Electron microscopy

A 3D map of atoms in 2D materials

Angus I Kirkland.

[1] Department of Materials, University of Oxford OX1 3PH, United Kingdom
[2] electron Physical Sciences Imaging Centre, Diamond Light Source, Didcot OX11 0DE, United Kingdom
[3] The Rosalind Franklin Institute, Harwell Campus, Didcot OX11 0FA, United Kingdom.

Scanning atomic electron tomography measurements reveal the 3D local structure around single dopant atoms in 2D transition metal dichalcogenides, providing essential information to investigate and predict their electronic properties.

Reliable deployment in applications of graphene and other 2D materials requires a complete understanding - at the atomic level - of the nature of defects that can significantly affect their physical properties. In particular, point defects, dislocations and dopant atoms are almost inevitably present in all as-synthesised materials, including graphene [1], hexagonal boron nitride [2] and 2D transition metal dichalcogenides [3]. However, with only limited exceptions [4], prior studies have mostly provided structural information projected on 2D images, whereas, to fully understand the structure and consequential effects of these defects, it is necessary to probe the full 3D atomic map of the investigated materials.

Now, writing in Nature Materials [5], an interdisciplinary team lead by John Miao has used aberration corrected scanning transmission electron microscopy to determine the full local 3D structure of the 2D MoS_2 lattice around single Re atom dopants with a precision down to 4 picometres. The obtained 3D atomic coordinates have been used as inputs for theoretical calculations that allowed the researchers to determine both the full local strain tensor and the accurate electronic band structure of the material.

The reported work is based on the use of electron tomography, in which multiple projections of an object over a wide range of tilt angles are used to reconstruct a 3D structure (Fig. 1a). This is a well-established method, applied routinely in both physical and biological sciences [6]. However, this approach has not been widely applied to studies of 2D materials, in part due to radiation damage of the specimen, which limits the number of projections that can be recorded and the resulting imaging resolution along the beam direction. To

overcome this issue, Miao and co-workers have developed a precise tomographic method, named scanning Atomic Electron Tomography (sAET), which requires only a limited range of tilt angles, thus reducing radiation damage. This method also provides a specific advantage when applied to 2D materials, as the number of projections needed to obtain a particular resolution along the z (beam) direction is proportional to the sample thickness. For 2D materials, which are synthesised as laterally extended thin films, the number of tilt angles that needs to be recorded is hence substantially reduced, without sacrificing precision in the measured atom coordinates.

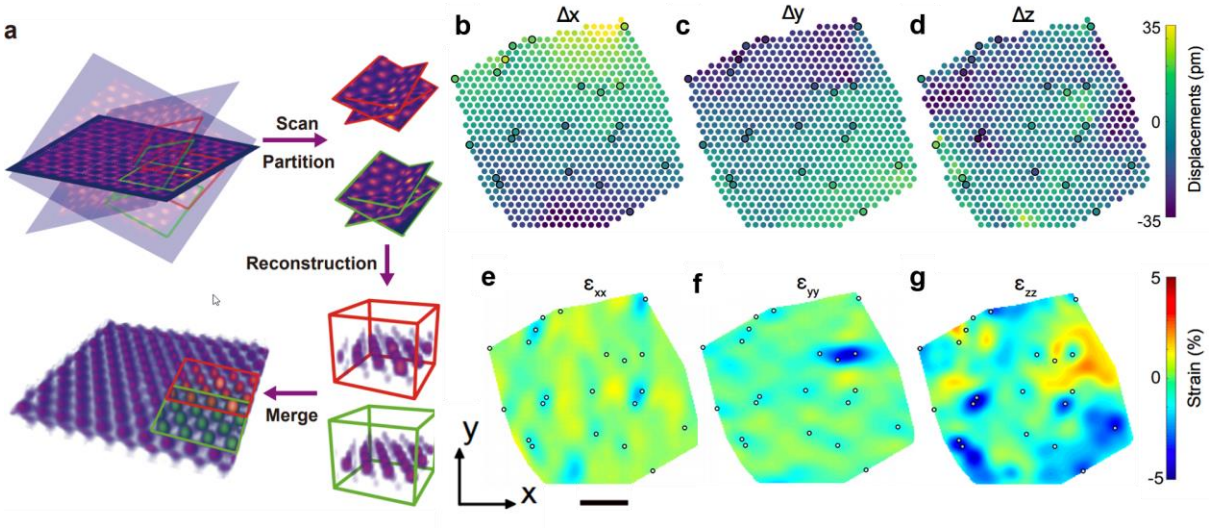


Figure 1. **a**, In scanning atomic electron tomography, a limited number of projections at different tilt angles are acquired from a 2D material or heterostructure. A small 3D window is then chosen and scanned along the x- and y-axis, maintaining a finite overlap between two neighbouring windows. At each scanning position, corresponding regions in the projections are identified for each window and all the projections are partitioned into a series of image stacks. Finally, the 3D windows are reconstructed from the image stacks and stitched together to form a full reconstruction of the atomic structure. **b-d**, Measured 3D atomic displacements of Mo (dots) and Re (circled dots) atoms along the x-, y- and z-axis, respectively. **e-g**, Three components of the strain tensor in the Mo/Re layer, where the Re dopants (circles) induce local strains in the ε_{xx}, ε_{yy}, and ε_{zz} maps. The x-, y- and z-axis are along the [1,0,0], [1,2,0] and [0,0,1] directions, respectively. Scale bar, 2nm. Adapted with permission from ref. 5, Springer Nature Ltd.

Miao and collaborators used their method to measure 3D atomic displacements (Fig. 1b-d) and calculate the full 3D strain tensor in 2D MoS_2 thin films doped with individual Re atoms (Fig. 1e-g). They showed that the out of plane strain, along the z-axis, is larger than the strain within the plane of the 2D sheet. This result has potentially significant impact for future fabrication of devices based on van der Waals heterostructures, where the mismatch between the lattices of different 2D materials stacked on top of each other plays an important role.

Moreover, it also enables us to understand a fundamental phase transition in Re doped MoS_2. Indeed, it has been previously reported that, at high doping concentrations, this material transforms between two closely related structures (the 1H and 1T forms) with different electronic properties [7] However, the mechanism by which this transition is initiated at single atom dopant sites is not clearly understood. The reported accurate sAET measurements of the local deviations in bond distances and angles around Re atoms offer an important insight into this mechanism and will be crucial for the fabrication of future devices in which the bonding environment and strain affect the local electronic properties.

Miao and colleagues have further extended the use of their structural data to calculate local band diagrams by using the 3D coordinates determined from sAET as an input to Density Functional Theory. Their calculations show that the local band structure has a metallic character, whereas the one of a relaxed extended lattice is semiconducting with a direct band gap. This demonstrates that the presence of dopants causes a localised metal-to-insulator transition at the atomic scale. The researchers have validated these theoretical predictions by performing local photoluminescence (PL) measurements. The results show that the macroscopic emission of the investigated material strongly depends on the Re dopant concentration: the PL peak consistent with a p-type semiconducting behaviour disappears due to quenching as the doping increases. This observation represents a remarkable evidence of the direct correlation between a key optical property and subtle local changes in bonding and strain at the atomic level.

In the immediate future, this work will guide manufacturing efforts in the design of materials with controlled adatom arrays and in quality control of unwanted defects. Looking further forward, the use of this approach could be extended to other technologically important thin film materials systems and further refined to allow data acquisition from even more beam sensitive samples, possibly including organic polymers in future solar cells and membranes for use in new fuel cells and batteries. Ultimately, it may be possible to use the method described to probe the local structure of biological membranes.

References.

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