

Characterization and Control of Dopants and Defects at the Single-Atom-Scale

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14. ABSTRACT We report outcomes for an NRL 6.1 Base Program toward development of methods for direct imaging and spectroscopic characterization of atomic-scale defects, and, where possible, electron-beam driven control of defect atom positions to add a new level of understanding and flexibility to the design and production of semiconducting and two-dimensional materials. This work focused on developing precise knowledge of, and control over, the placement of individual dopant atoms that will ultimately permit the tuning of optical and electrical properties of materials for quantum information and photonic applications.					
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EXECUTIVE SUMMARY

This document satisfies the closeout requirements for NRL base program 991L68: Characterization and Control of Dopants and Defects at the Single-Atom-Scale. It provides an overview of the technical objectives of the program, technical progress, and dissemination of research findings through publications, presentations, transitions, and awards.

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CLOSE OUT MEMORANDUM FOR NRL BASE PROGRAM 991L68: CHARACTERIZATION AND CONTROL OF DOPANTS AND DEFECTS AT THE SINGLE-ATOM-SCALE

PROGRAM DESCRIPTION

The objective of this program is to develop methods for direct imaging and spectroscopic characterization of atomic-scale defects, and, where possible, electron-beam driven control of defect atom positions to add a new level of understanding and flexibility to the design and production of semiconducting and two-dimensional materials. This work focused on developing precise knowledge of, and control over, the placement of individual dopant atoms that will ultimately permit the tuning of optical and electrical properties of materials for quantum information and photonic applications. The NRL UltraSTEM is ideally suited for characterization of nanomaterials at scales down to the individual atom. This class of electron microscope is the only tool capable of directly imaging sub-surface impurity atoms and vacancy defects with simultaneous spectroscopic characterization. Progress has been made in three systems of active interest to NRL, ONR and DoD in general: 1. Particulate nanodiamonds, 2. Wide-band gap semiconductors, and 3. Two-dimensional transition metal dichalcogenides (TMDs).

Direct Characterization and Positioning of Point Defects in Particulate Nanodiamonds

Through this program, significant advances were made in the ability to characterize and control dopant incorporation into nanodiamonds through aberration-corrected scanning transmission electron microscopy (STEM). The objective of this task was to directly image, characterize, and position single color-centers, particularly the nitrogen-vacancy (NV) center, in diamond – a single-atom defect that is a known quantum emitter. The defect incorporation was understood by using simultaneously acquired electron energy loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDS). By coupling these spectroscopic signals, we were able to experimentally verify that an EELS peak at 282.4 eV originates from the NV center and thereby image the location of a single NV center in a nanodiamond. Naturally-occurring nanodiamonds containing NV centers, sourced from the Murchison meteorite, provided a platform on which we optimized spectroscopic conditions necessary to unambiguously identify this single point-defect. Working with synthetic nanodiamonds obtained from the commercial vendor FND Biotech, NV centers were identified in samples that are more readily applicable to scalable quantum technologies than the meteoritic nanodiamond used to establish proof-of-concept, single-defect spectroscopy. An in-situ heating stage was also used to observe the temperature stability of N and noble gas dopants in diamond from room temperature to 1200°C. The N impurities were observed to change atomic configuration at temperatures between 400 and 600°C, well below typical temperatures in bulk diamond. We further established electron beam parameters that allowed us to reposition N atoms and/or NV centers in situ using the electron beam, demonstrating that the STEM beam can be used to reposition N atoms and/or NV centers in diamonds. Because the STEM beam is atomically-sharp and can be precisely positioned, this work indicates that controllable positioning of a single NV center should be possible. This is important progress toward individually positioning NV centers to create atomically precise single photon emitter arrays.

Atomic-Scale N Defects in Wide-Band Gap Semiconductors

Another objective of this work was to identify defect structures in transition metal nitride electronic materials and cubic boron nitride (c-BN) thin films, with applications in high power and superconducting electronics. Incorporation of NbN_x and Ta₂N together has the ability to produce defect-free SNS Josephson junctions that have been suggested as a programmable voltage standard. Our electron microscopy analysis provided a definitive determination that the structure of tantalum nitride films was the desired non-polar P63mmc phase, rather than related polar P63mc Ta₂N or P-31m TaN phases. This information gives promise for growing related wide band gap materials like AlN and GaN on Ta₂N, which may provide a new defect-free way to bridge lattice mismatch between SiC and conventional III-nitride semiconductors.

High-Sc fraction $\text{Sc}_x\text{Al}_y\text{-1N}$ films with $x > 0.4$ offer a 5x increase in piezoresponse compared to pure AlN and are the first experimentally demonstrated nitride ferroelectric material, expanding the range of possible nitride-based devices. Controlling the phase of epitaxially grown $\text{Sc}_x\text{Al}_y\text{-1N}$ is very challenging, and while theory predicts the wurtzite phase to be most stable, it is difficult to avoid cubic inclusions during growth. Using STEM, this program determined the presence and location of the fine-scale cubic inclusions, which are typically smaller than 5 nm. STEM imaging revealed that the initial film growth proceeds with narrow columnar domains that coarsen into larger domains with several inclined threading dislocations, consistent with strain relief. Cubic inclusions are found among the initial columnar growth features, and few-nm cubic grains are also found throughout the coarser grained regions of film near threading dislocations. EELS studies revealed a subtle difference between the cubic and hexagonal phases.

Additionally, STEM revealed the critical role of Mg dopants in the growth of c-BN on diamond substrates, illuminating a deeper understanding of c-BN growth necessary to produce these UWBG films.

Micron-Scale Modification of Two-Dimensional Transition Metal Dichalcogenides

Another objective of this project was modification of 2D materials for the precise, nanoscale tuning of material properties. In collaboration with Code 6390, we studied Bi_2Se_3 bilayers on monolayer WS_2 for spin-polarized and oxygen transport. In this work, we demonstrated a method to manipulate the valley polarization and degree of circular polarization (DoCP) across a large range using a low-power laser (0.762 μW) in ambient conditions and at room temperature. The changes are locally confined, enabling features as small as 814 nm, and are long-term stable (>334 days). Applying a laser in a vacuum controllably reverses changes to the photoluminescence (PL) and DoCP. The PL and DoCP can be reliably manipulated within a range, allowing the material to be erased and reused. Investigation of the laser-irradiated $\text{Bi}_2\text{Se}_3\text{-WS}_2$ material in an oxygen environment revealed a change from Bi_2Se_3 to a $\text{Bi}_x\text{O}_y\text{Se}_z$ nanothin film that strongly resembles a rare $R\bar{3}m$ Bi_2O_3 phase, a rare crystal form of Bi_2O_3 predicted to have superior oxygen-transport properties to the other experimentally-stabilized crystal structures. To the best of our knowledge, we have synthesized some of the most chemically pure $R\bar{3}m$ rhombohedral Bi_2O_3 reported. We were also the first to report synthesis of rhombohedral Bi_2O_3 in nano-thin morphology. The micron-scale, size-confined laser spots selectively transform Bi_2Se_3 to $R\bar{3}m$ $\text{Bi}_x\text{O}_y\text{Se}_z$ and allows for rapid oxygen transport near room temperature under laser exposure. This nano-thin $\text{Bi}_x\text{O}_y\text{Se}_z$ material is a promising, unexplored low temperature solid oxide fuel cells and improved syngas production. The fabrication mechanism of 2D material modification via laser irradiation can be applied to other 2D materials as a generalized method to manipulate their properties with high precision and sub-micrometer spatial resolution.

DISSEMINATION

Refereed Journal Publications

1. N. Lebedev, R.M. Stroud, M.D. Yates, and L.M. Tender “Spatially Resolved Chemical Analysis of *Geobacter sulfurreducens* Cell Surface,” *ACS Nano* **13**, 4834–4842 (2019).
2. M.J. Crane, A. Petrone, R.A. Beck, M.B. Lim, X. Zhou, X. Li, R.M. Stroud, and P.J. Pauzauskie “High-pressure, high-temperature molecular doping of nanodiamond,” *Science Advances* **5**, eaau6073 (2019).
3. L. Yu, B.M. Hudak, A. Ullah, M.P. Thomas, C.C. Porter, A. Thisera, R.H. Pham, M. De Alwis Goonatileke, and B.S. Guiton “Unveiling the Microscopic Origins of Phase Transformations: An in Situ TEM Perspective,” *Chemistry of Materials* **32**, 639–650 (2020).
4. O.S. Ovchinnikov, A. O’Hara, S. Jesse, B.M. Hudak, S.-Z. Yang, A.R. Lupini, M.F. Chisholm, W. Zhou, S.V. Kalinin, A.Y. Borisevich, and S.T. Pantelides “Detection of defects in atomic-resolution images of materials using cycle analysis,” *Advanced Structural and Chemical Imaging* **6**, 1–9 (2020).
5. D.R. Rolison, J.J. Pietron, E.R. Glaser, T.H. Brintlinger, J.P. Yesinowski, P.A. DeSario, J.S. Melinger, A.D. Dunkelberger, J.B. Miller, C.L. Pitman, J.C. Owrutsky, R.M. Stroud and M.D.

- Johannes "Power of Aerogel Platforms to Explore Mesoscale Transport in Catalysis." *ACS Applied Materials & Interfaces* **12**, 41277–41287 (2020).
6. C. Pitman, A.M. Pennington, T.H. Brintlinger, D.E. Barlow, L.F. Esparraguera, R.M. Stroud, J.J. Pietron, P. DeSario, and D. Rolison "Stabilization of Reduced Copper on Ceria Aerogels for CO Oxidation," *Nanoscale Advances* **2**, 4547–4556 (2020).
 7. V.J. Gokhale, B.P. Downey, D.S. Katzer, N. Nepal, A.C. Lang, R.M. Stroud and D. J. Meyer "Epitaxial bulk acoustic wave resonators as highly coherent multi-phonon sources for quantum acoustodynamics," *Nature Communications* **11**, 2314 (2020).
 8. J.J. Fonseca, A.L. Yeats, B. Blue, M.K. Zhalutdinov, T.H. Brintlinger, B.S. Simpkins, D.C. Ratchford, J.C. Culbertson, J.Q. Grim, S.G. Carter, M. Ishigami, R.M. Stroud, C.D. Cress and J.T. Robinson "Enabling remote quantum emission in 2D semiconductors via porous metallic networks," *Nature Communications* **11**, 5 (2020).
 9. T.H. Brintlinger, S. Buckhout-White, N.D. Bassim, D. Mathur, A. Samanta, J.T. Robinson, J.-C. Idrobo, R.M. Stroud, E.R. Goldman and M.G. Ancona "Chemical Mapping of Unstained DNA Origami Using STEM/EDS and Graphene Supports," *ACS Applied Nano Materials* **3**, 1123–1130 (2020).
 10. C.N. Chervin, R. DeBlock, J.F. Parker, B.M. Hudak, N.L. Skeelee, J.K. Ko, R.M. Stroud, D.R. Rolison, and J.W. Long, "Capacity and Phase Stability of Metal-Substituted α -Ni(OH)₂ Nanosheets in Aqueous Ni-Zn Batteries," *Materials Advances* **11**, 14495–14503 (2021).
 11. A.C. Lang, D.S. Katzer, N. Nepal, D.J. Meyer, and R.M. Stroud, "Phase Identification and Ordered Vacancy Imaging in Epitaxial Metallic Ta₂N Thin Films," *ACS Applied Materials & Interfaces* **13**, 12575–12580 (2021).
 12. R.C.Y. Auyeung, B.M. Hudak, R.M. Stroud, and N.A. Charipar "Nanodiamonds by laser filamentation in ethanol," *Synthesis and Photonics of Nanoscale Materials XVIII* **11675**, 1167506 (2021).
 13. B.M. Hudak and R.M. Stroud "Evolution of NV centers in nanodiamond using in situ heating with STEM-EELS/EDS," *Microscopy and Microanalysis* **27**, 3050–3052 (2021)
 14. A. Markevich, B.M. Hudak, J. Madsen, J. Song, P.C. Snijders, A.R. Lupini, and T. Susi, "Mechanism of Electron-Beam Manipulation of Single-Dopant Atoms in Silicon," *The Journal of Physical Chemistry C* **125**, 16041–16048 (2021).
 15. B.M. Hudak and R.M. Stroud, "Identification and Manipulation of NV Centers in Nanodiamond," *Microscopy and Microanalysis* **28**, 2410–2411 (2022).
 16. Z. Hennighausen, D. Wickramaratne, K. McCreary, B.M. Hudak, T.H. Brintlinger, H.-J. Chuang, M. Noyan, B. Jonker, R.M. Stroud, O. van't Erve, "Laser-patterned submicron Bi₂Se₃-WS₂ pixels with tunable circular polarization at room temperature," *ACS Applied Materials & Interfaces* **14**, 9504–9514 (2022).
 17. Z. Hennighausen, B.M. Hudak, M. Phillips, J. Moon, K.M. McCreary, H.-J. Chuang, M. R. Rosenberger, B.T. Jonker, C.H. Li, R.M. Stroud, and O.M.J. van 't Erve "Room-Temperature Oxygen Transport in Nanothin BixOySez Enables Precision Modulation of 2D Materials," *ACS Nano* **16**, 13969–13981 (2022).
 18. B.M. Hudak and R.M. Stroud "Atomically Precise Detection and Manipulation of Nitrogen-Vacancy Centers in Nanodiamonds," *ACS Nano* **17**, 7241–7249 (2023).
 19. B.M. Hudak, A. Markevich, T. Susi, A.R. Lupini, and R.M. Stroud "Direct Positioning of Point Defects in 3D Materials Using STEM," *Microscopy and Microanalysis* **29**, 1365 (2023).
 20. R. Dziobek-Garrett, S. Hilliard, S. Sriramineni, O. Ambrozaite, Y. Zhu, B.M. Hudak, T.H. Brintlinger, T. Chowdhury, and T.J. Kempa; "Controlling Morphology and Excitonic Disorder in Monolayer WSe₂ Grown by Salt-Assisted CVD Methods," *ACS Nanoscience Au* **3**, 441–450 (2023).

Patents

1. R.M. Stroud, M.J. Crane, and P.J. Pauzauskie, “Molecularly Doped Nanodiamond,” U.S. Patent No. 11325086, Oct. 5, 2022.
2. T.E. Sutto, A. Ng, N.D. Bassim, T.H. Brintlinger, M.S. Osofsky, and R.M. Stroud, “Method for Preparing Clean Insulating Single or Few Sheets of Topological Insulators Using an Ionic Liquid,” U.S. Patent No. 10640377, May 5, 2020.
3. Z.B. Hennighausen, B.M. Hudak, O.M.J. van't Erve, and M. Phillips, “Nano-thin $\text{Bi}_x\text{O}_y\text{Se}_z$ Low-temperature Oxygen Transporter Membrane for Oxygen Transport, Separation, and Two-dimensional (2D) Material Manipulation,” U.S. Patent No. 18113285, Aug. 24, 2023.

Invited Conference Presentations

1. R.M. Stroud, “The Universe is my Nano-Fab: scanning transmission electron microscopy of carbonaceous nanomaterials,” Michigan Microscopy and Microanalysis Meeting, Central Michigan University, November 2018.
2. R.M. Stroud, “The Universe is my Nano-Fab: scanning transmission electron microscopy of carbonaceous nanomaterials,” Australian Microbeam Analysis Society, Brighton, Australia, February 2019.
3. R.M. Stroud, “The Universe is my Nano-Fab: scanning transmission electron microscopy of carbonaceous nanomaterials,” Chesapeake Microscopy and Microanalysis Society, Baltimore, MD, May 2019.
4. R.M. Stroud, “Nanodiamonds from Earth to the Cosmos,” European Microbeam Analysis Meeting, Trondheim, Norway, May 2019.
5. R.M. Stroud, “From Earth to the Cosmos and Back in the Electron Microscope,” Nion Corporation Open House, Kirkland, WA, August 2019.
6. R.M. Stroud, “Structural and Elemental Transformation of Meteoritic Nanodiamonds During In Situ Heating in a UHV Scanning Transmission Electron Microscope,” 82nd Annual Meeting of The Meteoritical Society, Sapporo, Japan, July 2019.
7. R.M. Stroud, “Aberration-Corrected STEM Analysis of Impurities in Cosmic Nanodiamonds and Synthetic Analogs,” Microscopy and Microanalysis 2019, Portland, OR, August 2019.
8. R.M. Stroud, “The Universe is my nano-fab: scanning transmission electron microscopy of nanomaterials from space,” National Academies of Engineering EU-USA Frontiers of Engineering Forum, Stockholm, Sweden, November 2019.
9. R.M. Stroud, “The Universe is my nano-fab: scanning transmission electron microscopy of nanomaterials from space,” Arizona State University, School of Space Exploration and Engineering Seminar, virtual seminar, April 2020.
10. R.M. Stroud, “Temperature Dependence of Impurity Distributions in Nanodiamonds as Revealed by Coordinated UHV-STEM EDX and EELS Analysis,” Microscopy and Microanalysis 2020, virtual conference, August 2020.
11. B.M. Hudak, “Identification of NV Centers in Nanodiamond through STEM-EELS/EDS” TMS 2021, Anaheim, CA, February 2022.
12. B.M. Hudak, “Direct Positioning of Point Defects in 3D Materials Using STEM,” Microscopy and Microanalysis 2023, Minneapolis, MN, August 2023.

Transitions to External Programs

1. FY23 Applied Research for Advancement of S&T priorities (ARAP) “APEX: Advanced Power Electronics and eXtreme RF.”

Awards

1. MRS NM05 Young Researcher Award to B.M. Hudak for presentation titled “Locating NV Centers in Nanodiamond Using Simultaneous STEM-EELS/EDS” presented May 8, 2022 at the Spring MRS 2022 Meeting.
2. NRC/ASEE Postdoctoral Research Publication Award for publication titled “Room-Temperature Oxygen Transport in Nanoscale $\text{Bi}_x\text{O}_y\text{Se}_z$ Enables Precision Modulation of 2D Materials.”
3. 2023 Annual Research Publication Award for publication titled “Atomically Precise Detection and Manipulation of Nitrogen-Vacancy Centers in Nanodiamonds.”