

4550

- (52) Lillie, S. E.; Broadway, D. A.; Dontschuk, N.; Zavabeti, A.; Simpson, D. A.; Teraji, T.; Daeneke, T.; Hollenberg, L. C. L.; Tetienne, J.-P. *Phys. Rev. Materials* **2018**, *2*, 116002.
- (53) Tetienne, J.-P.; De Gille, R.; Broadway, D.; Teraji, T.; Lillie, S.; McCoey, J.; Dontschuk, N.; Hall, L.; Stacey, A.; Simpson, D.; Hollenberg, L. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, *97*, 085402.
- (54) Tsubouchi, N.; Ogura, M.; Horino, Y.; Okushi, H. Appl. Phys. Lett. 2006, 89, 012101.
- (55) Forneris, J.; Traina, P.; Monticone, D. G.; Amato, G.; Boarino, L.; Brida, G.; Degiovanni, I. P.; Enrico, E.; Moreva, E.; Grilj, V. *Sci. Rep.* **2015**, *5*, 15901.
- (56) Olivero, P.; Bosia, F.; Fairchild, B. A.; Gibson, B. C.; Greentree, A. D.; Spizzirri, P.; Prawer, S. *New J. Phys.* **2013**, *15*, 043027.
- (57) Simpson, D. A.; Tetienne, J. P.; McCoey, J. M.; Ganesan, K.; Hall, L. T.; Petrou, S.; Scholten, R. E.; Hollenberg, L. C. *Sci. Rep.* **2016**, *6*, 22797.
- (58) Brookes, C. Nature 1970, 228, 660.
- (59) Gogotsi, Y. G.; Kailer, A.; Nickel, K. G. J. Appl. Phys. 1998, 84, 1299-1304.
- (60) Dub, S.; Lytvyn, P.; Strelchuk, V.; Nikolenko, A.; Stubrov, Y.; Petrusha, I.; Taniguchi, T.; Ivakhnenko, S. *Crystals* **2017**, *7*, 369.
- (61) Wort, C. J. H.; Balmer, R. S. Mater. Today 2008, 11, 22-28.
- (62) Tetienne, J.-P.; Dontschuk, N.; Broadway, D. A.; Lillie, S. E.; Teraji, T.; Simpson, D. A.; Stacey, A.; Hollenberg, L. C. L. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2019**, *99*, 014436.
- (63) Jingu, Y.; Hirama, K.; Kawarada, H. IEEE Trans. Electron Devices 2010, 57, 966-972.
- (64) Hoshino, Y.; Kato, H.; Makino, T.; Ogura, M.; Iwasaki, T.; Hatano, M.; Yamasaki, S. *Phys. Status Solidi A* 2012, 209, 1761–1764.
- (65) Hirama, K.; Takayanagi, H.; Yamauchi, S.; Jingu, Y.; Umezawa, H.; Kawarada, H. High-performance p-channel diamond MOSFETs with alumina gate insulator. 2007 IEEE International Electron Devices Meeting; pp 873–876.
- (66) Wildanger, D.; Maze, J. R.; Hell, S. W. Phys. Rev. Lett. 2011, 107, 017601.
- (67) Chen, X.-D.; Li, S.; Shen, A.; Dong, Y.; Dong, C.-H.; Guo, G.-C.; Sun, F.-W. Phys. Rev. Appl. **2017**, 7, 014008.
- (68) Kleinsasser, E. E.; Stanfield, M. M.; Banks, J. K. Q.; Zhu, Z.; Li, W.-D.; Acosta, V. M.; Watanabe, H.; Itoh, K. M.; Fu, K.-M. C. *Appl. Phys. Lett.* **2016**, *108*, 202401.
- (69) Jamali, M.; Gerhardt, I.; Rezai, M.; Frenner, K.; Fedder, H.; Wrachtrup, J. *Rev. Sci. Instrum.* **2014**, *85*, 123703.
- (70) Babinec, T. M.; Hausmann, B. J. M.; Khan, M.; Zhang, Y.; Maze, J. R.; Hemmer, P. R.; Loncar, M. Nat. Nanotechnol. **2010**, *5*, 195–199.
- (71) Appel, P.; Neu, E.; Ganzhorn, M.; Barfuss, A.; Batzer, M.; Gratz, M.; Tschöpe, A.; Maletinsky, P. *Rev. Sci. Instrum.* **2016**, *87*, 063703.
- (72) Khanaliloo, B.; Jayakumar, H.; Hryciw, A. C.; Lake, D. P.; Kaviani, H.; Barclay, P. E. *Phys. Rev. X* **2015**, *5*, 041051.
- (73) Riedrich-Möller, J.; Kipfstuhl, L.; Hepp, C.; Neu, E.; Pauly, C.; Mücklich, F.; Baur, A.; Wandt, M.; Wolff, S.; Fischer, M.; Gsell, S.; Schreck, M.; Becher, C. *Nat. Nanotechnol.* **2012**, *7*, 69–74.
- (74) Burek, M. J.; De Leon, N. P.; Shields, B. J.; Hausmann, B. J. M.; Chu, Y.; Quan, Q.; Zibrov, A. S.; Park, H.; Lukin, M. D.; Lončar, M. *Nano Lett.* **2012**, *12*, 6084–6089.
- (75) Faraon, A.; Santori, C.; Huang, Z.; Acosta, V. M.; Beausoleil, R. G. *Phys. Rev. Lett.* **2012**, *109*, 033604.
- (76) Hausmann, B. J. M.; Bulu, I. B.; Deotare, P. B.; McCutcheon, M.; Venkataraman, V.; Markham, M. L.; Twitchen, D. J.; Loncar, M. *Nano Lett.* **2013**, *13*, 1898–1902.
- (77) Tao, Y.; Boss, J. M.; Moores, B.; Degen, C. L. Nat. Commun. 2014, 5, 3638.