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ABSTRACT

Epitaxial lattice-matched TiN/(Al,Sc)N metal/semiconductor superlattices have attracted significant interest in recent years for their potential applications in thermionic emission-based thermoelectric devices, optical hyperbolic metamaterials, and hot-electron-based solar-energy converters, as well as for the fundamental studies on the electron, photon, and phonon propagation in heterostructure materials. In order to achieve high efficiency devices and for the quest to discover new physics and device functionalities, it is extremely important that the superlattices exhibit atomically sharp and abrupt interfaces with minimal interface mixing and surface roughness. Moreover, as the energy transport across the cross-plane direction of these superlattices depends on the interface-properties, it is important to characterize the interfacial electronic structure and the chemistry of bond formation. Employing a combination of soft x-ray scattering techniques such as x-ray diffraction and synchrotron-based x-ray reflectivity, in this article, we demonstrate sharp and abrupt TiN/(Al,Sc)N superlattice interfaces with an asymmetric interface roughness ranging from two-to-three unit cells. Synchrotron-based soft x-ray absorption analysis revealed similar peak positions, line shapes, and absorption edges of different atoms in the individual thin films and in the superlattices, which demonstrate that the oxidation state of the atoms remains unchanged and rules-out the secondary structure or phase formation at the interfaces. The x-ray scattering results were further verified by aberration-corrected high-resolution scanning transmission electron microscopy imaging and energy dispersive x-ray spectroscopy mapping analysis. These results will be important for understanding of the transport properties of metal/semiconductor superlattices and for designing superlattice-based energy conversion devices.

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I. INTRODUCTION

Heterostructure metamaterials have been at the forefront of modern technological innovation and revolution over five-to-six decades and are researched extensively to develop a wide variety of electronic and optoelectronic devices ranging from solid-state lighting, digital and analog optoelectronics, optical communication, consumer electronics, solid-state energy conversion, etc.^{1,2} Such artificially structured materials have been also employed extensively for the fundamental physics, materials science, and device engineering studies that have led to the discoveries of the quantum Hall

effect,^{3,4} quantum confinement of elementary particles,^{5,6} development of quantum well lasers,^{7,8} quantum cascade lasers,^{9,10} etc., with large-scale societal impacts.¹¹ While most of these heterostructures are composed of lattice-matched semiconductors such as GaAs/AlAs with their electronic band-offset providing essential functionalities,^{12,13} metal/semiconductor superlattice (SL) heterostructures have not gained much attention until very recently.¹² Epitaxial single-crystalline metal/semiconductor superlattices with tunable Schottky barrier heights could lead to highly efficient thermionic emission-based thermoelectric energy converters,¹ hot-electron devices for solar-energy conversion,^{18,19} terahertz optoelectronics, exotic optical metamaterials with hyperbolic dis-²³ However, persions and large densities of photonic states, etc.²⁰ the material's compatibility and growth challenges had primarily limited the progress in the development of such "man-made" crystals for a long time.^{14,2}

Epitaxial TiN/Al_{0.72}Sc_{0.28}N metal/semiconductor superlattices are the first demonstration of such single-crystalline metamaterials without the presence of a significant amount of extended defects such as dislocations.^{21,26} Due to the similarity in the crystal structure and the lattice-constant of the component TiN and Al_{0.72}Sc_{0.28}N and substrate MgO, these rocksalt superlattices exhibit near defect free interfaces with high mechanical hardness, chemical stability, and thermal stability up to ~1000 °C.^{27,28} In terms of the thermal transport properties, TiN/Al_{0.72}Sc_{0.28}N metal/semiconductor superlattices have demonstrated phonon wave-effects in heterostructure materials and with the incorporation of heavy tungsten (W) atoms as alloys in TiN, their thermal conductivity was reduced to less than 1.7 W/m K at room temperature that would make them useful for thermoelectric applications.^{29,30} Similarly, TiN/ Al_{0.72}Sc_{0.28}N superlattice metamaterials have also exhibited photonic hyperbolic dispersion^{21,22} of the isofrequency surfaces and large enhancement in their densities of photonic states that could be engineered for several quantum electronic device applications. Currently, significant efforts are underway to engineer their electronic properties and design Schottky barrier height-based thermionic energy conversion devices for waste-heat recycling as well as optoelectronic devices operating from the terahertz-to-near-UV spectral ranges.^{31–33} In addition, rocksalt ScN has also attracted significant interest in recent years for its large thermoelectric power factors and potential thermoelectric applications.³

However, in order to achieve high device efficiencies, it is essential that these superlattices exhibit structural qualities such as atomically smooth interfaces with minimal interface atomic mixing or roughness.^{36,37} Moreover, since the cross-plane energy transport critically depends on the interfacial properties, it is also important to determine their electronic structure and the chemistry of bondformation at the interfaces, particularly to ascertain the presence or absence of any interfacial layers that could impact device properties. In this article, the interface chemistry and the electronic structure of the epitaxial TiN/Al_{0.72}Sc_{0.28}N metal/semiconductor superlattices are determined by employing a combination of highresolution XRD, XRR, and XAS analysis. Furthermore, HRSTEM imaging and EDS mapping analysis were performed to demonstrate atomically sharp interfaces and to show the absence of any otherwise interfacial layers. Though the superlattice interface could have been studied by HRSTEM analysis only, TEM images result from a small sample area at the interfaces. At the same time, the XAS signal from the interface is much less compared to the signals from the rest of the films. Therefore, a combination of XRR and HRSTEM was employed to analyze the interface properties.

II. EXPERIMENTAL DETAILS

Five thin film and superlattice samples [~100 nm TiN, ~240 nm ScN, ~120 nm TiN/Al_{0.72}Sc_{0.28}N, and TiN/Al_{0.72}Sc_{0.28}N superlattices with 6 nm (3 nm/3 nm) and 20 nm (10 nm/10 nm) period thicknesses with 250 nm of total thicknesses, respectively] were deposited with the reactive DC-magnetron cosputtering technique (PVD Products, Inc.) on MgO (001) substrates with a base pressure of 2×10^{-8} Torr. The Sc (99.99% purity on metal basis), Ti (99.995% on metal basis), and Al (99.999% on metal basis) targets had dimensions of 2 in. diameter and 0.25 in. thickness. All depositions were performed with an Ar-N₂ gas mixture of 4 SCCM of Ar and 6 SCCM of N₂ at a deposition pressure of 10 mTorr. The targets were sputtered in a constant power-mode with a substrate temperature of 750 °C during the depositions. More details about the growth process can be found in Ref. 22.

X-ray diffraction (symmetric $2\theta - \omega$ diffraction spectra) studies on the thin films were performed using Cu-K α_1 radiation in a Panalytical X'pert diffractometer. The diffractometer is equipped with a triple-bounce monochromator to remove any contribution from Cu-K α_2 .

Synchrotron-based soft XRR analysis was utilized at the BL-03³⁸ of the Indus-2 synchrotron facility at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India to determine the interfacial properties. A monochromatic soft x-ray beam of 455 eV energy was used to achieve the contrast in the refractive index between TiN and Al_{0.72}Sc_{0.28}N. The beamline provides a high photon flux (~10⁹-10¹¹ photons/sec) with a moderate spectral resolution $\left(\frac{E}{\Delta E} \sim 1000 - 6000\right)$ using a varied line spacing plane grating monochromator having three gratings that are interchangeable in situ without breaking the vacuum. The reflectometer consisted of a two axes high-vacuum compatible goniometer with an x-y-z sample manipulation stage. The scattering geometry was in the vertical plane, which is suitable for the s-polarized reflectivity measurements as synchrotron light is plane polarized in the horizontal plane. The sample and the detector were mounted on the $\theta - 2\theta$ axes, respectively. The experimental XRR pattern was fitted with SRXRR software³⁹ based on the recursive Parart formalism. An overall uncertainty of about 2–3 Å, i.e., about half a unit cell was recorded in the determination of the interface roughness. The uncertainty analysis was performed by keeping all parameters in the XRR data fitting as constant and systematically varying the interface roughness from the mean value. The R-squared value was taken as a metric in determining the quality of the fitting.

The electronic structure and the chemical bonding at the $TiN/Al_{0.72}Sc_{0.28}N$ superlattice interfaces were further evaluated with soft XAS measurements recorded in a total electronic yield (TEY) mode at the SXAS beam line (BL-01) of the Indus-2 Synchrotron source.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging along with EDS mapping was performed using an image and probe corrected and



monochromated FEI Themis 60-300 microscope equipped with a ChemiSTEM EDS detector system for ultrahigh count rates and operated at 300 kV. EDS maps were recorded with the probe forming a diameter smaller than 0.07 nm and total counts of the presented maps used for quantification were above 1×10^6 counts for a robust statistics and error estimation.

The TEM lamella was prepared with a Helios Hydra dual beam plasma focused ion beam (FIB). Films were coated with a 20 nm of Au to prevent charging prior to the FIB process. For TEM sample preparation, a 100 nm Pt + C protective cap was deposited with 5 kV electron beam followed by a 1 μ m Pt + C protective cap with a 12 kV Xe beam. A 30 kV Xe beam at 60, 15, and 4 nA was used for trenching and lift out. The TEM specimens were welded to Mo grids using Xe beam Pt welding. Thinning was achieved with tilt angles of ±1.5° with currents of 300 and 100 pA. Final thinning was done with 30 kV at 30 pA, checking for electron transparency using a 5 kV electron beam with a secondary electron (SE) detector. When the region of interest was thin enough, it was finally polished with 5 kV electron beam with an SE detector.

III. RESULTS AND DISCUSSION

HRXRD analysis revealed that all of the thin films and superlattices grow with 002 orientations on (002) MgO substrates with a small degree of mosaicity (see Fig. 1). The TiN 002 peak was found to be located at 42.48° in the symmetric $2\theta - \omega$ XRD diffractogram representing a *c* axis lattice constant of 4.24 Å which is consistent with previous literature reports.^{36,40} The full-width-at-the-half-maxima



FIG. 1. XRD diffractogram of TiN, TiN/Al_{0.72}Sc_{0.28}N, and 10 nm/10 nm TiN/ Al_{0.72}Sc_{0.28}N metal/semiconductor superlattice deposited on MgO (002) substrates are presented that show 002 oriented epitaxial growth. Interference fringes resulting from x-ray interference from multiple interfaces are visible in the superlattices. The XRD patterns of TiN and TiN/Al_{0.72}Sc_{0.28}N are adopted from our previous work (Ref. 31) and replotted here for the comparison of results. Reproduced with permission from Nayak *et al.*, Appl. Phys. Lett. **115**, 25 (2019). Copyright 2019, AIP Publishing LLC 2019.

(FWHM) of the rocking curve corresponding to the 002 peak was found to be 0.045° (not shown here) that indicates its nominal single-crystalline nature. Since the Al_{0.72}Sc_{0.28}N thin film with 72% AlN mole-fractions is metastable in the rocksalt crystal structure,¹² prior to the Al_{0.72}Sc_{0.28}N deposition, a 20 nm TiN seed layer was deposited on MgO substrates. HRXRD analysis revealed that the TiN/Al_{0.72}Sc_{0.28}N film grows with the 002 orientations on the MgO substrate with a lattice-constant of 4.27 Å. It is important to note that the 72% AlN mole-fraction in $Al_{0.72}Sc_{0.28}N$ was chosen to lattice-match $\mathrm{Al}_{0.72}\mathrm{Sc}_{0.28}\mathrm{N}$ with TiN for the superlattice deposition. Similar to their component thin films, the superlattices were found to grow with 002 orientations on the (002) MgO substrates with an out-of-plane lattice-constant of 4.26 Å (for 10 nm/10 nm superlattice). Distinct interference fringes were observed in the XRD pattern of the superlattices that arise from the x-ray diffraction caused by the periodic nature of the superlattices. Such sharp and clear interference fringes are the fingerprint of high-quality interfaces with minimal interface roughness. From the position of these fringes, a period thickness of 17 nm was measured. Prior reciprocal space x-ray mapping on the similar superlattices had revealed that the in-plane lattice-constant of the superlattices was pseudomorphically lattice-matched with that of the MgO substrate at 4.21 Å and a slight c axis relaxation.²



FIG. 2. Soft x-ray reflectivity pattern of a nominal 10 nm/10 nm TiN/ $AI_{0.72}Sc_{0.28}N$ superlattice is presented. The experimental data (blue sphere) was fitted with four different models with different interlayer roughnesses as presented in the inset. Model C that takes into account two interlayers per period thickness was found to best fit the experimental data.



The specular XRR pattern of the nominal 10 nm/10 nm TiN/Al_{0.72}Sc_{0.28}N superlattice with a total of 10 periods amounting to 200 nm of total thickness exhibits (see Fig. 2) periodic fringes that arise due to the x-ray reflection from the individual interfaces. In XRR patterns, the sharpness and the intensity of the peaks also known as Kiessig fringes is related to the interface sharpness and atomic mixing, while their positions signify the layer thickness and the periodicity.⁴¹ A sharp decrease in the intensity with increasing incident angles signifies higher interface roughness and atomic intermixing, while higher peak intensity at higher angles represents atomically sharp interfaces. The Kiessig fringes of the TiN/ Al_{0.72}Sc_{0.28}N superlattice in Fig. 2 appear sharp and intense that suggests atomically smooth and abrupt interfaces. To gain further quantitative information, the experimental XRR pattern was fitted with four models with each having distinct interface roughness pattern presented in Fig. 2 (inset). Since the differences in the models arise from the description of the interface roughness, results show that all of the four models fit the position of the fringes accurately. The TiN layer thickness was found to be 9.3 nm, while the Al_{0.72}Sc_{0.28}N layer thickness was 9.5 nm in the superlattice. It is important to note here that the layer thicknesses are very close to the experimentally targeted thickness of 10 nm for both of the layers during the deposition process that are calibrated from the growth rates and is also consistent with the periodicity obtained from the HRXRD interference fringe separations (see Fig. 1).

A comparison of the experimental XRR pattern with that of the modeling analysis reveal that model A, where interfaces are assumed to be ideal with no roughness fit the experimental data moderately (R-squared value 0.8214). The intensity of the Kiessig fringe peaks is larger in modeling compared to the ones in the experimental observation (see Fig. 2) since ideal interfaces with no interface roughness is assumed. Inclusion of interface roughness on single interfaces, i.e., either on the TiN/Al_{0.72}Sc_{0.28}N interface (B) or on the Al_{0.72}Sc_{0.28}N/TiN interface (B') was found to fit the experimental XRR pattern much better with a roughness of ~1 unit cell (I_1) and 3 unit cells, respectively (I_2) (R-squared values for models B and B' are 0.8753 and 0.8301, respectively). In other words, the interface roughness of TiN deposited on Al_{0.72}Sc_{0.28}N was found to exhibit three times more roughness than that of Al_{0.72}Sc_{0.28}N deposited on TiN layers. The experimental XRR pattern was found to fit best when interface roughness was included in both of the TiN/Al_{0.72}Sc_{0.28}N (I₃) and Al_{0.72}Sc_{0.28}N/ TiN (I_4) interfaces. Results show that the best fit was achieved with a roughness of ${\sim}2$ unit cells for the TiN/Al_{0.72}Sc_{0.28}N and ${\sim}3$ unit cells for Al_{0.72}Sc_{0.28}N/TiN interfaces, respectively (R-squared value 0.8928).

Such higher roughness of TiN growth on $Al_{0.72}Sc_{0.28}N$ layers can be explained by the surface energy mismatch of the constituent materials. Metallic TiN exhibits a surface energy of 63.2 mJ/m² for the (200) surfaces, which is smaller than that of most noble metal's surface energies of 1-3 J/m², such as Au and Ag.⁴²⁻⁴⁴ On the other hand, due to their saturated chemical bonds and semiconducting nature, $Al_{0.72}Sc_{0.28}N$ is expected to exhibit much smaller surface energies than TiN; though the exact value remains to be measured (surface energy of AlN^{45} is 38 mJ/m², while for ScN, it remains to be measured and/or calculated). Therefore, it would be comparatively difficult for TiN to wet on the $Al_{0.72}Sc_{0.28}N$ surface than the vice versa, leading to the observed higher TiN interface roughness on Al_{0.72}Sc_{0.28}N layers. It is important to note here that though previous²² laboratory source XRR measurements on similar superlattices deposited with different growth conditions had exhibited a smaller interface roughness of half a unit cell and one unit cell in TiN/Al_{0.72}Sc_{0.28}N and Al_{0.72}Sc_{0.28}N/TiN interfaces, respectively, it still showed higher TiN interface roughness on the Al_{0.72}Sc_{0.28}N layers than the vice versa. The higher interface roughness found here, therefore, could be due to changes in the growth environment or due to the fact that the present XRR analysis uses much intense synchrotron radiation compared to lab-source XRR, as well as differences in the scattering length contrast between the soft-XRR and laboratory source XRR. In addition to the surface energy mismatch, the higher roughness of TiN growth on Al_{0.72}Sc_{0.28}N layers could have been triggered due to a small atomic-scale asymmetric interdiffusion of atoms at the interfaces, though this suggested mechanism requires a detailed modeling and experimental analysis remains to be performed.

Nevertheless, the present XRR analysis reveal epitaxial TiN/ Al_{0.72}Sc_{0.28}N metal/semiconductor superlattices with very sharp interfaces that are comparable to the well-known oxide materials such as SrTiO₃/LaAlO₃ or GaAs/AlAs semiconductor superlattice interfaces.^{46,47} The smaller interface roughness in TiN/Al_{0.72}Sc_{0.28}N metal/ semiconductor superlattices is particularly interesting as metals and semiconductors exhibit inherent surface energy mismatches that though is much small in the present case, but could lead to large roughness in many other material systems. For example, in elemental noble metal and oxide insulator based metal/semiconductor multilayers^{48,49} such as Au/SiO₂, Ag/TiO₂, the interfaces were found to be much rough and with a significant extent of interdiffusions. For semiconductor superlattices with much smaller surface energies of the constituent semiconductors, it was expected to achieve relatively lower interface roughness, since semiconductors were expected to easily wet the surface of the grown films for another layer to form.

Having addressed the interface roughness and intermixing, SXAS is used to determine the electronic structure and the chemical bonding at the $TiN/Al_{0.72}Sc_{0.28}N$ superlattice interfaces. The XAS spectrum spanning an energy range from 390 eV to 420 eV represents [presented in Fig. 3(a)] unoccupied densities of NK edge and Sc L-edge states for TiN, ScN, Al_{0.72}Sc_{0.28}N component thin films and the 3 nm/3 nm as well as 10 nm/10 nm TiN/ Al_{0.72}Sc_{0.28}N metal/semiconductor superlattices, respectively. The absorption threshold, peak positions, and line shapes of ScN, Al_{0.72}Sc_{0.28}N and 10 nm/10 nm TiN/Al_{0.72}Sc_{0.28}N XAS spectra appear very similar with one other, albeit two additional pronounced peaks in the $Al_{0.72}Sc_{0.28}N$ film and $10\,nm/10\,nm$ TiN/ Al_{0.72}Sc_{0.28}N superlattices that are not clearly visible in the ScN film [see Fig. 3(a)]. All three of these materials exhibit four peaks located at 400.8 eV (I), 403.1 eV (II), 405.3 eV (III), and 407.6 eV (IV) with similar absorption thresholds [see Fig. 3(b)]. In addition to these four peaks, $Al_{0.72}Sc_{0.28}N$ and 10 nm/10 nm TiN/ Al_{0.72}Sc_{0.28}N superlattices exhibit two clear and distinct additional peaks located at 401.7 eV and 405.7 eV, respectively [see Fig. 3(a)]. Close inspection of the first derivative of the ScN XAS also revealed the existence of the peaks albeit with much diminished intensities. The similarity of the XAS spectrum of 10 nm/10 nm TiN/ Al_{0.72}Sc_{0.28}N superlattices with ScN and Al_{0.72}Sc_{0.28}N is not





FIG. 3. (a) Soft x-ray absorption spectra of Sc L-edge, N K-edge, and Ti L-edge in ScN, $AI_{0.72}Sc_{0.28}N$, TiN, and 3 nm/3 nm as well as 10 nm/10 nm TiN/ $AI_{0.72}Sc_{0.28}N$ metal/semiconductor superlattices are presented. The spectral position and absorption thresholds are very similar to one another in thin films and superlattices suggesting the absence of any other phase formed at the interfaces. (b) First derivative of SXAS data denotes the absorption edges.

surprising given that the top layer of the superlattice is 10 nm $Al_{0.72}Sc_{0.28}N$ and XAS in general probes about a few tens of nm of depth beneath the sample's surface. A small shouldering in the XAS spectrum of $Al_{0.72}Sc_{0.28}N$ and 10 nm/10 nm TiN/Al_{0.72}Sc_{0.28}N superlattice is also observed that resulted most likely from the defect induced smearing of the electronic bands. The similarities in their peak positions and line shapes signify their similar rocksalt crystal structure and bonding coordination.

A comparison of the observed SXAS spectra with literature reports⁵⁰ show that the spectral features observed in the 400–420 eV range arise from the Sc L-edge and N K-edge transitions. Because of spin–orbit coupling, Sc-L edge splits into L₃ and L₂ edges. Due to octahedral symmetry, the L₃ and L₂ peaks further split into t_{2g} and e_g suborbitals with the e_g states occupying higher energy as expected. As the peak positions of Sc L-edge and N K-edge

transitions overlap with one another, the full potential multiscattering (FMS) theory⁵¹ simulations of the experimental spectra are performed to decipher the origin of the peaks (see Fig. 4).

The peak positions at 400.8 eV (I) and 403.1 eV (II) were found to arise from the Sc- $2p_{3/2}$ orbitals to the unoccupied d-orbital transitions representing the L₃ edge, while the peaks corresponding to the 405.3 eV (III) and 407.6 eV (IV) exhibit the $Sc-2p_{1/2}$ orbitals to unoccupied *d*-orbital transitions representing the L₂ edge. It is important to note here that the extent of the spin-orbit splitting (ζ_{2p}) of the Sc-L edge, i.e., $(L_2(t_{2g}) - L_3(t_{2g}))$ was found to be very similar in ScN, Al_{0.72}Sc_{0.28}N and 10 nm/ 10 nm TiN/Al_{0.72}Sc_{0.28}N superlattices, respectively, with a value of 4.5 eV that is not only consistent with the previous reports⁴⁵ of ScN but also is in the same range as other 3d material systems.^{52,53} The extent of the spin-orbit splitting (ζ_{2p}) from the e_g states of L₂ and L_3 peaks also exhibit a very similar value of 4.5 eV. The crystal field splitting energy (10Dq) estimated from the energy differences from t_{2g} and e_g peaks in L₃ and L₂ edges in Fig. 3 exhibit a value of \sim 2.3 eV that is close to the FMS modeling result of 2.1 eV. While the four common peaks from these three films are explained well by the Sc L-edge transitions, the two additional peaks at 401.6 eV (V) and 405.7 eV (VI), respectively, can be attributed to the N-K edge transitions that are contributed by unoccupied N-2p-derived states and the states of neighboring cations, which have significant p-symmetry components projected onto N-sites and defect induced local changes in the electronic structure. It is important to note here that these N K-edge transitions are also present in TiN and 3 nm/3 nm TiN/Al_{0.72}Sc_{0.28}N superlattices as would be expected.

The SXAS spectrum of pure TiN film and the 3 nm/3 nm TiN/Al_{0.72}Sc_{0.28}N superlattice appears very similar to one another with the presence of two clear and distinct peaks at 398.2 eV and 401.1 eV (transition from N-2*p* orbital hybridized with Ti-3*d* states), respectively, that is not present in other films. The other two peaks at 405.3 and 409.5 eV arise due to the transition from N-2*p* hybridized with Ti-4*sp* orbitals.⁵⁴ Since the periodicity of the superlattice is 6 nm, the SXAS signal in-principle should arise from the TiN, Al_{0.72}Sc_{0.28}N layers and from the interfaces.

The SXAS of Ti L-edge spectra from TiN and both of the superlattices were also obtained which show four distinct peaks in



FIG. 4. Theoretical (dotted lines) and experimental (solid lines) XAS spectrum of (a) ScN, (b) $AI_{0.72}Sc_{0.28}N$, and (c) TiN. Theoretical data were obtained using the full potential multiscattering theory.



all three of the samples with similar absorption thresholds and spectral line shapes. The peak positions are very close to one another and located at 458.2 eV, 459.7 eV, 463.8 eV, and 465.1 eV. Similar to Sc, Ti L-edge also splits into L₃ and L₂ subshells due to the spin-orbit interactions. The L3 edge arises from the transitions from Ti- $2p_{3/2}$ to the unoccupied Ti-*d* orbitals, while the L₂ subshell results from the Ti- $2p_{1/2}$ to the unoccupied Ti-*d* orbital transitions. Due to the Ti-atom's octahedral bonding environment, both of the L_3 and L_2 states further splits into t_{2g} and e_g orbitals (shown in Fig. 5). Since the Ti L-edge spectrum does not exhibit any peak-overlap issues and are explained well with literature reports, FEFF simulations are not perfomed. Unchanged absorption threshold, peak-positions, and line-shapes between the component materials and the superlattice, therefore, clearly show that the oxidation states of each of the atoms remains unchanged in superlattices with respect to the individual layers. In addition, the absence of any additional peaks and the similarity of spectral line-shape verify absence of secondary phase formation or precitipation at the superlattice interfaces, as well as perturbation of crystal structure and atomic coordination at the superlattice interfaces.

A high-resolution TEM micrograph along with individual elemental maps and line-scans of the superlattice is presented in



FIG. 5. Soft x-ray absorption spectra of Ti L-edge in TiN as well as in the 3 nm/ 3 nm and 10 nm/10 nm TiN/Al_{0.72}Sc_{0.28}N superlattice are presented. The L-edge splits into L₃ and L₂ peaks due to spin–orbit coupling and each of these peaks further splits due to crystal field splitting. The crystal field splitting in 10 nm/ 10 nm superlattice is not that pronounced and the intensities are less, since 10 nm Al_{0.72}Sc_{0.28}N is the top layer of the superlattice that results in reduced TiN intensity.

Fig. 6. The high-resolution STEM micrograph and its inset FFT (Fast Fourier Transform) demonstrates high quality epitaxial crystal growth, with no sign of any misfit-dislocations at the interfaces. The individual cations (Ti, Al and Sc) show little diffusion into the adjacent layers. The EDS line-scans (integrated throughout the entire width of the image and quantified to atomic percent after absorption correction, using Cliff–Lorimer coefficients and Brown–Powell ionization cross-section models) show that the superlattice



FIG. 6. (a) HAADF-STEM micrograph of the TiN/Al_{0.72}Sc_{0.28}N metal/semiconductor superlattice interface and FFT (inset) demonstrates high-quality epitaxial crystal growth with substrate on top. (b) STEM-EDS line-scans across the superlattice interfaces (with interface line markers placed at the points from where the respective elemental signal starts decreasing and interfacial region marked by dashed lines) extracted from the EDS maps in (c)–(e) are presented. An interface roughness of 1.18 and 0.87 nm for the Al_{0.72}Sc_{0.28}N/TiN and TiN/Al_{0.72}Sc_{0.28}N interfaces, respectively was measured that is in agreement with the spatially averaged XRR measurements. Individual EDS maps of (c) Ti, (d) Al, (e) Sc, and (f) N atoms are shown.



layer are well separated and exhibit ~1 nm wide interface regions with little atomic intermixing (marked by dashed lines) due to diffusion. This is important, since previous studies in similar nitride superlattices have reported diffusion of metal atoms between the layer along various structural defects.^{27,56,57} Errors in quantification stem from the peak overlap between the N and Sc L lines, however, are below 2 atomic percent due to the high count rates. Nevertheless, from the imaging an interface roughness of 1.18 nm was measured for the $Al_{0.72}Sc_{0.28}N/TiN$ (I_4) interfaces, while for the TiN/Al_{0.72}Sc_{0.28}N (I_3) interface, the roughness was measured to be 0.87 nm, which are in excellent agreement with the XRR results.

IV. SUMMARY AND CONCLUSIONS

In conclusion, interface electronic structure and bond formation, as well as the interface roughness, of epitaxial lattice-matched TiN/Al_{0.72}Sc_{0.28}N metal/semiconductor superlattices are determined with soft x-ray scattering techniques and verified by transmission electron microscopy imaging analysis. The superlattices are found to exhibit sharp interfaces with asymmetric interface roughness of three and two unit cells for the Al_{0.72}Sc_{0.28}N/TiN and TiN/ Al_{0.72}Sc_{0.28}N, respectively. Such asymmetry in the interface roughness arises due to a surface energy difference between the TiN and Al_{0.72}Sc_{0.28}N layers. X-ray absorption studies showed that the electronic structure of the atoms remains unchanged from the individual layer to the superlattices and no changes in the oxidation state or the formation of secondary phase at the interfaces. These results are important for achieving TiN/Al_{0.72}Sc_{0.28}N metal/semiconductor superlattice-based energy conversion devices and for the use of such materials for fundamental heat, current, and light propagation studies.

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