www.advmat.de



Atomic Defects in Two Dimensional Materials

Haider I. Rasool, Colin Ophus, and Alex Zettl*

Atomic defects in crystalline structures have pronounced affects on their bulk properties. Aberration-corrected transmission electron microscopy has proved to be a powerful characterization tool for understanding the bonding structure of defects in materials. In this article, recent results on the characterization of defect structures in two dimensional materials are discussed. The dynamic behavior of defects in graphene shows the stability of zigzag edges of the material and gives insights into the dislocation motion. Polycrystalline graphene is characterized using advanced electron microscopy techniques, revealing the global crystal structure of the material, as well as atomic-resolution observation of the carbon atom positions between neighboring crystal grains. Studies of hexagonal boron nitride (hBN) are also visited, highlighting the interlayer bonding, which occurs upon defect formation, and characterization of grain boundary structures. Lastly, defect structures in monolayer polycrystalline transition metal dichalcogenides grown by CVD are discussed.

1. Introduction

Characterization of atomic defects is important for fundamental understanding of material properties. The nature of the atomic bonding structure gives direct information regarding the bulk electronic and mechanical properties. For high spatial resolution studies, both scanning probe microscopy (SPM) and aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) can give insights into the bonding structure of atoms as well as local properties such as electronic structure information.^[1–5] For two-dimensional (2D) materials, such as graphene,^[6–8] TEM is an ideal characterization tool since it can image the materials with both high spatial and temporal resolution without a supporting substrate.^[9] In addition, large area imaging and diffraction can be performed to gain information regarding the crystallinity of synthesized materials.^[10,11]

Several advances have been critical in the field of electron microscopy which have allowed for atomic resolution imaging of defects in 2D materials. Hardware aberration corrector electron optics dramatically minimizes the affects of intrinsic spherical aberrations of electron lenses and chromatic aberration correctors or monochromators can reduce the energy spread of the electron beam illumination for sub-ångstrom imaging.^[12] One critical factor has been the development of imaging at low accelerating voltages of 80 or 60 kV, which dramatically reduces damaging affects of the illuminating electrons on sample specimens.^[9,13] In addition. the electron-ion scattering cross-section increases as voltage decreases, producing more contrast for a given illumination dose. Lastly, electron scintillator cameras have lower point-spread-functions at lower operating voltages, leading to sharper images.

In this article, we discuss recent studies of atomic defect structures in 2D mate-

rials. We start by looking at defect dynamics of graphene holes and dislocations under the influence of an electron beam energy bath.^[9,12] The atomic rearrangement processes provide valuable insight into the stability of graphene edge structures. Further observations of dislocation movement through the carbon lattice with single atom resolution provides fundamental information regarding plastic deformation of the 2D sheet,^[12] which is necessary for understanding the failure behavior of the material. In addition, characterization of polycrystalline graphene grown by chemical vapor deposition (CVD) is discussed. Advanced electron microscopy techniques have been used to map the large scale crystal structure and the atomic structure of grain boundaries (GBs) which stitch together neighboring crystallites.^[10,11] Imaging extended stretches of the GBs has revealed that they are comprised of conserved atomic bonding sequences with similar strain profiles.^[14]

Beyond graphene, we visit work on the related material, hexagonal boron nitride (hBN). The bulk material has a layered structure, similar to graphene, with boron and nitrogen occupying each sub-lattice of the hexagonal structure.^[15] The

Dr. H. I. Rasool, Prof. A. Zettl Department of Physics University of California at Berkeley Berkeley, CA 94720, USA E-mail: azettl@berkeley.edu Dr. H. I. Rasool, Prof. A. Zettl Materials Science Division Lawrence Berkeley National Laboratory (LBNL) Berkeley, CA 94720, USA

DOI: 10.1002/adma.201500231

Adv. Mater. 2014, DOI: 10.1002/adma.201500231 Dr. C. Ophus National Center for Electron Microscopy (NCEM) Molecular Foundry Lawrence Berkeley National Laboratory (LBNL) Berkeley, CA 94720, USA Prof. A. Zettl Kavli Energy NanoSciences Institute at the University of California Berkeley, California 94720, USA





Figure 1. Defect dynamics in monolayer graphene. A) Edge configuration of an electron beam created hole in graphene highlighting the armchair edge. B) Growth of the hole showing an extended zigzag edge. C) Atomic structure of a hole showing armchair edges during initial stages of a Monte Carlo simulation. D) Further simulation results showing the faceting of the edge structure into zigzag edges. E) Initial frame of the conversion of an armchair edge to a zigzag edge. F) Subsequent frame of the conversion. The two atoms marked in blue are removed and four new carbon atoms shown in red result in the conversion. A–F) Reproduced with permission.^[9] Copyright 2009, American Association for Advancement of Science. G) Pentagon and heptagon dislocation pair in monolayer graphene. H) Perpendicular strain field measured by GPA. I–N) AC-HRTEM images and atomic structures of the dislocation pair movement with the carbon lattice. G–N) Reproduced with permission.^[12] Copyright 2012, American Association for Advancement of Science.

two-atom composition of this material and partial ionic bonds allows for interlayer bonding at single atom defect sites and edges of holes.^[16,17] The closed loops formed at the edges of holes have distinctly different electronic structure when compared to their non-bonded counterparts. In addition, the atomic structure of GBs in polycrystalline hBN grown by CVD are discussed.^[18,19]

The structurally more complex transition metal dichalcogenides (TMDs) are discussed in the final section of the article. These semi-conducting materials have recently gained attention within the scientific community due to their layer dependent optical and electronic properties with monolayers exhibiting a direct bandgap.^[20-22] The added structural complexity comes from the chemical nature of the two different types of elements comprising the crystal lattice and the three sets of atomic planes within a single monolayer. The observation of a variety of unique atomic defect structures, which include antisite defects, has recently been accomplished in these materials.^[23] Studies of CVD grown polycrystalline molybdenum disulfide have revealed interesting dislocations at both tilt and mirror GBs.^[24,25] The atomic structure of these boundaries directly influences the optical and electronic properties of the material.

2. Defect Dynamics in Graphene

Using AC-HRTEM it is possible to gain insights into the dynamic behavior of defect structures in graphene. During imaging, the electron beam can be used to create defect structures while simultaneously providing the necessary energy required to induce atomic motion of the sample. In this way, the dynamics of carbon atoms at the edge of an electron beam induced hole were observed, giving insight into the relative stability of the zigzag edge versus the armchair edge.^[9] Monitoring the atomic rearrangements and beam etching of the edge atoms revealed the higher stability of the zigzag edge through its slower erosion when compared to armchair edges. Figure 1A shows an electron beam generated hole with armchair edges highlighted. As the armchair edges erode, the hole shows a more faceted structure with zigzag edges, which can be seen in Figure 1B. This observed experimental behavior is consistent with Monte Carlo simulations of hole dynamics which predict the reconfiguration of a zigzag edge from a hole with rough armchair edges (Figure 1C and 1D).

The observed stability can be explained by a simple model that takes into consideration the coordination of active edge sites. In a zigzag edge, the carbon atoms are bonded to either two or three

www.MaterialsViews.com



Figure 2. Grain boundaries in polycrystalline graphene. A) Real space distribution of crystal grains constructed from nanodiffraction data. B) Histogram of relative orientation of tilt boundaries. A,B) Reproduced with permission.^[10] Copyright 2011, American Chemical Society. C) Diffraction pattern taken from a polycrystalline region of graphene. D) Dark field image created from collection of electrons from the selected spot in (C). E) Diffraction pattern from (C) showing the various locations of the objective aperture used to create a real space map (F) of the crystallites. C–F) Reproduced with permission.^[11] Copyright 2011, Nature Publishing Group. G) AC-HRTEM image of a GB. Reproduced with permission.^[10] Copyright 2011, American Chemical Society. H) AC-STEM image of a GB. Reproduced with permission.^[11] Copyright 2011, Nature Publishing Group. I,J) EWR intensity of two regions of a graphene GB with conserved atomic bonding sequences. K,L) Atomic models highlighting the conserved sequence. M,N) Parallel strain fields illustrating similar strain profiles for the conserved regions. I–N) Reproduced with permission.^[14] Copyright 2014, American Chemical Society.

neighboring atoms. The doubly coordinated sites are expected to be preferentially removed, leaving behind a vacancy without any dangling bonds. In contrast, when an atom is ejected from an armchair edge, a high energy dangling bond is left behind that must migrate to a nearby vacancy site. As these dangling bonds erode, so does the armchair edge. Figure 1E and 1F show high magnification images of the transformation of an armchair edge to a zigzag edge by atom migration.

The dynamics of dislocations in graphene has also been studied in a similar manner.^[12] A pair of dislocations, each comprised of an adjoining pentagon and heptagon, was created using an electron beam and subsequently used to drive the movement of the dislocation within the lattice and image the process with very clear identification of every atom in the lattice. An AC-HRTEM image of a dislocation pair is shown in Figure 1G. In this study, the atomic scale strain fields surrounding each dislocation were measured using gradient phase analysis (GPA). Each dislocation showed strain dipoles centered at the 5-7 defect structure. On the pentagon side of the dislocation, the carbon-carbon bonds are contracted, creating a tensile strain in the surrounding lattice. On the heptagon side, the bonds are expanded, creating a compressional strain. The perpendicular strain fields, highlighting the dipoles centered at the dislocations, is shown in Figure 1H.

After the formation of the dislocation pair, the beam drives motion of the pair within the lattice. This motion occurs

through a combination of climb (Stone–Wales bond rotation) and glide (removal of two carbon atoms) processes and allows the pair to migrate through the crystal as a united object. The captured dynamics of both processes and corresponding atomic models are presented in Figure 1I to 1N.

3. Polycrystalline Graphene

Growth of graphene on copper substrates^[26] by CVD produces a polycrystalline sheet with macroscopic lateral dimensions and a thickness of one layer of carbon atoms. Each single crystal region can range from hundreds of nanometers in size to tens of microns and are covalently connected together at the grain boundaries of the crystallites. These boundaries are of interest for fundamental structural studies as well as for practical purpose. The nature of the bonding between crystals^[27,28] and density of defects is expected to have pronounced affects on the materials properties.^[29–31]

Using nano-diffraction, it is possible to map the spatial distribution of the single crystal regions by rastering the electron beam over the sample and collecting the crystal diffraction pattern at each point within a defined field of view of the sample.^[10] **Figure 2** shows a constructed real space mapping of the different crystal regions of a graphene sheet acquired by scanning diffraction and a histogram of the relative orientations

www.advmat.de

ADVANCED MATERIALS



of the crystallites. In addition, standard dark field imaging techniques can be used to visualize the spatial distribution of single crystal regions of the material.^[11] Briefly, an objective aperture is placed in the back focal plane of the microscope to image specific crystalline regions in real space (Figure 2C and 2D). Selecting different diffraction spots taken from a specific illuminated region, allows for the construction of a composite real space image of the crystal distribution of the material (Figure 2E and 2F). These techniques can be useful for characterizing growth conditions and can serve as non-destructive tools to further characterize the electronic and mechanical properties of the material.^[32–34]

Once a samples crystal structure is mapped, it is possible to use AC-HRTEM to image the grain boundaries that join individual single crystal regions. For 2D materials the grain boundaries that connect adjoining crystals are 1D structures that depart from the standard bonding of the bulk. In graphene, tilt grain boundaries that join misoriented crystals are comprised of adjoining pentagons and heptagons. These boundaries have recently been observed using bright field AC-HRTEM and aberration-corrected scanning TEM (AC-STEM). In these studies short lengths of grain boundaries were imaged and shown to have significant line curvature (Figure 2G and 2H). This line curvature persists even after extensive imaging, which can cause atom dynamics at the boundaries.^[35] This departure from theoretically studied boundaries is likely caused by the roughness of growing edges prior to crystal stitching during the synthesis.

Further study of graphene GBs reveal that these structures are comprised of conserved atomic bonding sequences, where similar structural building blocks were found to exist along the length of the boundary.^[14] In the study, exit wave reconstructions (EWR) were performed on focal series images taken at GBs. The EWR allows for the calculation and correction of residual aberrations present in the collected data, which allows for the precise measurements of the atomic positions. Images of two different grain boundary regions with conserved dislocation sequences is shown in Figure 2I and 2J with atomic models highlighting the regions in Figure 2K and 2L. Measurements of the deviation from the ideal lattice are used to calculate the spatial distribution of the strain fields present at the boundaries (Figure 2M and 2N). These strain fields are organized into dipoles of compressive and tensile strain which are localized at the boundary with a spatial extent of 1 to 2 nanometers. The low strain magnitudes of 1 to 2% contribute to the high strength of the grain boundaries when compared to the bulk crystal.^[33]

4. Hexagonal Boron Nitride Defect Structures

Hexagonal boron nitride (hBN) is a 2D layered material with similar structural characteristics to graphite with similar crystal lattice and layer spacing. In contrast to graphite, a semimetal with a high in-plane conductivity, hBN is an insulating material with a large bandgap across and within the stacked layers. Each individual sheet is comprised of boron and nitrogen atoms arranged in a honeycomb lattice with partial ionic bonds. The bulk material is comprised of these individual sheets stacked with boron and nitrogen atoms stacked alternatively down the column (**Figure 3**A). This AA'A stacking is in contrast to the ABA stacking commonly found in graphite, which is known as the Bernal structure.^[15]

Using a combination of EWR phase and image summation, for increased signal to noise, it is possible to unambiguously identify the thickness of few layer hBN and the atomic positions of the boron and nitrogen within the lattice. Once all the atoms are identified it was found that the boron atoms are predominately ejected from the lattice due to electron beam damage. As holes grow larger, they develop into triangular shaped voids which are terminated by nitrogen atoms. An AC-HRTEM image of a boron monovacancy and extended triangular hole with schematic models are presented in Figure 3B to 3D.

When defects and voids are created in bilayer hBN the material undergoes significant interlayer bonding, which is in contrast to bilayer graphene where vacancies and holes remain independent between the layers.^[16] For a single boron vacancy, two types of interlayer bonding behaviors have been identified. In the two configurations, a single bond occurs between either one nitrogen or two nitrogen atoms in the layer with the defect and one or two boron atoms from the intact layer. Experimental images and schematic models of these defect sites are presented in Figure 3E to 3K. This bonding results in significant vertical and lateral atomic displacements at the defect site and is evidenced by the reduction in symmetry of the vacancy from three to two fold, which is consistent with simulated images of interlayer bonded structures (Figure 3G and 3J).

In addition to interlayer bonding due to isolated defects, hBN undergoes interlayer bonding at the edges of holes in a bilayer sheet.^[17] A row of boron atoms at the zigzag edge of one layer bonds to the nitrogen atoms of the lower zigzag edge, creating a closed loop structure that effectively turns the two sheets into a continuous folded structure. Significant distortion of the hexagonal structure is observed in AC-STEM images of these structures (Figure 3L and 3M). This interlayer bonding maintains the insulating electronic structure of the two sheets, which is in stark contrast to the predicted metallic behavior that is expected for zigzag terminated hBN nanoribbons. An atomic model and calculated unoccupied orbital map of the closed loop structure are depicted in Figures 3N and 3O.

With the ability to accurately determine the layer thickness and identify atomic species in hBN samples, it opens up the possibility to study grain boundary defect structures in polycrystalline samples.^[18,19] Similar to graphene, hBN can be synthesized on macroscopic length scales on appropriate growth substrates such as copper or nickel with boron and nitrogen containing precursors. Individually nucleated islands grown on metallic substrates, extend over the surface with various crystallographic orientations, and fuse to form continuous 2D sheets.

The GBs between two single crystal regions were found to be connected via pentagons and heptagons (5|7) defects rather than square and octagon (4|8) defects (Figure 3P and 3Q), which are predicted to be more stable primarily because it avoids homonuclear bonding at the defect sites.^[19] While both structures are energetically stable, the local strain in the sheet may affect which defects are preferred. In the experimental structures, noticeable strain is present as evidenced by dynamic



Figure 3. Atomic defects in hBN. A) Atomic model of stacking structure in hBN. B) AC-HRTEM image of hBN showing a single boron vacancy and nitrogen terminated hole. C) Atomic model of hBN vacancy. D) Atomic model of triangular hole with nitrogen atom termination. A–D) Reproduced with permission.^[15] Copyright 2009, American Physical Society. E) Large area image of hBN showing different single atom boron vacancies. F) Model of single bond formation generated after a boron vacancy is formed. G,H) Simulated and AC-HRTEM image of the single interlayer bonding structure depicted in (F). I) Model of two interlayer bonds created upon boron vacancy creation. J,K) Simulated and AC-HRTEM image of the double interlayer bonding structure depicted in (I). E–K) Reproduced with permission.^[16] Copyright 2011, American Physical Society. L,M) Images of a closed edge of a bilayer hole in hBN acquired by AC-STEM. Mapping of the atomic positions highlights the distorted hexagons along the edge. N) Top view of closed loop structure. O) Side view of edge structure with overlaid EELS unoccupied orbital map. L–O) Reproduced with permission.^[17] Copyright 2012, American Physical Society. P) Tilt GB in polycrystalline hBN with a 21° relative angle. Q) Magnified region from (P) highlighting the pentagons (yellow), heptagons (red), and hexagons (blue) at the boundary. P,Q) Reproduced with permission.^[18] Copyright 2013, American Chemical Society.

observations of lattice relaxations and dislocation motion during imaging, which may favor 5|7 dislocations.

5. Defects in Transition Metal Dichalcogenides

Transition metal dichalcogenides (TMDs) are a class of layered materials that have recently received a great deal of interest within the scientific community. Of particular interest are the disulfides and diselenides of molybdenum and tungsten, which have interesting optical and electronic properties that depend strongly on the number of layers. These materials are comprised of a layer of transition metal atoms (molybdenum or tungsten) positioned between two layers of chalcogen atoms (sulfur or selenium). In the pristine crystal structures, each metal atom is six fold coordinated and the chalcogen atom is three fold coordinated. With these three layers of atoms for each isolated monolayer, the structures have a greater degree of complexity when compared with either the monoatomic graphene or diatomic hBN.

Recently, progress has been made on the CVD synthesis of these materials on insulating substrates for potential device applications.^[24,25] Similar to graphene, the grown films are polycrystalline and transferrable to a variety of substrates with appropriate processing. Using low-resolution dark-field imaging, the real space crystal distribution of grown films reveals the presence of isolated single crystal and polycrystalline monolayer islands with both tilt and mirror grain boundaries (**Figure 4**A to 4D). Characterization by high-resolution electron microscopy has also been accomplished to understand the atomic scale defects, which include monovacancies, multi atom vacancies, and grain boundary structures.^[23] Both tilt and mirror grain boundaries appear frequently, each having their own unique optical and electronic properties. By using AC-STEM imaging, the atomic structure of the different defect and boundary structures provides the necessary information to understand measured bulk properties.

One unique feature of TMDs when compared to graphene or hBN is the existence of antisite defect structures where metal atoms can occupy the sites of chalcogen atom pairs or a pair of chalcogen atoms can occupy metal atom sites. Antisite defects in MoS2 reveal that when molybdenum atoms replace a sulfur pair within the lattice, a break in the symmetry of the hexagonal network is observed, whereas a sulfur pair will replace molybdenum atoms while maintaining the crystal lattice symmetry (Figure 4E to 4H).

The complex bonding capability of the atomic constituents of TMDs allows for interesting boundary structures. In tilt boundaries, new 4|6 and 6|8 dislocations have been observed along with conventional 5|7 dislocations and are believed to be the result of variations in the local concentrations of reactant species during growth. A collection of dislocation structures observed in MoS_2 tilt boundaries is shown in Figure 4I to 4M. In mirror boundaries, 4|4 and 4|8 line defects exist between neighboring crystalline domains and contain kink sites that have four fold over coordinated metal atoms junctions. The AC-STEM



Makrials Views www.MaterialsViews.com



Figure 4. Atomic defects in polycrystalline molybdenum disulfide. A) False-color DF-TEM images of polycrystalline MoS₂ islands grown by CVD. B) False color DF-TEM image of a bicrystal with a tilt boundary. C,D) DF-TEM images of polycrystalline islands with mirror boundaries. A–D) Reproduced with permission.^[25] Copyright 2013, Nature Publishing Group. E,F) Antisite defects with molybdenum or two-atom sulfur replacement, respectively. G,H) Atomic models of (E) and (F) with molybdenum atoms shown in magenta and sulfur atoms shown in yellow. I) Tilt boundary in MoS₂ with a 18.5° angle. J,K) 5/7 and 6/8 dislocations taken from (I). L,M) Pristine and molybdenum substituted 4/6 dislocations observed in tilt boundaries, respectively. 2D and 3D models are presented along with AC-STEM images in (J) to (M). N) Image of a mirror boundary in MoS₂. O) Kink in an MoS₂ mirror boundary with 4-fold coordinated molybdenum atom. P) 4/4 mirror boundary AC-STEM image. Q) Atomic model of boundary in (N). R) 4/8 mirror boundary structure, representing highest possible kink density. E–R) Reproduced with permission.^[23] Copyright 2013, American Chemical Society.

images and atomic structures are shown in Figure 4N to 4R. Additionally, phase boundaries and their dynamic behavior can be observed in these materials, where a metallic (1T) and semiconducting (2H) phase simultaneously exist in a monolayer.^[36]

6. Conclusions and Outlook

The study of the atomic structure of defects in 2D materials is a rich field with a bright future. While the provided discussion is not exhaustive, we have sought to highlight important results obtained by advanced electron microscopy. Each section illustrates how the different materials are related, yet unique and interesting in their own right. Work on the monoelemental graphene has served as a strong foundation for future research on the whole class of 2D materials. For example, the work on combining the mapping of the large area crystal structure and high-resolution atomic structure of graphene has inspired recent work on TMDs. These studies built upon previous work by including electrical device characterization and optical photoluminescence measurements on single crystal and GB regions of the CVD grown material.

Knowledge gained from high-resolution imaging will continue to contribute to our understanding of the bulk properties of 2D materials. Recent work has shown that graphene's elastic stiffness can increase when sparse defects are intentionally created in the material.^[35] It would be interesting to perform similar studies on both monolayer and bilayer hBN samples. The interlayer bonding that occurs during defect creation in hBN is expected to alter the elastic properties of the material when compared to defect free layers. Additionally, controlled and patterned fabrication of holes with closed edges in hBN may prove to have interesting mechanical properties. For TMDs, mechanical measurements of the elastic stiffness and failure strength of different defect densities and GB structures has yet to be accomplished. It would be interesting to create and characterize



/ww.advmat.de



www.MaterialsViews.com

different vacancies and antisite defects in TMDs with the goal of making mechanical measurements. For example, one could intentionally create vacancies and subsequently back fill these sites with the same or different atomic species as the parent lattice and measure the failure behavior.

As the field of 2D materials grows, it is clear that high-resolution electron microscopy will continue to play an important role in its progress. Additionally, developments within the field of electron microscopy will make new experiments possible for characterization of 2D materials. This can be seen in recent results acquired on hBN, where high-resolution vibrational spectroscopy is now possible using a newly developed TEM with an electron beam source that has a remarkable energy spread of 12meV.^[37] Further studies from the developing fields will surely produce important fundamental knowledge for the scientific community.

Acknowledgements

H.I.R and A.Z. acknowledge support in part by the Director,Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract DE-AC02-05CH11231, within the sp2-bondedMaterials Program; the National Science Foundation under grant DMR-1206512; and the Office of Naval Research under grant N00014-12-1-1008. C.O. acknowledges support by the National Center for Electron Microscopy (NCEM)of the Lawrence Berkeley National Laboratory (LBNL), under Contract DE-AC02-05CH11231.

> Received: January 19, 2015 Revised: February 19, 2015 Published online:

- [1] L. Gross, F. Mohn, P. Liljeroth, J. Repp, F. J. Giessibl, G. Meyer, Science 2009, 324, 1428.
- [2] J. Repp, G. Meyer, S. Paavilainen, F. E. Olsson, M. Persson, *Science* 2006, 312, 1196.
- [3] L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer, Science 2009, 325, 1110.
- [4] S. Uhlemann, M. Haider, Ultramicroscopy 1998, 72, 109.
- [5] D. A. Muller, L. Fitting Kourkoutis, M. Murfitt, J. H. Song, H. Y. Hwang, J. Silcox, N. Dellby, O. L. Krivanek, *Science* 2008, 319, 1073.
- [6] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10451.
- [7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* 2005, 438, 197.
- [8] Y. Zhang, Y-W. Tan, H. L. Stormer, P. Kim, Nature 2005, 438, 201.
- [9] C. O. Girit, J. C. Meyer, R. Erni, M. D. Russell, C. Kisielowski, L. Yang, C-H. Park, M. F. Crommie, M. L. Cohen, S. G. Louie, A. Zettl, *Science* 2009, *323*, 1705.
- [10] K. Kim, Z. Lee, W. Regan, C. Kisielowski, M. F. Crommie, A. Zettl, ACS Nano 2011, 5, 2142.

- [11] P. Y. Huang, C. S. Ruiz-Vargas, A. M. van der Zande, W. S. Whitney, M. P. Levendorf, J. W. Kevek, S. Garg, J. S. Alden, C. J. Hustedt, Y. Zhu, J. Park, P. L. McEuen, D. A. Muller, *Nature* **2011**, *469*, 389.
- [12] J. H. Warner, E. R. Margine, M. Mukai, A. W. Robertson, F. Giustino, A. I. Kirkland, *Science* 2012, *337*, 209.
- [13] K. Suenaga, M. Koshino, *Nature* **2010**, *468*, 1088.
- [14] H. I. Rasool, C. Ophus, Z. Zhang, M. Crommie, B. Yakobson, A. Zettl, Nano Lett. 2014, 14, 7057.
- [15] N. Alem, R. Erni, C. Kisielowski, M. D. Rossell, W. Gannett, A. Zettl, *Phys. Rev. B* 2009, *80*, 155425.
- [16] N. Alem, O. V. Yazyev, C. Kisielowski, P. Denes, U. Dahmen, P. Hartel, M. Haider, M. Bischoff, B. Jiang, S. G. Louie, A. Zettl, *Phys. Rev. Lett.* **2011**, *106*, 126102.
- [17] N. Alem, Q. M. Ramasse, C. R. Seabourne, O. V. Yazyev, K. Erickson, M. C. Sarahan, C. Kisielowski, A. J. Scott, S. G. Louie, A. Zettl, *Phys. Rev. Lett.* 2012, 109, 205502.
- [18] A. Gibb, N. Alem, J-H. Chen, K. J. Erickson, J. Ciston, A. Gautam, M Linck, A. Zettl, J. Am. Chem. Soc. 2013, 135, 6758.
- [19] Y. Lou, X. Zou, B. I. Yakobson, ACS Nano 2012, 6, 7053.
- [20] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, Phys. Rev. Lett. 2012, 105, 136805.
- [21] A. Splendian, L. Sum, Y. Zhang, T. Li, J. Kim, C-Y Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, *10*, 1271.
- [22] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, Nat. Nanotechnol. 2012, 7, 699.
- [23] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P. M. Ajayan, B. I. Yakobson, J-C. Idrobo, *Nano Lett.* **2013**, *13*, 2615.
- [24] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J-C. Idrobo, P. M. Ajayan, J. Lou, *Nat. Mater.* **2013**, *12*, 754.
- [25] A. M. van der Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G-H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, J. C. Hone, *Nat. Mater.* **2013**, *12*, 554.
- [26] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science* 2009, 324, 1312.
- [27] Y. Liu, B. I. Yakobson, Nano Lett. 2010, 10, 2178.
- [28] O. V. Yazyev, S. G. Louie, Phys. Rev. B 2010, 81, 195420.
- [29] R. Grantab, V. B. Shenoy, R. S. Ruoff, Science 2010, 330, 946.
- [30] Y. Wei, J. Wu, H. Yin, X. Shi, R. Yang, M. Dresselhaus, Nat. Mater. 2012, 11, 759.
- [31] O. Yazyev, S. G. Louie, Nat. Mater. 2010, 9, 806.
- [32] G-H. Lee, R. C. Cooper, S. J. An, S. Lee, A. van der Zande, N. Petrone, A. G. Hammberg, C. Lee, B. Crawford, W. Oliver, J. W. Kysar, J. Hone, *Science* **2013**, *340*, 1073.
- [33] H. I. Rasool, C. Ophus, W. S. Klug, A. Zettl, J. K. Gimzewski, Nat. Commun. 2013, 4, 2811.
- [34] A. W. Tsen, L. Brown, M. P. Lavendorf, F. Ghahari, P. Y. Huang, R. W. Havener, C. S. Ruiz-Vargas, D. A. Muller, P. Kim, J. Park, *Science* **2012**, *336*, 1143.
- [35] S. Kurasch, J. Kotakoski, O. Lehtinen, V. Skakalova, J. Smet, C. E. Krill, A. V. Krasheninnikov, U. Kaiser, *Nano Lett.* 2012, *12*, 3168.
- [36] Y-C. Lin, D. O. Dumcenco, Y-S. Huang, K. Suenaga, Nat. Nanotechnol. 2014, 9, 391.
- [37] G. Lopez-Polin, C. Gomez-Navarro, V. Parente, F. Guinea, M. I. Katsnelson, F. Perez-Murano, J. Gomez-Herrero, *Nat. Phys.* 2015, 11, 26.
- [38] O. L. Krivanek, T. C. Lovejoy, N. Dellby, T. Aoki, R. W. Carpenter, P. Rez, E. Soignard, J. Zhu, P. E. Batson, M. J. Lagos, R. F. Egerton, P. A. Crozier, *Nature* 2014, 514, 209.