

In-situ Microscopy / Dynamic Processes

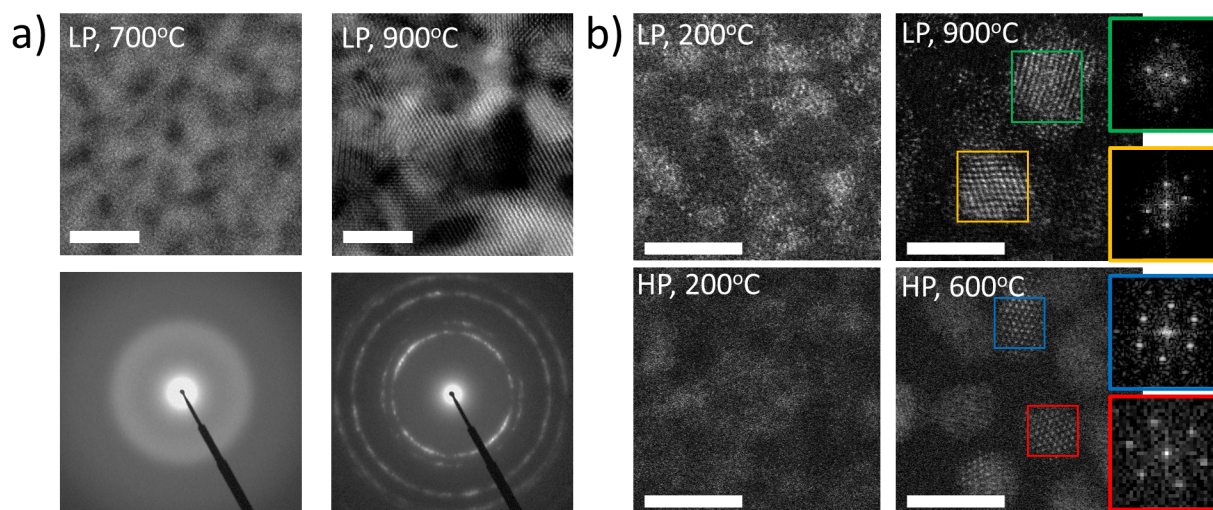
In-situ Oxidation in Environmental Transmission Electron Microscopy for Engineering	
Dielectric/2D Semiconductor Interfaces	188
Anisotropic 2D van der Waals Magnets Hosting 1D Spin Chains	189
Observing Nanoscale Transformations between Quicklime and Slaked Lime in an Environmental Transmission Electron Microscope.....	190
Revealing Metal Redox Pathways up to Ambient Pressure via in-situ Transmission Electron Microscopy	191

In-situ Oxidation in Environmental Transmission Electron Microscopy for Engineering Dielectric/2D Semiconductor Interfaces

R. Kothari, Z. Liu, H. Wu, P. J. Knight, P. Miller, R. Jaramillo, F. M. Ross

Two-dimensional (2D) semiconductors have emerged as an exciting and promising opportunity to expand electronics beyond the capabilities of silicon. They offer high mobility in the ultrathin limit and can be used as components in sensors or flexible electronics. One key challenge is the integration of 2D semiconductors, such as molybdenum disulfide (MoS_2), with the high-performance dielectrics used to separate the semiconducting channel from the metal gate in field-effect transistors. As a strategy to create high-quality semiconductor/dielectric interfaces, we use crystalline, epitaxial hafnium oxide (HfO_2) as a seed layer on which we deposit hafnium-based oxides by atomic layer deposition (ALD), a scaled technology in silicon electronics. To optimize this strategy, we need to understand both (1) the initial oxidation of Hf metal and (2) the crystallization of Hf-based ALD oxides. We use the Hitachi HF5000 Environmental S/TEM at Characterization.

nano (ETEM) to perform these experiments. Figure 1a shows the crystallization of a sputtered Hf film on the thin silicon nitride (SiN_x) membrane of an ETEM chip in response to temperature. Future work will probe this transformation for Hf on MoS_2 . Figure 1b shows the crystallization of Hf-zirconium oxide (HZO) from an initially amorphous state. The HZO de-wets from the SiN_x membrane and crystallizes in response to heating. Our past experiments could be carried out only at low oxygen pressures (10^{-7} atm), but recent improvements to the ETEM allow up to atmospheric pressures to be maintained during imaging, where similar HZO films were observed to crystallize at lower temperatures. We are also exploring the use of a TiN base layer to improve ALD adhesion and better replicate other studies of HZO's ferroelectric properties and structural modifications during switching.



▲ Figure 1: (a) Crystallization of HfO_2 formed from 15-nm sputtered Hf metal at low O_2 pressure (LP, 10^{-7} atm). Top-HAADF STEM, bottom-TEM diffraction; (b) HAADF STEM of ALD HZO at LP and HP O_2 (1 atm) before and after crystallization in response to heating. Insets show FFTs of corresponding regions, consistent with monoclinic and orthorhombic phases. All scale bars are 5 nm.

FURTHER READING

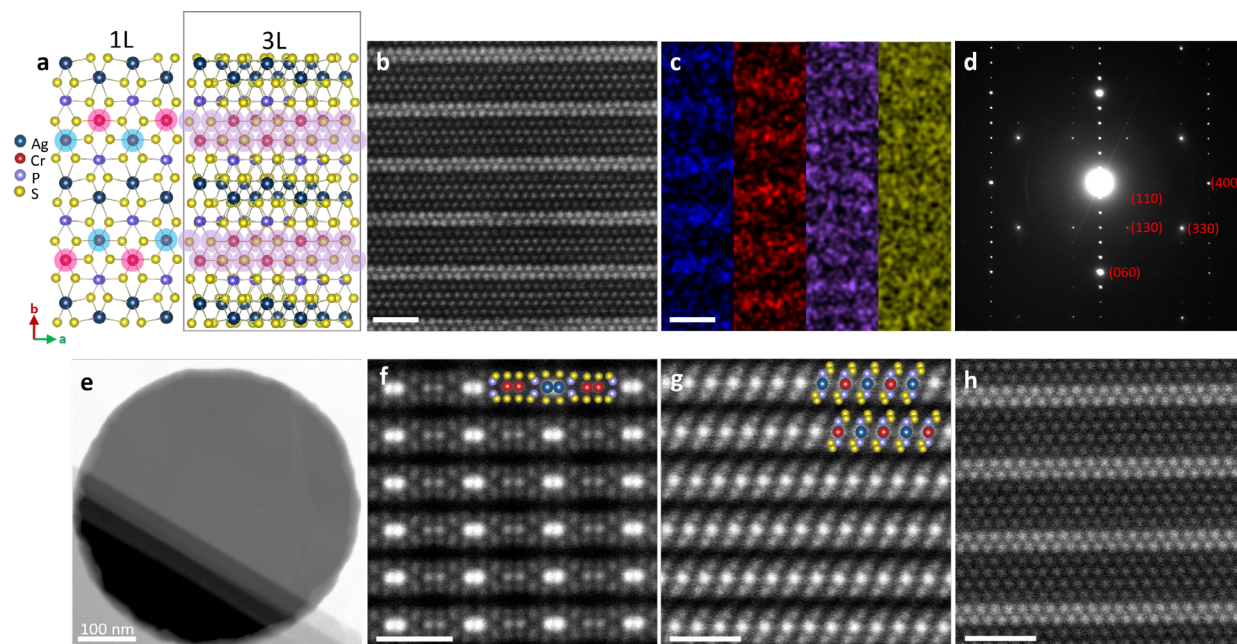
- A. Pannone, A. Raj, H. Ravichandran, et al., "Robust Chemical Analysis with Graphene Chemosensors and Machine Learning," *Nature*, vol. 634, pp. 572–578, 2024. DOI.org/10.1038/s41586-024-08003-w
- A. K. Katiyar, A. T. Hoang, D. Xu, et al., "2D Materials in Flexible Electronics: Recent Advances and Future Prospectives," *Chemical Reviews*, vol. 124, pp. 318–419, 2024. DOI.org/10.1021/acs.chemrev.3c00302
- Z. Liu, Q. Mao, V. Kamboj, et al., "Epitaxial Formation of Ultrathin HfO_2 on Graphene by Sequential Oxidation," arXiv 2504.11693, 2025. DOI.org/10.48550/arXiv.2504.11693

Anisotropic 2D van der Waals Magnets Hosting 1D Spin Chains

E. Park, J. P. Philbin, H. Chi, J. J. Sanchez, C. Occhialini, G. Varnavides, J. B. Curtis, Z. Song, J. Klein, J. D. Thomsen, M. G. Han, A. C. Foucher, K. Mosina, D. Kumawat, N. Gonzalez-Yepe, Y. Zhu, Z. Sofer, R. Comin, J. S. Moodera, P. Narang, F. M. Ross
Sponsorship: MathWorks, Department of Energy BES QIS Program, ARO Multidisciplinary University Research Initiative

The exploration of one-dimensional (1D) magnetism, frequently portrayed as spin chains, constitutes an actively pursued research field that illuminates fundamental principles in many-body problems and applications in magnonics and spintronics. The inherent reduction in dimensionality often leads to robust spin fluctuations, impacting magnetic ordering and resulting in novel magnetic phenomena. Here, we explore structural, magnetic, and optical properties of highly anisotropic two-dimensional (2D) van der Waals antiferromagnets that uniquely host spin chains. First-princi-

ples calculations reveal that the weakest interaction is interchain, essentially leading to 1D magnetic behavior in each layer. With the additional degree of freedom arising from its anisotropic structure, we engineer the structure by alloying, varying the 1D spin chain length using electron beam irradiation, or twisting for localized patterning, and calculate spin textures, predicting robust stability of the antiferromagnetic ordering. Comparing them with other spin chain magnets, we anticipate these materials to bring fresh perspectives on harvesting low-dimensional magnetism.



▲ Figure 1: STEM structural characterization of 2D van der Waals magnets with 1D magnetic chains. a) Schematic of structure of AgCrP_2S_6 shown for monolayer (1L) and tri-layer (3L). Zig-zag chains of Cr atoms are highlighted in blue (spin up) and pink (spin down) for 1L and purple for 3L. b) Plan view STEM image of AgCrP_2S_6 . c) EDS map of AgCrP_2S_6 with Ag, Cr, P, and S indicated in blue, red, purple, and yellow, respectively. d) Diffraction pattern corresponding to area shown in b. e) Low magnification STEM image showing different layer numbers of flake. f-g) STEM images of the cross sections in crystallographic a and b directions, respectively, with atomic structures overlaid. h) Plan view STEM image of AgVP_2S_6 . Scale bars in b, c, f-h, 1 nm.

FURTHER READING

- E. Park et al., "Anisotropic 2D van der Waals Magnets Hosting 1D Spin Chains," *Advanced Materials*, vol. 36, p. 2401534, 2024.

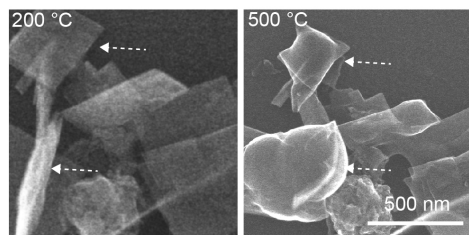
Observing Nanoscale Transformations between Quicklime and Slaked Lime in an Environmental Transmission Electron Microscope

E. Vaserman, H. Wu, F. M. Ross, A. Masic

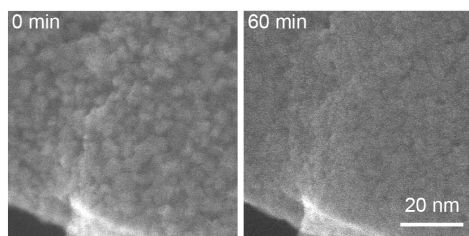
Quicklime (CaO) and slaked lime (Ca(OH)_2) are among the oldest material systems used by humans for construction, with a history spanning over 9,000 years. Today, the lime cycle (transformation between calcium carbonate (CaCO_3), CaO , and Ca(OH)_2) plays vital roles in modern construction sustainability, carbon sequestration, and various other industrial applications. Quicklime reacts exothermically with water to form slaked lime, which can reversibly decompose back to CaO and water upon heating. This CaO - Ca(OH)_2 cycle is fundamental to thermochemical energy storage technology and strongly influences the mechanical strength, durability, and carbonation behavior of ordinary Portland cement (OPC) and lime-based mortars and concretes. Although lime hydration and dehydration have been studied for centuries, the nanoscale mechanisms underlying these transformations remain poorly understood. In particular, the effect of environmental factors such as humidity and temperature on the hydration kinetics and the resulting morphology, microstructure, and porosity of slaked lime is not fully characterized.

In this work, we study the transformation between quicklime and slaked lime at the nanoscale using Characterization.nano's Hitachi HF5000-IS Environmental Transmission Electron Microscope (ETEM). In addition to conventional transmitted electron signals, the ETEM is equipped with a secondary electron (SE) detector, enabling simultaneous SE imaging of surface morphology evolution during the lime reactions. We observe the transformation of plate-like Ca(OH)_2 into stacked CaO nanoparticles in vacuum at different temperatures (Figure 1a), followed by their "fusion" back into Ca(OH)_2 under varying water vapor pressures (Figure 1b). Interestingly, during dehydration, some Ca(OH)_2 nanoplates appear to expand, possibly driven by internal steam pressure accumulation. Our atomic-resolution SE results also reveal the formation of edge dislocations in newly formed CaO (Figure 1c). These new insights are important for understanding the long-term durability of historical lime-based materials and modern OPC-based cements and will guide the design of next-generation cementitious systems.

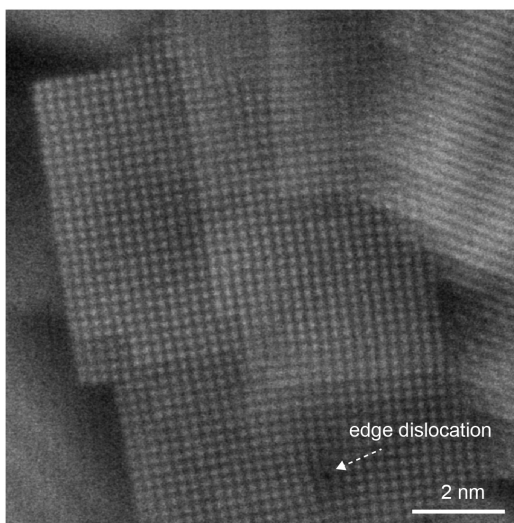
a Dehydration of slaked lime in vacuum



b Hydration of quicklime in water vapor



c Atomic-resolution SE imaging of quicklime



▲ Figure 1: SE images showing morphological evolution of lime during (a) Ca(OH)_2 dehydration in vacuum and (b) rehydration of the resulting CaO under water vapor. (c) Atomic-resolution SE image of CaO acquired in vacuum at 650 °C.

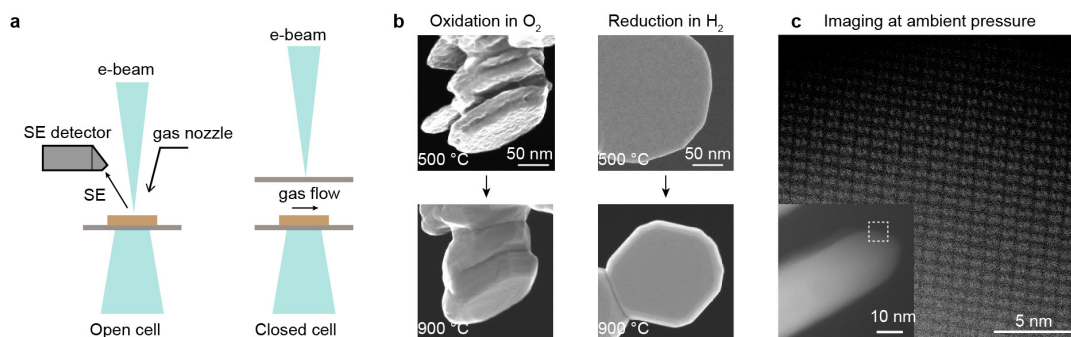
Revealing Metal Redox Pathways up to Ambient Pressure via in-situ Transmission Electron Microscopy

H. Wu, F. M. Ross

Sponsorship: Center for Entrepreneurship Development and Incubation, Seagate

Metal redox reactions are ubiquitous in nature (e.g., geological processes) and industrial applications. Understanding how materials evolve in morphology and structure at the nanoscale during such reactions in gaseous environments is critical for advancing catalysis, energy storage, and semiconductor technologies. Advances in transmission electron microscopy (TEM), microfabrication, and microelectromechanical systems have enabled the direct exposure of samples to a controlled gas environment at elevated temperatures within the microscope column. Gas can be introduced at low pressures (up to tens of millibars) using differential pumping or confined between two thin silicon nitride membranes in a closed-cell specimen holder (up to ambient pressure). Both approaches have proven effective in revealing atomistic mechanisms governing metal redox reactions. However, the effects of gas pressure on kinetic phase transformation pathways, particularly on transient surface morphological evolution during redox reactions, remain poorly understood.

In this project, we investigate metal redox reactions in various gaseous environments across different pressures using Characterization.nano's Hitachi HF5000-IS environmental TEM (ETEM) with a secondary electron (SE) detector. We visualize redox reactions occurring in a range of metal and alloys (Fe-, Zn- and Ni-based alloys) under gases, including H_2 , O_2 , methanol, and water vapor, up to ambient pressure. These experiments demonstrate that atomic resolution can be obtained under ambient pressure conditions and enable us to identify several transient phase transformation pathways during the early stages of oxidation and reduction of metals. The simultaneous SE imaging enabled us to understand the surface morphological changes taking place during these reactions, including the removal of surface ligand layers and the development of surface faceting. We anticipate that these advances will broaden the application of in-situ gas phase TEM for studying dynamic material process.



▲ Figure 1: (a) Schematics of setups for gas-phase TEM imaging. (b) SE images showing the morphological evolution of magnetite oxidation in O_2 (left) and hematite reduction in H_2 (right). (c) Atomic-resolution image of magnetite in O_2 at ambient pressure.