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# The Atomic Structure of Epitaxial Metallic Transition Metal Nitride $TaN_x$ by STEM-ABF and HAADF

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A long-standing material science challenge has been the difficulty of epitaxial integration of metals and semiconductors. Recently there have been several successes combining metallic transition metal nitrides (TMNs), $TaN_x$ and $NbN_x$ with III-nitride semiconductors, AlN, GaN, and related substrate material SiC[1]. Due to the rigid Ta sublattice conventional diffraction techniques have difficulty discriminating between common $TaN_x$ structures, therefore aberration-corrected STEM imaging and direct comparison to image simulation is necessary to determine the exact phase of epitaxial $TaN_x$ films. The majority of experimentally measured hexagonal $TaN_x$ phases consist of the same Ta-sublattice with only a differing N-sublattice. An open question remains, will epitaxially grown $TaN_x$ will adopt the same polar crystal structure as GaN and SiC, $P6_3mc$, or retain the non-polar $P6_3mmc$ of $\gamma$-$Ta_2N$ ($TaN_{0.5}$)? The answer to this question could have wide ranging effects on the properties of devices incorporating epitaxial $TaN_x$ and other epitaxially grown TMNs on polar substrates.

In this study we examine the structure of $TaN_x$ films grown on 6H-SiC via radio-frequency plasma molecular-beam epitaxy with aberration-corrected scanning transmission electron microscopy (STEM). We performed a combination of annular bright-field (ABF) and high-angle annular dark-field (HAADF) imaging and ABF/HAADF image simulation via Prismatic[2]. Experimental HAADF and ABF images were acquired on an aberration-corrected Nion UltraSTEM 200X operated at 200 kV, with a convergence angle of 27mrad, as stacks of 50 frames, and later cross-correlated and summed to reduce noise. Initial image analysis revealed that the structure of $TaN_x$/6H-SiC films readily agrees with the lattice constants determined by x-ray diffraction. Due to the similarity of the Ta sublattice in candidate structures, HAADF imaging is insufficient for determination of $TaN_x$'s space group (Figure 1, top), but ABF imaging and simulation, (Figure 1, bottom) reveal the structure to be that of $\gamma$-$Ta_2N$. This demonstrates that epitaxially grown $Ta_2N$ adopts the non-polar phase.

Rutherford backscattering spectrometry (RBS) and energy-dispersive x-ray spectroscopy (EDS) suggest that the films are off stoichiometry, containing approximately 3-5 at% less Ta than stoichiometric $\gamma$-$Ta_2N$. STEM imaging down the [10-10] zone axis reveals several line defects (Figure 2a) which appear to contain ordered Ta vacancies. In order to quantify the Ta column occupancy, we simulated HAADF images for a range of Ta column occupancies. The best-fit image simulation (Figure 2b, c) confirms that the defect columns have approximately 40-50% Ta occupancy. The observed defect column concentration and estimated the Ta occupancy are consistent with an approximate decrease of 3-4 at% Ta globally throughout the entire film, which is in agreement with RBS and low magnification off zone-axis acquired EDS values. This suggests that the sub-stoichiometric Ta composition is due to the formation of Ta vacancies during growth. STEM imaging and corroboration with advanced image simulation is crucial to understanding the microstructure of grown epitaxial TMN films and will continue to play vital role in the future design and optimization of this new class of materials.

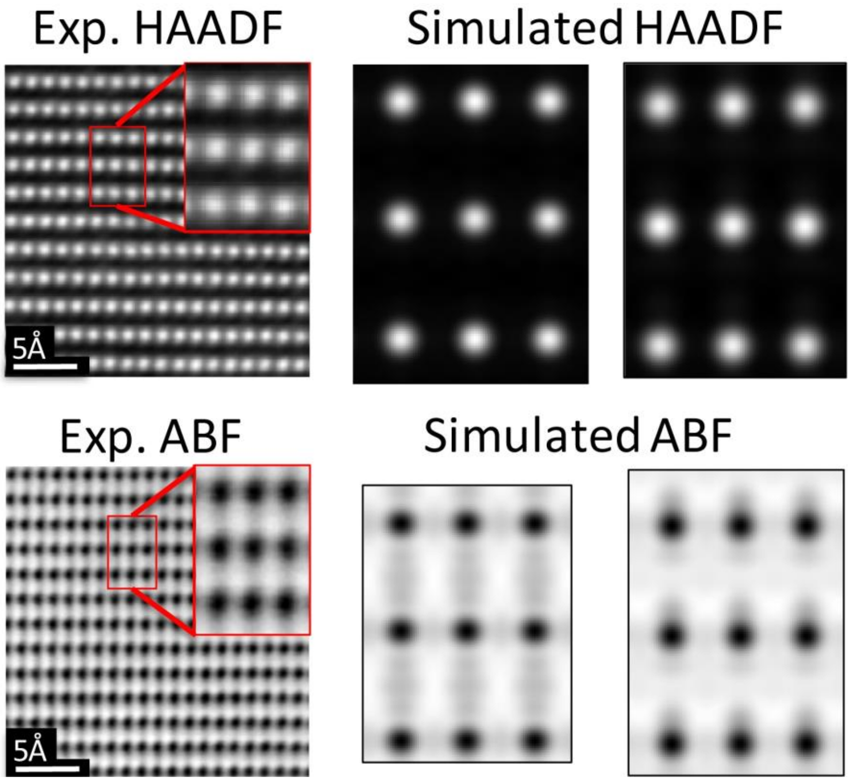

**Figure 1.** (Top left) Experimental HAADF image acquired from [10-10] oriented Ta2N, corresponding simulated HAADF images for P63mmc; (Top middle) and P63mc, top right, TaNx structures. Simulated HAADF images were created by selecting virtual detector angles >70 mrad. (Bottom left) Experimental ABF image acquired from [10-10] oriented Ta2N with corresponding simulated ABF images for P63mmc (Bottom middle); and P63mc (Bottom right). Simulated ABF images were created by selecting virtual detector angles 9-15mrad. Experimental and simulated images have a convergence angle of 27mrad.

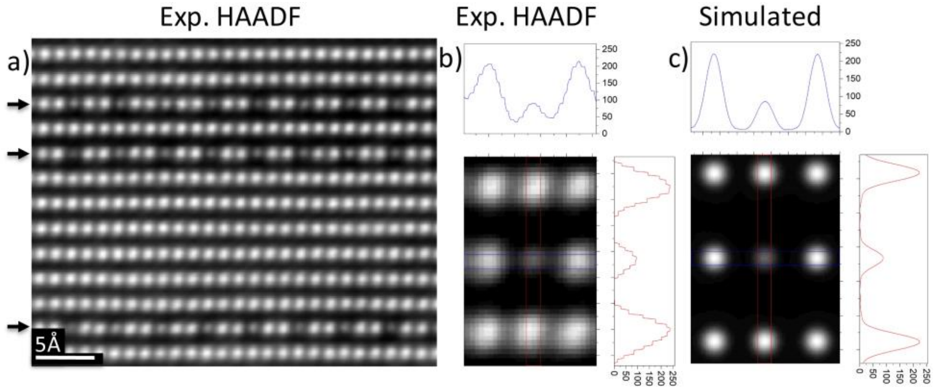

**Figure 2.** (a) Experimental HAADF image acquired from [10-10] showing the regular line defect structures in Ta2N. Line profiles extracted from (b) the experimentally acquired HAADF, and (c) the 50% Ta column occupancy simulated HAADF, respectively. The simulated HAADF image was created by selecting virtual detector angles >70mrad. Experimental and simulated images have a convergence angle of 27mrad.

References

[1] Katzer, D. S. et al., *Physica Status Solidi (a)* **217** (3) (2019).
[2] Ophus, C., *Adv Struct Chem Imaging* **3** (1), 13 (2017).