# Rocksalt nitride metal/semiconductor superlattices: A new class of artificially structured materials

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### APPLIED PHYSICS REVIEWS—FOCUSED REVIEW

# Rocksalt nitride metal/semiconductor superlattices: A new class of artificially structured materials

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Artificially structured materials in the form of superlattice heterostructures enable the search for exotic new physics and novel device functionalities, and serve as tools to push the fundamentals of scientific and engineering knowledge. Semiconductor heterostructures are the most celebrated and widely studied artificially structured materials, having led to the development of quantum well lasers, quantum cascade lasers, measurements of the fractional quantum Hall effect, and numerous other scientific concepts and practical device technologies. However, combining metals with semiconductors at the atomic scale to develop metal/semiconductor superlattices and heterostructures has remained a profoundly difficult scientific and engineering challenge. Though the potential applications of metal/semiconductor heterostructures could range from energy conversion to photonic computing to high-temperature electronics, materials challenges primarily had severely limited progress in this pursuit until very recently. In this article, we detail the progress that has taken place over the last decade to overcome the materials engineering challenges to grow high quality epitaxial, nominally single crystalline metal/semiconductor superlattices based on transition metal nitrides (TMN). The epitaxial rocksalt TiN/(Al,Sc)N metamaterials are the first pseudomorphic metal/semiconductor superlattices to the best of our knowledge, and their physical properties promise a new era in superlattice physics and device engineering. Published by AIP Publishing. https://doi.org/10.1063/1.5011972

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#### I. INTRODUCTION

Ever since the theoretical proposal of Esaki and Tsu et al.<sup>1-5</sup> of bandstructure engineering of materials by employing superlattices, semiconductor-based superlattices and heterostructures have changed the world in many profound ways. Several novel scientific concepts (such as fractional quantum Hall effect,<sup>6,7</sup> electron and photon confinement,<sup>8,9</sup> and intersubband emission<sup>10,11</sup>) and technologically important devices (such as quantum well lasers,<sup>12,13</sup> quantum cascade lasers,<sup>14,15</sup> and high speed optoelectronic devices<sup>16,17</sup>) have emerged from semiconductor superlattices or the "man-made crystals" as Esaki called them over half a century ago. Lattice matched epitaxial semiconductor superlattices<sup>18–20</sup> (such as GaAs/AlAs) are not only the most celebrated semiconductor heterostructures ever developed but they have also captured the imaginations of generations of researchers working in materials science, physics, and device electronics. Yet, there is a widespread realization within the heterostructure community today that the current scientific and engineering challenges of our society such as renewable energy, secure information technology, imaging, and sensing require more advanced materials, new physics, and device designs that are currently difficult or impossible with present materials and technologies.

Metal/semiconductor superlattice heterostructures have the potential to overcome some of the limitations of semiconductor superlattice and heterostructures and could also offer novel solutions in many areas of modern science and technology.<sup>21–23</sup> In contrast to semiconductor superlattices, the development of metal/semiconductor superlattice heterostructures, however, had not progressed to an appreciable degree until very recently (see Fig. 1) due to materials compatibility limitations.<sup>21,24</sup> Metal/semiconductor superlattices should have several advantages over an all semiconductor superlattice and heterostructures and could lead to many scientific and technological breakthroughs in electronic, optoelectronic, plasmonic, and thermal transport research fields. For example, in terms of its electrical and optoelectronic properties, metal/semiconductor superlattice and heterostructures should have greater conductance of carriers in the active regions of an electronic device (reduced series resistance) and should also provide means to control electron potential locally. Such advantageous properties would have positive implications in thermionic energy conversion applications $^{25-27}$  and hot-electron based solar energy conversion devices.<sup>28</sup> Electron confinement<sup>29–31</sup> in the metallic layers and electron sub-bands inside the superlattices could also lead to high temperature intersubband absorption and emission devices suitable for terahertz applications that are currently not achievable with all-semiconductor heterostructures due to bipolar conduction at higher temperature. The ability to inject carriers at high current densities and extreme anisotropy in practically all-electronic properties are some of the numerous characteristics that could be explored.

Metal/semiconductor heterostructures and superlattices also offer an ideal testbed to verify various advanced hypotheses of thermal conduction mechanisms in nanostructured materials.<sup>32,33</sup> While thermal transport in semiconducting materials and heterostructures are primarily governed by lattice vibrations or phonons, electrons dominate heat-transport in metals. Metal/semiconductor superlattice and heterostructures, therefore, present an intriguing heat transport paradox, where thermal energy must be exchanged between electrons and phonons for efficient heat transport at the interfaces. While such phenomena could be and have been utilized to lower thermal conductivity for applications such as in thermoelectricity and thermionics,<sup>34,35</sup> the same materials should also serve as model systems where electron-phonon coupling methods<sup>36,37</sup> could be tested and verified. Broadly speaking, metal-based superlattice heterostructures furthers electron and thermal transport concepts and knowledge in heterostructure materials and are expected to offer new device functionalities.

Surface plasmons and surface plasmon-polaritons at the metal/semiconductor interfaces add to a whole new paradigm of exciting scientific concepts that remain relatively unexplored. While a highly doped semiconductor heterostructure such as InGasAs/InAlAs and others<sup>38,39</sup> will only offer plasmon resonance in the mid-to-long infrared spectral range, metal/semiconductor superlattices exhibit optical properties in the visible to near IR spectral ranges,<sup>39–41</sup> thus enabling novel energy conversion applications. Metal/semiconductor superlattices have already demonstrated hyperbolic metamaterials (HMM) properties,<sup>42,43</sup> enhancement of the densities of photonic states,<sup>43</sup> and promise for hyperthermal conductivity.<sup>44–46</sup>

Given such enormous promise and potential, it was indeed surprising that until as recently as 2005, examples of metal/semiconductor heteroepitaxy were only limited to a handful of material systems such as Si/CoSi<sub>2</sub>/Si,<sup>47,48</sup> AlAs/ NiAl/AlAs,<sup>49,50</sup> and GaAs/ErAs/GaAs.<sup>51,52</sup>

Over the last decade (2005–2016), however, this situation has changed considerably thanks to the vision and continued funding by Defense Advanced Research Projects Agency (DARPA), National Science Foundation (NSF), Department of Energy (DOE), and Air Force Office of



Journey of Metal/Semiconductor Heteroepitaxy and Superlattices

FIG. 1. Historic timeline of the metal/semiconductor heteroepitaxy and superlattice development. Three different phases of heterostructure development are shown in the image. During the period from 1965 to 1976, Jaklevic and Lambe *et al.*<sup>78,80</sup> performed seminal tunneling experiments on polycrystalline-metal/amorphous-semiconductor/polycrystalline-metal heterojunctions at Ford Motor Company. Several other theoretical and experimental researches were also performed in Bell Communications Laboratory (Sze *et al.*<sup>235</sup>) and in California Institute of Technology (Mead *et al.*<sup>207</sup>). From 1983–1993, Palmstrom and Sands *et al.*<sup>21,49–52,83–85</sup> developed crystalline semiconductor/metal/semiconductor heterojunctions based on III-V semiconductors and Si in Bellcore, Inc. Defect free epitaxial single crystalline metal/semiconductor superlattices and heterostructures were developed based on rocksalt transition metal nitrides<sup>42,43,53–56</sup> (TMN) in Purdue University (2005–2017).

Scientific Research (AFOSR). With an initial motivation to develop high-temperature thermionic materials to convert waste heat energy directly into electrical power, Saha *et al.*<sup>42,43,53–56</sup> have developed the epitaxial, metal/semiconductor superlattice, and heterostructure systems based on TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N. This research demonstrated that transition metal nitrides (TMN) offer an opportunity to develop interesting metals, semiconductors, and epitaxial metal/semiconductor superlattice heterostructures that could be useful for a range of energy conversion applications both for ambient and harsh environmental conditions. The thin film and superlattice heterostructures developed with TMNs are mechanically hard,<sup>55</sup> corrosion resistant, and are stable at high operating temperatures<sup>57,58</sup> in excess of about 900 °C. The superlattices are also amenable to doping, alloying, and quantum size effects, which could be engineered into the next generations of optoelectronic and quantum electronic applications.

While significant challenges related to device fabrication, characterization, and high temperature measurements remain to be addressed in greater details, the demonstration of epitaxial, nominally single crystalline metal/semiconductor superlattices has opened up a myriad of new research directions. In this article, we attempt to describe various aspects of the development of metal/semiconductor superlattice heterostructures, highlighting the choice of materials, state of the art in this research field, growth, structural characterization, and measurement of physical properties. We also highlight several future research directions that will further the metal/semiconductor superlattice heterostructure research.

#### **II. WHY IS IT DIFFICULT TO GROW SUPERLATTICES?**

Growth of epitaxial, single crystalline, lattice matched metal/semiconductor superlattice or for that matter, any epitaxial superlattice, is extremely challenging. The superlattice growth process (see Fig. 2) has to satisfy several criteria,<sup>59,60</sup> such as

- Metals and semiconductors have to be from the same family of materials (such as oxides, nitrides, or arsenides). Growth of superlattices based on materials from different materials families may be possible, but this approach offers significant practical challenges due to extreme mismatches in bonding and materials properties across interfaces.
- 2. The crystal structures of the metal and semiconductor must be the same. Moreover, the crystal structure of the



FIG. 2. Schematic diagram of thin film and superlattice growth modes in coordinates of interfacial lattice constant misfit (x-axis) and surface-energy difference (y-axis) between two materials A and B. The dashed curve separates the Stranski-Krastanov and the Weber-Volmer growth modes. Superlattices can be grown when the interfacial misfit and surface energy differences are very small (within the circled regions as shown). Reprinted with permission from K. N. Tu, IBM J. Res. Dev. **34**, 868 (1990). Copyright 2018 IEEE.

substrate should also be identical. Failure to match the crystal structure would result in space-group symmetry mismatch and the nucleation of defects that propagate with the growth interface, thereby disrupting epitaxial growth.

- 3. The lattice constants of the metal and the semiconductor also have to be very similar with each other and with that of the substrate. Lattice mismatch of more than a few percentage is enough to nucleate misfit dislocations at the interface.
- 4. Excess surface energies of the metal and semiconductor have to be very small and similar for proper wetting of the materials on one another. Excess interface energies also have to be very small for maintaining lattice coherency.
- 5. The metal and semiconductor crystal phases must have compatible growth conditions, morphological stability, and coefficient of thermal expansion.

Given such stringent requirements, it is not surprising that the growth of epitaxial, lattice matched metal/semiconductor superlattices has been extremely difficult.

#### III. MATERIALS CHALLENGES OF METAL/ SEMICONDUCTOR SUPERLATTICE GROWTH

Metals and semiconductors are different not only in electronic conduction but also in almost every basic scientific and material property.<sup>61</sup> To name a few, while metals have high surface energies due to their unsaturated dangling bonds, semiconductors usually possess strong covalent character, and saturated surface states that results in much lower surface energies. The strong metallic bonds (arising due to the interactions of the conduction electrons) ensure that metals usually crystalize in simple closed packed structures such as FCC, BCC, or HCP. On the other hand, covalent bonds allow semiconductors to crystallize in relatively complex structures such as zincblende, wurtzite, and others with mostly tetrahedral coordination. Such fundamental differences in the basic chemical bonding and atomic coordination numbers gives rise to fundamentally different electronic, optical, thermal, and mechanical properties in metals and semiconductors, which cause their atomic scale arrangements to be extremely challenging.<sup>21</sup>

Elemental metals (such as Al, Au, Ag, Cu, and others) usually crystallize in cubic lattice-structures, while elemental semiconductors, such as Si and Ge on the other hand, have diamond crystal structure.<sup>61,62</sup> Moreover, most elemental metals do not wet most substrates properly because of their extremely high surface energies (in several J/m<sup>2</sup>), resulting in polycrystalline thin film growth with high surface roughness. There have been some recent reports on the growth of polycrystalline<sup>40,63</sup> Au/SiO<sub>2</sub>, Ag/TiO<sub>2</sub> multilayers, but such structures are usually accompanied with rough and atomically diffused interfaces.

Compound semiconductors such as III-arsenides or IIIphosphides crystallize in the zincblende structure;<sup>61,62</sup> however, the arsenide or phosphide families do not have any metallic counterpart that share the common zincblende crystal structure to be explored for the development of metal/ semiconductor superlattices. In late 1980s, Palmstrom *et al.*<sup>21,50–52</sup> developed semi-metallic rare-earth ErAs. But ErAs exhibits the rocksalt crystal structure, which though allows for the development of bilayers with semiconducting GaAs, albeit with defects, it does not allow for superlattice growth. Like ErAs, several<sup>64,65</sup> rare-earth arsenides (like TbAs) can be grown epitaxially on GaAs, but fundamental mismatch in crystal structure and lattice constants forbids the development of superlattices.

In case of nitrides,<sup>61,62</sup> the most celebrated and technologically important semiconductors such as III-V GaN, AlN, and InN all have the wurtzite crystal structure, but similar to the arsenide family, the nitride family does not include any wurtzite metals that can be integrated with nitride semiconductors to grow superlattices. Similarly, some Pb based chalcogenide semiconductors adopt the rocksalt crystal structure<sup>66,67</sup> (such as PbTe), but there are no rocksalt metals. It is indeed surprising that among the hundreds of thousands of naturally occurring or artificial inorganic materials, compatible metals and semiconductors that share structural commonality for growing superlattices are so difficult to find.

A window of opportunity, however, exists within the TMN family (see Table I, for a survey of material properties) where commensurate crystal structure, highly conductive metals, and semiconductors can be found.<sup>68–73</sup> Most TMNs crystallize in the rocksalt structure with octahedral coordination having high degrees of ionicity in their chemical bonds. For example, TiN, ZrN, HfN, VN, and others are good metals with high electrical conductivities, and their physical properties have been studied for decades for corrosion resistant hard coating applications. In comparison to the TMN metals, not much attention has been devoted historically to search for semiconductors within the TMN family. However, TMNs such as III(B)-nitrides ScN, YN, and LaN have

TABLE I. Lattice constant ( $a_0$ ), bulk modulus (B), heat of formation ( $\Delta H_f^0$ ), melting temperature ( $T_M$ ), mechanical hardness (H), electrical conductivity at room temperature ( $\sigma_{300K}$ ), and thermal conductivity at room temperature ( $\kappa_{300K}$ ) of rocksalt TMNs are presented. First-principles modeling results are presented (Refs. 68–70, 74, and 75) with superscript "t," where experimental values are not known.

	$\overset{a_0}{(\text{\AA})}$	B (GPa)	$\Delta H_f^0$ (eV)	$T_M$ (°C)	H (GPa)	σ <sub>300K</sub> (S/m)	$\frac{\kappa_{300K}}{\left(\frac{W}{mK}\right)}$
Metals							
TiN	4.24	301	4.36 <sup>t</sup>	2930	23	$1.5 \times 10^7$	63
ZrN	4.61	289 <sup>t</sup>	4.48 <sup>t</sup>	2980	30	$3.7 \times 10^{6}$	47
HfN	4.52	294 <sup>t</sup>	4.13 <sup>t</sup>	3305	35	$3.1 \times 10^{6}$	37
VN	4.14	233	2.78 <sup>t</sup>	2050	30	$1.6 \times 10^{6}$	
NbN	4.39	317 <sup>t</sup>	2.65 <sup>t</sup>	2573	26	$1.8 \times 10^{6}$	4.2
TaN	4.38	338 <sup>t</sup>	2.48 <sup>t</sup>	3090	23	$5.5 \times 10^5$	5.5
CrN	4.08	361 <sup>t</sup>			24	$1.5 \times 10^5$	
MoN	4.21	354 <sup>t</sup>			23		
WN	4.31	394 <sup>t</sup>					
Semico	nductors						
ScN	4.52	365	4.80 <sup>t</sup>	2600	28	$1.3 \times 10^5$	10.6
YN	4.87	204 <sup>t</sup>	4.33 <sup>t</sup>				
LaN	5.29	148 <sup>t</sup>	3.20 <sup>t</sup>				

semiconducting properties with indirect bandgaps.<sup>68,74–76</sup> Unfortunately, YN and LaN are not stable in ambient conditions and readily oxidize which limits their suitability for practical applications. Apart from the commonality in crystal structure and diverse electrical properties, TMNs are also known to be mechanically hard, corrosion resistant, and possess extremely high melting temperatures ( $\sim$ 3000 °C) that should help design devices for harsh environmental conditions. Therefore, ScN as the semiconducting component material, and TMNs such as TiN, ZrN, HfN, and others as metals, remain the only possible and potential material options that can be explored for the development of metal/ semiconductor superlattices.

#### IV. A BRIEF HISTORY OF METAL/SEMICONDUCTOR HETEROEPITAXY

The history of metal/semiconductor heteroepitaxy research dates back to mid-1960 during the time semiconductor heterostructures also saw rapid development. Jaklevic and Lambe et al.77-80 at Ford Motor Company had performed seminal tunneling experiments on polycrystalline metal (e.g., Pb, Al)/amorphous semiconductor (e.g., Al<sub>2</sub>O<sub>3</sub>, MgO) tunnel junctions (e.g., Pb/Al<sub>2</sub>O<sub>3</sub>/Al). Their work demonstrated electron quantization in metallic films and tunneling across the commensurate states in metals, which were significant milestones in early metal/semiconductor research. Their subsequent research on the spectroscopy of trapped molecules at a metal/metal-oxide interface led to the development of inelastic molecular vibrational spectroscopy,<sup>78</sup> which is used widely today to study the vibration of molecular adsorbates on hetero-interfaces. However, materials challenges in those early years were extremely difficult to overcome, and as a result, though the semiconductor heterostructure research field made unprecedented progress, metal/ semiconductor heterostructures remained in obscurity for several decades.

The second generations of the metal/semiconductor heteroepitaxy research were performed in the mid-to-late 1980s.<sup>21</sup> As the silicon transistor technology was on the ascent, the motivation was to develop metal-base or permeable-base transistors that could operate with high onstate current. Several researchers in the early 1980s in Japan and US had also developed silicide<sup>47,48,81,82</sup> based Si/CoSi<sub>2</sub>/ Si and Si/NiSi<sub>2</sub>/Si semiconductor/metal/semiconductor (S/ M/S) heterostructures (see Fig. 3). Independent research works by Sands et al. and Palmstrom et al. led to the development of crystalline<sup>21,49–52,83–85</sup> AlAs/NiAl/AlAs and GaAs/ErAs/GaAs S/M/S heterostructures, respectively (see Fig. 3). In all of the three material systems, researchers were able to demonstrate resonant electron tunneling and associated negative differential resistance (NDR). However, none of the three heterostructures satisfies the growth criteria of a superlattice highlighted in Sec. II. Fundamentally, the crystal structures of the metals (NiAl, CoSi2, and semimetallic ErAs) were different from the zincblende arsenide semiconductors (GaAs and AlAs) and from that of the diamond crystal structured Si. As an example, in the case of the AlAs/ NaAl/AlAs system, NiAl has a cubic (CsCl) crystal structure, while AlAs have zincblende crystal structure. Because of this crystal structure mismatch, though the initial NiAl layer grows on AlAs surface without significant defects; the growth of AlAs on NiAl was usually accompanied by severe defect nucleation, and further epitaxial defect free growth of the metal (NiAl) on AlAs became impossible [see Fig. 3(a)]. In the case of GaAs/ErAs/GaAs, apart from the crystal structure and lattice constant mismatch issues, it was also found that the ErAs does not wet the GaAs, which leads to island growth of the semiconductor over layers [see Fig. 3(b)]. Therefore, even with the initial excitements and continued effort for over next several years, epitaxial, metal/semiconductor superlattice growth remained a challenge.

#### V. SILICIDE/SILICON AND RARE-EARTH ARSENIDE/III-ARSENIDE HETEROSTRUCTURES

While the development of epitaxial metal/semiconductor superlattice heterostructures remained a difficult challenge for



FIG. 3. High-resolution transmission electron microscopy (HRTEM) images of (a) AlAs/NiAl/AlAs, (b) GaAs/ErAs/GaAs, and (c) Si/CoSi<sub>2</sub>/Si semiconductor/ metal/semiconductor heterojunctions. The metal layers grow epitaxially with minimal defects on the bottom semiconductor layers. However, the top semiconductor overlayers were usually defective because of lattice constant, space group symmetry and surface energy mismatches. Further growths of defect-free metal layers on top of the semiconductor overlayer were not possible. Reproduced with permission from Sands *et al.*, Mater. Sci. Rep. **5**, 99–170 (1990), Copyright 1990 Elsevier B.V. and reproduced with permission from Tsuji *et al.*, Thin Solid Films **516**, 3989–3995 (2008). Copyright 2008 Elsevier B.V.

several decades, the requirement of efficient metallic contacts with semiconductors continues to be an integral performance determinant in microelectronics. The possibility of using metallic silicides as conductors (i.e., as Schottky barriers and contacts as well as gate-metals and interconnects) in silicon Integrated Circuits (ICs) has motivated research<sup>86-88</sup> on epitaxial silicide/silicon heterostructures since 1970s. Silicides exhibit<sup>89</sup> low resistivity, relative ease in patterning and fabrication for nanofabrication, stability in oxidizing environment, smooth surface, mechanical integrity and good adhesion, efficient device characteristics, and lifetime necessary for applications in modern ICs. Moreover, epitaxial silicides (such as NiSi<sub>2</sub>, CoSi<sub>2</sub>, and others) offer several advantageous characteristics in comparison to their polycrystalline counterparts, including greater stability, lower stress at the interfaces, alleviation of grain boundary effects, as well as conductivity improvements.

More than half of the elements in the periodic table react with silicon to form one or more silicides, and many of the silicides exhibit metallic characteristics. Traditionally, two techniques are used for the development of silicides on Si, (a) by reaction of the metallic film with Si substrate, and subsequent thermal annealing, and (b) by co-deposition of silicide films using evaporation, sputtering, chemical vapor deposition (CVD), and molecular beam epitaxy (MBE) methods. Commonly known silicides,<sup>90</sup> such as PtSi and Pd<sub>2</sub>Si, were used extensively in early years to lower contact resistance of Al alloys, as well as to serve as a diffusion barrier layer between aluminum alloy films and Si. And for last 20 years or so, various IC manufacturers have also used TiSi<sub>2</sub>, WSi<sub>2</sub>, and TaSi<sub>2</sub>.

Like the silicides, several rare-earth semi-metallic arsenides have been grown inside and/or on semiconducting IIIarsenides such as GaAs, InGaAs, and others.<sup>21,49–52,83–85</sup> Thermoelectric and optoelectronic nano-composite devices fabricated with such arsenides have demonstrated superior device performance. For example, ErAs nano-precipitate inside InGaAs matrix has been utilized to demonstrate high thermoelectric *figure-of-merits (ZT)* at higher operating temperatures.<sup>91–93</sup> ErAs nano-particle inclusion inside the InGaAs matrix was shown to reduce the thermal conductiviey<sup>93</sup> of the matrix by a significant amount, thus realization of higher *ZT*. ErAs nano-islands inside GaAs matrix were also shown to exhibit photo-conductive antennas for terahertz wave detection and emission.<sup>94–97</sup> The nano-composite devices demonstrated superior performance with respect to low temperature GaAs, and radiation damaged Si on sapphire samples, which is traditionally used for terahertz detectors. The ErAs/InAlGaAs nanocomposites have also exhibited millimeter wave detection<sup>97</sup> properties with excellent efficiencies.

# VI. PROMISE FOR THERMOELECTRICITY AND PLASMONICS

The resurgence of metal/semiconductor superlattice heterostructures came about in the beginning of the current century when Mahan, Bowers, and Shakouri et al.25,26,98-102 theoretically proposed that metal-based superlattices could drastically improve the efficiency of thermoelectric devices through thermionic emission principles, whereby hotelectrons are selectively emitted over the Schottky barriers in a metal/semiconductor superlattice (see Fig. 4). Theoretical models showed that degenerate semiconductor or metal based superlattices with optimized barrier heights could result in thermoelectric figure-of-merits (ZT) of 3-4 at hightemperatures ( $\sim$ 800 K). Since environmentally friendly renewable source of energy is an urgent societal requirement, the promise for the highly efficient thermoelectric and thermionic devices through metal/semiconductor superlattice heterostructures immediately attracted attention and catalyzed research efforts.



FIG. 4. (a) Schematic description (left panel) of a thermoelectric device for refrigeration applications. Under the influence of an externally applied potential bias, electrons in the metal absorb heat from the lattice at cold side of the thermoelectric device and release the heat at the hot side, which results refrigeration. A Schottky barrier exists at the metal/semiconductor interface, which controls the flow of electrons by selectively allowing the high-energy hot electrons to pass through, while blocking the low energy cold electrons. This selective emission of electrons over the Schottky barrier height is known as energy filtering, which is expected to increase the efficiency of the thermoelectric device. (b) Nanoscale metal/semiconductor superlattice leads to hyperbolic photonic dispersion of the iso-frequency surfaces.

During the same time period, researchers in plasmonics and nano-photonics research community<sup>23,103,104</sup> were also actively looking for metal/dielectric heterostructures and superlattices, where exotic optical phenomena such as hyperbolic dispersion of photons, negative refraction, hyperlens, and enhancement of photonic densities of states could be demonstrated (see Fig. 4). Initial demonstrations of such interesting optical properties were realized in Au/SiO<sub>2</sub>, Ag/ TiO<sub>2</sub>, and similar polycrystalline noble-metal/dielectric multilayers.<sup>40,41</sup> But the poor material quality, diffused and intermixed interfaces made unambiguous demonstration of the optical properties extremely difficult. It was realized that lattice matched defect free superlattices are essential, which polycrystalline noble metals could not provide. Therefore, the two research fields, thermoelectricity and plasmonics, catalyzed by two totally different physics based device principles, motivated research on metal/semiconductor superlattice and heteroepitaxy.

#### **VII. DEVELOPMENT OF SEMICONDUCTORS**

Unlike the traditional III(A)-V wurtzite nitride semiconductors such as AlN, GaN, or InN, ScN had not attracted significant attention until very recently. Therefore, before discussing ScN based metal/semiconductor superlattices, in this section, the physical properties of ScN and subsequently developed rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N semiconducting alloys are addressed.

### A. Scandium nitride (ScN): The case for a rocksalt semiconductor

Scandium nitride (ScN) is a group III-B TMN that crystalizes in the rocksalt structure with octahedral coordination and a lattice constant<sup>74</sup> of 4.50 Å. Like most other TMNs, ScN is mechanically hard (23 GPa), corrosion resistant, stable in ambient conditions, and has an extremely high melting temperature of  $2600 \,^{\circ}C^{69,70,74}$  In early years, researchers were actively pursuing ScN as a hard coating materials for tribology applications,<sup>105</sup> however, more recently, ScN has attracted significant interests for its potential thermoelectric applications<sup>106–111</sup> and as a substrate material for the growth of high quality GaN thin films.<sup>112–114</sup>

Molecular Beam Epitaxy<sup>115–118</sup> (MBE), dc-magnetron sputtering,<sup>106,119,120</sup> and hybrid vapor phase epitaxy<sup>121-123</sup> (HVPE) methods have been employed over the years to deposit epitaxial ScN thin films on MgO and Al<sub>2</sub>O<sub>3</sub> (sapphire) substrates. In an early report of ScN growth in 1972, Dismukes *et al.*<sup>121,122</sup> used HVPE to grow epitaxial ScN films in the 850 °C-930 °C temperature range on Al<sub>2</sub>O<sub>3</sub> (sapphire) substrates. Any deviations in the growth temperature were found to result in polycrystalline film growth. This early investigation of ScN was also important, given that the authors also studied the electrical properties and reported that the HVPE-deposited epitaxial ScN exhibited high *n*-type carrier concentrations of 10<sup>20</sup>-10<sup>21</sup> cm<sup>-3</sup>. Doping of ScN with C and Si neither did result in p-type ScN nor did postgrowth annealing in Mg or Zn vapor. More recently, Oshima et al.<sup>123</sup> used a similar HVPE method for the growth of ScN and reported high mobility of  $284 \text{ cm}^2/\text{V}$  s at  $3.7 \times 10^{18} \text{ cm}^{-3}$ 

*n*-type carrier density. They speculated that high growth rates in HVPE in orders of 100s of nm/min were perhaps the reason for such low carrier concentration and high mobilities in ScN. In terms of MBE growth, Smith et al. 115,116 demonstrated that ScN grows with [001] orientation with very small surface roughness on [001] MgO substrates. Several studies<sup>115,116,124</sup> have also shown that ScN grow with (111) orientation on [0001] sapphire. Sputter-deposited ScN has a room temperature resistivity of 0.22 m $\Omega$  cm, and a moderate electron mobility of 106 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. High-resolution transmission electron microscopy (HRTEM) imaging by Burmistrova et al.<sup>106,107</sup> on ScN deposited on [001] MgO substrates by magnetron sputtering showed that the films are highly textured with a cube-on-cube epitaxial relationship of ScN(001)[001] MgO(001)[001] and very low densities of misfit dislocations [see Fig. 5(b)]. The dislocation density analysis, however, remains to be addressed.

In terms of the electronic structure of ScN, researchers contradicted each other for several decades. Early research reports in 1980s and 1990s (both experimental and well as first-principles based modeling analysis) have claimed that ScN is a semimetal.<sup>124,125</sup> However, subsequent improvements in density functional theory (DFT) have led to the prediction that ScN is an indirect bandgap semiconductor. 68,74,126,127 Experimentally, the controversy about the origin of the exact nature of ScN's electronic structure lies in the thin film growth process, where large background carrier concentrations in magnetron sputtering usually dope the material unintentionally *n*-type with a large carrier concentrations of (1-6)  $\times 10^{20}$  cm<sup>-3</sup>. Burmistrova *et al.*<sup>106</sup> used Nuclear Reaction Analysis (NRA) along with Rutherford Back Scattering Spectrometry (RBS) to show that the sputter deposited ScN thin films possess  $1.6 \pm 1$  atomic percentage of oxygen as impurity, which is one of the main reasons of such high carrier concentrations. Several other researchers<sup>128</sup> have also suggested the presence of fluorine (F) and hydrogen (H) atoms inside the ScN during HVPE and sputtering growth that would also dope the material heavily *n*-type. Though nitrogen vacancies could also be a source of *n*-type carriers, Dismukes et al.<sup>121,122</sup> concluded that the concentrations of nitrogen vacancies in HVPE-deposited ScN should be quite small.

The controversies of ScN's electronic properties were resolved by careful DFT based modeling,<sup>68,126</sup> subsequent optical absorption, and emission-based spectroscopic analysis,<sup>74,119</sup> and by the development of p-type Sc<sub>x</sub>Mg<sub>1-x</sub>N and  $Sc_xMn_{1-x}N$  thin film alloys. <sup>110,111,119</sup> The electronic structure of ScN [presented in Fig. 5(a)] demonstrated that ScN is an indirect bandgap semiconductor with an indirect  $\Gamma$ -X bandgap of 0.9 eV and a direct Γ-Γ gap of 2.2 eV. DFT based modeling analysis<sup>106</sup> also showed that the presence of oxygen impurities shifts the Fermi energy from inside bandgap to the conduction band. Landauer theory and Boltzmann transport equation based analysis of the electrical conductivity and Seebeck coefficient measurements have suggested that the Fermi level of sputter deposited ScN resides approximately 0.06-0.09 eV above the conduction band-edge at room temperature.<sup>106,111</sup> Theoretical modeling analysis of the position of the Fermi energy as a function of the carrier concentration<sup>111</sup> clearly showed that in as-deposited films



FIG. 5. (a) Electronic structure of ScN calculated with density functional theory (DFT) with a Hubbard U-parameter along with generalized gradient approximation of the exchange correlation functional. ScN is an indirect bandgap semiconductor with an indirect gap of 0.9 eV and direct gap of 2.9 eV (in the DFT calculations). (b) HRTEM microscopy image of ScN/MgO interface shows coherent, epitaxial crystal growth, with cube-on-cube epitaxy. (c) Electrical resistivity and Seebeck coefficient of ScN presented as a function of temperature showed the resistivity increases with temperature, which suggest its degenerate nature. Seebeck coefficient increased from ~60  $\mu$ V/K at room temperature to ~160  $\mu$ V/K at 850 K, which resulted ScN to achieve large thermoelectric powerfactor. (d) Incorporation of Mg<sub>x</sub>N<sub>y</sub> (which acts as a hole-dopant) inside ScN matrix, increased resistivity and decreased n-type carrier concentrations, eventually turning ScN into a p-type semiconductor. Reproduced with permission from J. Appl. Phys. **107**, 033715 (2010), copyright 2010 AIP Publishing LLC and reproduced with permission from Appl. Phys. Lett. **110**, 252104 (2017). Copyright 2017 AIP Publishing LLC.

having *n*-type carriers greater than  $1.0 \times 10^{19} \text{ cm}^{-3}$ , the Fermi energy would be inside the conduction band, which would make the material a highly degenerate semiconductor or even a semi-metal in terms of its electrical properties.

Thermoelectric properties of ScN have been investigated independently by Burmistrova et al.106,107 and Kerdsongpanya *et al.*<sup>108</sup> with both studies exhibiting that unintentional doping helps ScN to achieve a suitable carrier concentration of  $\sim (1-5) \times 10^{20} \text{ cm}^{-3}$  for high thermoelectric power factor. Burmistova et al.<sup>106</sup> measured [presented in Fig. 5(c)] the Seebeck coefficient of ScN to be  $-70 \,\mu\text{V/K}$  at room temperature, which increases to  $-156 \,\mu\text{V/K}$  at 840 K. Along with the electrical conductivity measurements, they have demonstrated that ScN has thermoelectric power factor of  $3.5 \times 10^{-3}$  W/m K<sup>2</sup> at 600 K, which is higher than that of the best known thermoelectric materials<sup>129</sup> Bi<sub>2</sub>Te<sub>3</sub> at 400 °C, as well as a well-known high-temperature thermoelectric materials like  $La_3Te_4^{130}$  at 600 K. However, the value of power factor is comparable to undoped crystalline SiGe<sup>131</sup> in the same temperature ranges. The thermal conductivity of ScN films measured with a time-domain thermoreflectance (TDTR) technique<sup>111</sup> showed a value of 14 W/m K at 300 K, which is factor of  $\sim 10 \times$  higher than that of Bi<sub>2</sub>Te<sub>3</sub>, at room temperature. Because of such high thermal conductivity, ScN demonstrates a moderate ZT of 0.3 at high temperatures  $(\sim 800 \,\mathrm{K})$ . Nano-particle inclusion, phase separation, and others effective strategies will have to be developed for reducing the thermal conductivity of ScN without changing its electrical properties for high thermoelectric *figure-of-merit* (ZT).

Photoluminescence (PL) from ScN films grown on [001] MgO substrates at 2.2 eV originating from the direct bandto-band transitions was demonstarted.<sup>119</sup> Though the exact mechanism of the observed PL remains to be explained, the authors showed that the intensity of the luminescence was proportional to the laser input-power, suggesting faster electron-hole recombination rates with respect to thermalization time of the electrons to the indirect X valley. Since the green-gap in photovoltaics (PV) and light emitting diode (LED) technologies is still an active research direction,<sup>132</sup> ScN could potentially offer a solution, though further analysis on its luminescence efficiency will be required.

Large *n*-type carrier concentration in as-deposited ScN, though, is good for thermoelectricity; it is significantly detrimental for ScN's potential usefulness in metal/semiconductor superlattice heterostructures, as the depletion width at the metal/semiconductor interface is expected to be very small with high carrier densities. Moreover, practically any ScN based electronic and optoelectronic devices would also require control of its carrier concentrations with dopants and also a *p*-type ScN thin film. Saha *et al.*<sup>110</sup> have recently demonstrated that by alloying ScN with Mg<sub>x</sub>N<sub>y</sub> or with Mn<sub>x</sub>N<sub>y</sub> (both of which act as hole dopants), the carrier concentrations can be reduced, eventually turning ScN into a *p*-type semiconductor [presented in Fig. 5(d)]. A minimum *n*-type carrier concentration of  $2 \times 10^{18}$  cm<sup>-3</sup> has been achieved with Mg<sub>x</sub>N<sub>y</sub> doping inside the ScN matrix, before the film turns into a *p*-type semiconductor. The *p*-type ScN exhibits a maximum room temperature mobility of  $\sim 23 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , hole concentrations as high as  $(1-3) \times 10^{20} \text{ cm}^{-3}$ , and also high thermoelectric power factor<sup>111</sup>  $0.8 \times 10^{-3} \text{ W/m K}^2$  at 800 K. The mobility and thermoelectric power-factors can be improved by altering the deposition technique (such as HVPE method) and growth conditions of the *p*-type films.

# B. Development of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N: A novel nitride semiconductor

While ScN is an attractive semiconducting mono-nitride material for the development of single crystalline epitaxial metal/semiconductor superlattices with metallic rocksalt TMN, a lattice mismatch of 6.6% between ScN and MgO (substrate) severely affects the crystal quality of ScN/metal (ZrN or HfN)-based multilayers grown on MgO substrates (as will be discussed in Sec. VIII). The lattice mismatch between the film and the substrate gives rise to misfit dislocations, which thread through the film and render defect-free growth of superlattices extremely challenging. Motivated by the necessity of reducing the lattice mismatch between the semiconducting nitride films with that of the MgO substrate, rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N solid-solution alloys have been developed<sup>54</sup> on [001] MgO substrates, and their structural, electronic, and optical properties were studied.

Pure AlN thin films are known to exhibit the wurtzite crystal structure under ambient conditions; however, pure-AlN also adopts a high-pressure rocksalt crystal structure<sup>133–136</sup> with a lattice constant of 4.08 Å. Madan et al.<sup>137</sup> have demonstrated previously that AlN can be stabilized in the rocksalt phase inside a TiN/AlN multilayer with a critical thickness of about 2 nm, beyond which, it undergoes a metastable rocksalt to stable wurtzite structural phase transition. Since such a small a critical thickness of rocksalt-AlN was not suitable for most practical device applications, AlN was alloyed with ScN, and the rocksalt phase of Al<sub>x</sub>Sc<sub>1-x</sub>N thin films was stabilized. When Al<sub>x</sub>Sc<sub>1-x</sub>N thin films were deposited directly on [001] MgO substrates, the rocksalt phase could be stabilized with a maximum AlN mole fraction of  $\sim$ 52%, beyond which the films undergo the rocksalt-to-wurtzite structural phase transition.<sup>54</sup> Such observations agreed well with previous reports.<sup>138,139</sup> However, exact lattice matching of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N with the MgO substrate is possible only when the lattice constant of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N is reduced to  $\sim$ 4.21 Å, which would require further increases in the AlN mole fractions in the Al<sub>x</sub>Sc<sub>1-x</sub>N matrix. The maximum AlN mole fraction was increased to 82% for the stability of its rocksalt phase with  $\sim$ 120 nm critical thickness by using an epitaxial stabilization technique. TiN seed layers of 20 nm in thickness were deposited on MgO substrate before the Al<sub>x</sub>Sc<sub>1-x</sub>N film growth during the sputtering process, which reduced the lattice mismatch between the film/substrate interfaces and overcame the bond-polarity mismatch. For a rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N film with 72% mole fraction of AlN, the critical thickness for stabilizing the rocksalt phase was found<sup>54</sup> to exceed  $\sim 120 \text{ nm}$ . HRTEM analyses clearly showed sharp and abrupt TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N interfaces with the cube-on-cube epitaxial relationship. No clear signatures of any misfit dislocations were observed in the microscopy images, which guaranteed lattice matching and pseudomorphic crystal growth.

Structural characterization revealed<sup>54</sup> that the lattice constant of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N decreased monotonically from 4.50 Å to 4.15 Å with the increase in AlN mole-fractions. The tunability of the lattice constant of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N with respect to AlN mole fractions results in its lattice matching with almost the entire spectrum of TMN metals as shown in Fig. 6.

Optical and electrical properties of the rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N alloys were evaluated in detail<sup>54</sup> as a function of AlN mole fraction. The optical direct bandgap of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N alloy showed bandgap bowing, with a bowing parameter of 1.4 eV<sup>2</sup>. The direct bandgap of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N alloy films varied from 2.2 eV to about 4.3 eV, before the Al<sub>x</sub>Sc<sub>1-x</sub>N transitions into wurtzite crystal phase. The bandgap analysis also demonstrates that cubic-AlN should have a bandgap of 4.7 eV, smaller than stable wurtzite-AlN<sup>140</sup> which has a direct bandgap of 6.2 eV. Room temperature electrical properties (measured by the Hall Effect system) showed that incorporation of AIN inside ScN increased the resistivity by a factor of  $\sim 200 \times$  within the rocksalt crystal phase, and the carrier concentrations remaining in high  $10^{19}$ – $10^{20}$  cm<sup>-3</sup>. Since the origin of such high carrier concentration should be related to the presence of defects (such as oxygen impurity or nitrogen vacancies), the observed high carrier densities in rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N even with very large AlN mole-fractions are not surprising. The carrier concentration, however, decreased significantly for the wurtzite-Al<sub>x</sub>Sc<sub>1-x</sub>N film.

# VIII. DEVELOPMENT OF MULTILAYERS AND SUPERLATTICES

Having presented the development of semiconducting ScN and rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N thin film alloys, the growth and structural materials properties of the metal/semiconductor multilayers and superlattices are discussed in this section.

# A. Structural characterization of (Hf,Zr)N/ScN multilayers

ZrN/ScN, HfN/ScN, and (Zr,W)N/ScN metal/semiconductor multilayers were deposited on [001] MgO substrates by Rawat *et al.*,  $^{34,141-144}$  Schroeder *et al.*,  $^{57,145,146}$  and Burmistrova et al.<sup>147</sup> X-ray diffraction (XRD) spectrum of a ZrN/ScN multilayer (characteristic for other multilayers) showed 002 oriented epitaxial crystal growths. The fullwidth-at-half-maximum (FWHM) of the rocking curve ( $\omega$ -scan) were measured to be  $0.8^{\circ} - 1.3^{\circ}$  suggesting textured thin film growth.<sup>34</sup> Satellite peaks due to X-ray interference from different multilayer interfaces were clearly seen in the XRD spectrum [see Fig. 7(a)] suggesting periodic and coherent layer-by-layer epitaxial crystal growth. The main 002-diffraction peaks of the multilayers was used to extract out-of-plane lattice constants of 4.55 Å, 4.52 Å, and 4.54 Å for the ZrN/ScN, HfN/ScN, and (Zr,W)N/ScN multilayers, respectively.<sup>147</sup> It is important to note here that the lattice constant of ZrN (4.59 Å) and HfN (4.50 Å) are very close to



FIG. 6. (a) X-ray diffraction spectra of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N alloy films deposited directly on [001]-MgO substrates. The full-width-at-half-maxima (FWHM) of the rocking curves, representing the crystal quality decrease with the increase in the AlN mole fractions. (b) The stability of the rocksalt Al<sub>x</sub>Sc<sub>1-x</sub>N alloys was increased from x = 0.62 to x = 0.82 by employing an epitaxial stabilization technique by growing 20 nm of TiN on MgO substrates as seed layers. (c) HRTEM image of a metastable-Al<sub>0.72</sub>Sc<sub>0.28</sub>N alloy grown on 20 nm TiN seed layer. Epitaxial cube-on-cube crystal growth with no misfit dislocations can be observed in the micrograph. (d) Direct bandgap of the rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N alloys are presented as a function of their lattice constants. Lattice parameters of the rocksalt nitride metals are also plotted in the same figure, which shows that the rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N can be lattice matched with most other metallic TMN for superlattice growth. Reproduced with permission from Saha *et al.*, Phys. Status Solidi B **252**, 251 (2015). Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

that of the ScN (4.52 Å), and as a result the measured c-axis lattice constants of the multilayers were found to be an averaged value of the component materials.

Though the nitride metal and semiconductor components of the multilayers were lattice matched, careful HRTEM analysis<sup>54,147</sup> showed that the lattice mismatch between the nitrides (film) and the substrate (MgO) results in columnar grain formation, with grain boundaries at an interval of a few 10s to 100s of nanometers. The grain boundaries extend almost vertically throughout the films perpendicular to the film/substrate interface [see in the HAADF-STEM micrograph in Fig. 7(b)]. The micrograph also showed that the individual layers within the multilayer curve towards the grain boundaries in the vicinity of the substrates to form V-shaped structural defects. Hultman et al.<sup>148</sup> had previously identified such grain boundaries and V-shaped defects in sputter deposited nitride films, and attributed the presence of such defects to the threading dislocations forming at the substrate/film interface as a result of surface cusps on the substrate during the growth process. The HRTEM image [Fig. 7(b)] also show that though the layers curve towards the grain boundaries, they still maintain lattice coherency for the as-deposited films. Garbrecht et al.<sup>54</sup> have performed detailed analysis of such grain boundaries with HRTEM and have found that the origin of such grain boundaries lies in the nitride/MgO interface as arrays of edge dislocations arising due to the lattice mismatch, thus supporting the previous claims. Within the individual grains, however, the interfaces are coherent and lattice constants are matched as expected.

Since the densities of the dislocations and associated grain boundaries in these materials are quite large<sup>54</sup>  $(\sim 10^{14} - 10^{15} \text{ cm}^{-2})$ , the ZrN/ScN, HfN/ScN, and (Zr,Hf)N/ ScN heterostructures were referred to as "multilayers" rather than "superlattices." Moreover, the presence of such grain boundaries (and dislocations) are always detrimental for the cross-plane transport measurements especially for electrical transport since the boundaries could potentially (as will be presented later) result in electrical shunts along the crossplane transport direction. Several<sup>147</sup> cross-plane electrical measurements with (Hf, Zr)N/ScN multilayers have shown that leakage currents or/and shunt currents dominate the device characteristics over the thermionic transport. However, a set of device measurements has demonstrated thermionic emission<sup>149,150</sup> in ZrN/ScN multilayers with a Schottky barrier height of 0.28 eV. While it is not proper to attribute the leakage and shunt currents entirely to the dislocations and grain boundaries, there is no doubt that for reproducible electrical measurements, epitaxial superlattices devoid of extended defects would be necessary.



FIG. 7. (a) X-ray diffraction spectrum of HfN/ScN multilayer shows 002oriented film growth. Satellite peaks arising due to X-ray interference are also observed in the spectrum. (b) HRTEM micrograph of HfN/ScN multilayer showed vertical defect lines that originate at the multilayer/MgO interface and propagate through the multilayers to the surface. (c) Inset from Fig. 7(b) shows that along the defect lines individual layers curve towards the MgO substrate. Reproduced with permission from Garbrecht *et al.*, J. Mater. Sci. **51**, 8250 (2016). Copyright 2016 Springer International Publishing AG.

# B. Structural characterization of TiN/(Al,Sc)N superlattices

The epitaxial, pseudomorphic metal/semiconductor superlattices were developed by Saha *et al.*<sup>43,53,54</sup> with rock-salt-TiN/Al<sub>x</sub>Sc<sub>1-x</sub>N material system. Metallic TiN thin films have a lattice parameter of 4.24 Å, which is very close to the

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lattice parameters of the MgO (4.21 Å) substrate. To latticematch TiN and MgO, the Al<sub>x</sub>Sc<sub>1-x</sub>N alloy semiconductor was chosen with x = 0.72. Al<sub>0.72</sub>Sc<sub>0.28</sub>N alloys have a lattice parameter of 4.26 Å and therefore should result in nearly perfect lattice matching with TiN and MgO.

The XRD spectrum of TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N metal/semiconductor superlattices showed 002 oriented crystal growth on the [001] MgO substrates with a very small FWHM of the rocking curve ( $\omega$ -scan) of 0.05° due to a small degree of mosaicity [see Fig. 8]. Clear and sharp interference fringes were observed in the symmetric 2  $\theta - \omega$  XRD spectrum, which suggested layer-by-layer epitaxial crystal growth with coherent and abrupt interfaces.<sup>42</sup> Reciprocal space XRD map (RSM) showed that the asymmetric peaks such as 024-MgO peak, 024-superlattice peak, and all the interference fringes were all aligned vertically, which confirmed that along the in-plane directions, TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers have acquired the lattice constants of the MgO substrate (i.e.,  $a_{\parallel -TiN} = a_{\parallel -(Al,Sc)N} = a_{\parallel -MgO} = 4.21$ Å). Along the out-of-plane (c) direction, the lattice constants of TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N were found to be 4.23 Å, and 4.26 Å, respectively, which are very close to the thin film lattice constants of TiN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers, respectively.<sup>42</sup> The close lattice matching between the substrate and nitrides ensured very little strain in the superlattice, as was shown in RSM image.<sup>53</sup> X-ray reflectivity (XRR) measurements and subsequent data fitting have conclusively demonstrated that the interface mixings were of the order of oneto-two atomic layers.<sup>42</sup> When TiN grows on Al<sub>0.72</sub>Sc<sub>0.28</sub>N, the interface mixing was found to be about one monolayer, while the growth of Al<sub>0.72</sub>Sc<sub>0.28</sub>N on TiN resulted in a mixing of about two monolayers. The XRD analysis, therefore, have clearly demonstrated that the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N metal/ semiconductor superlattices were epitaxial, nominally single crystalline, devoid of any extended defects, such as dislocations, and possess coherent epitaxial layers with abrupt interfaces.

HRTEM microscopy analysis corroborated<sup>42,53</sup> the XRD analysis as well-defined sharp and coherent layers were clearly seen in the micrographs. Even a thin 2 nm  $Al_{0.72}Sc_{0.28}N$  layer deposited in-between 20 nm TiN layers



FIG. 8. X-ray diffraction spectra of a  $20 \text{ nm}/20 \text{ nm} \text{TiN/Al}_{0.72}\text{Sc}_{0.28}\text{N}$  superlattice showed 002-oriented growth. Superlattice satellite peaks are clearly observed indicating sharp interfaces. The FWHM of the rocking curve is  $0.05^{\circ}$ , suggesting that the superlattices are epitaxial and nominally single crystalline with a very small degree of mosaicity. (b) Reciprocal space XRD map (RSM) of the superlattice shows main 024 MgO, superlattice and satellite peaks all aligned vertically indicating that the superlattices are pseudomorphic and grow with very little strain. Reprinted with permission from Naik *et al.*, Proc. Natl. Acad. Sci. U. S. A. **111**, 7546 (2014). Copyright (2014) National Academy of Sciences.



FIG. 9. (a) HRTEM image of TiN/ metal/semiconductor Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice that shows coherent epitaxial layer-by-layer crystal growth. The interfaces are visibly sharp with the  $2\,nm$   $Al_{0.72}Sc_{0.28}N$  layer clearly visible in the image. (b) HRTEM image that showed lattice-fringes at the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N interface. Due to the close lattice matching, interfaces are atomically sharp with no sign of any extended defects. (c) HAADF-STEM micrograph of the superlattice showed coherent layer growth. Some V-shaped structural defects were observed. Reproduced with permission from Saha et al., Phys. Rev. B 90, 125420 (2014), Copyright 2014 American Physical Society and reprinted with permission from Naik et al., Proc. Natl. Acad. Sci. U. S. A. 111, 7546 (2014). Copyright (2014) National Academy of Sciences.

were clearly seen in microscopy images (see Fig. 9). The lattice-resolved high-magnification image showed coherent lattice fringes, and cube-on-cube epitaxial crystal growth. No sign of any misfit dislocations were observed at the interfaces between the nitride layers, and between the nitrides/ MgO interfaces. In the STEM image of a TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N multilayer, where Al<sub>0.72</sub>Sc<sub>0.28</sub>N layer thickness was varied, while the TiN layer thickness was held constant at 20 nm, some voided structures deficient of nitrogen atoms were apparant.<sup>150,151</sup> For more regular x nm/x nm superlattices, no such voids were ever observed.

Lattice matched Ti<sub>0.7</sub>W<sub>0.3</sub>N/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices were also deveoped<sup>53</sup> to reduce the thermal conductivity of the superlattices by alloying TiN with W<sub>2</sub>N. Like TiN/ (Al,Sc)N superlattices, the XRD spectrum showed nominally single crystalline and epitaxial growth of the Ti<sub>0.7</sub>W<sub>0.3</sub>N/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices on the [001] MgO substrates. The HRTEM-EDX maps showed excellent structural and interface quality of these heterostructures. HRTEM images (presented in Fig. 10) verified layer-by-layer coherent growth and demonstrated the spatial distribution of various elements in the superlattice system.



FIG. 10. (a) HRTEM-EDX analysis of a  $Ti_{0.7}W_{0.3}N/Al_{0.72}Sc_{0.28}N$  superlattice is presented. Ti, W, Al, Sc, and combined elemental maps are collected from the HRTEM image in (a) and presented in (b), (c), (d), (e), and (f), respectively. The elements are confined within their respective layers and the interfaces are very sharp. An HRTEM and HAADF-STEM image of the superlattices is also presented in (i) and (j), respectively, which showed coherent interfaces with layer-by-layer epitaxial crystal growth. Reproduced with permission from Saha *et al.*, Phys. Rev. B **93**, 045311 (2016). Copyright 2016 American Physical Society.

#### IX. THERMAL STABILITY

Thermal stability of the nitride multilayers and superlattices is extremely important for thermoelectric, thermophotovoltaic and all other high temperature applications. As the constituent TMNs possess high melting temperatures in excess of 3000 °C, the structural stability of the individual nitride materials should not be of great concern in 300–1500 °C temperature range, except for the fact that most of the TMNs oxidize at higher temperatures (as an example, TiN starts oxidizing at  $\sim$ 550 °C). The thermal stability of the multilayers and superlattices, however, are more important as the structures comprise dissimilar materials, separated by interfaces, where diffusion, intermixing, and other physical phenomena could occur. Schroeder et al.57 and Grabrecht et al.58 have employed a combination of synchrotron based XRD measurements and HRTEM techniques to analyze the thermal stability of the multilayers and superlattices after annealing them at high temperatures (up to 1050 °C, for up to 120 h) in vacuum and in forming-gas annealing environments. The results demonstrate interlayer diffusion and phase transformation in TiN-based superlattices primarily, while the HfN/ScN and ZrN/ScN multilayers demonstrated dislocation pipe diffusion in lattice-resolved microscopy for the first time, to the best of our knowledge.

#### A. Dislocation pipe-diffusion

HRTEM micrographs (see Fig. 11) of as-deposited and annealed HfN/ScN multilayer (representative of ZrN/ScN and (Zr,Hf)N/ScN multilayers) showed<sup>58,152</sup> that the characteristic shape and well-defined interfaces within the individual multilayer grains for the as-deposited samples remains unchanged even after annealing at 950 °C for 120 h. The column boundaries, however, clearly evolve during the annealing process. Garbrecht et al.<sup>152</sup> studied diffusion along the threading dislocations in nitride superlattices through carefully-designed as-deposited and annealed samples at 950 °C for 24, and 48 h, respectively. HRTEM results showed that diffusion of Hf atoms along the dislocations had already started in an as-deposited sample owing to the high growth temperature (850 °C). Subsequent annealing of the sample for 24 h resulted in further diffusion along the dislocation lines, and eventually after 48 h of annealing, the Hf atoms traveled through the ScN layers forming a metallic bridge. As Hf atoms diffuse inside ScN, Hf depleted HfN layers curve away from the interface. This phenomenon of atoms diffusing along the dislocation lines is termed as dislocation pipe diffusion and was first theoretically proposed<sup>153,154</sup> in 1960s. While the mechanism<sup>153-156</sup> has been probed by indirect methods such as radiation tracer and others in several materials, lattice-resolved microscopy demonstration of Garbrecht et al.<sup>152</sup> was the first of its kind.

Away from the boundaries, the layers remain well separated without any significant intermixing or diffusion of atoms at the interfaces. Further analysis of the diffraction spectra showed sporadic zincblende ZrN (HfN, (Hf,Zr)N) grains along the boundaries that form bridges across the layers.

#### as-deposited 950°C, 24 hours 950°C, 120 hours



FIG. 11. HRTEM micrograph of an HfN/ScN multilayer (a) as-deposited, (b) annealed at 950 °C for 24 h, and (c) annealed at 950 °C for 120 h. The micrographs clearly show that with increase in temperatures, the inherent multilayers remains intact with well-defined interfaces, and the boundaries clearly evolve due to annealing process. Hf atoms are seen to diffuse along the threading dislocation lines leading to metallic bridge formation shown in (d) and (e). Such diffusions are known as the dislocation pipe diffusion. Two dislocation short circuits are seen in a cross-sectional micrograph. Reproduced with permission from Garbrecht *et al.*, J. Mater. Sci. **51**, 8250 (2016), Copyright 2016 Springer International Publishing AG and Reproduced with permission from Garbrecht *et al.*, Sci. Rep. **7**, 46092 (2017). Copyright 2017 Macmillan Publishers Limited, part of Springer Nature.

The rocksalt-to-zincblende structural phase transition triggered by hydrostatic pressure in HfN, ZrN, and other TMNs had been discovered previously;<sup>157</sup> however, in ZrN/ScN (or HfN/ScN and (Hf,Zr)N/ScN) multilayers, such transition are expected to be triggered by defects during the annealing process.

#### **B. Bulk diffusion**

The thermal stability of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices was evaluated by following the same annealing procedure as mentioned for the HfN/ScN multilayers. However, in addition to the HRTEM, Schroeder *et al.*<sup>57</sup> has also performed synchrotron-based XRD measurements to obtain information from larger sample areas. The synchrotron measurement showed (see Fig. 12) that the as-deposited superlattices exhibit cubic diffraction patterns as expected. However, annealing the superlattices at 950 °C (and 1050 °C) for 120 h resulted in the observation of 12 equally spaced diffraction spots in the synchrotron spectra. The diffraction spots were 30° apart from each other suggesting a rocksalt-to-wurtzite structural phase transformation of the Al<sub>0.72</sub>Sc<sub>0.28</sub>N layer. Interestingly, as-deposited Al<sub>x</sub>Sc<sub>1-x</sub>N thin film alloys grown (directly on MgO substrates) at the cusp of rocksalt-to-

950°C, 24 hours

s 950°C, 120 hours



FIG. 12. HRTEM micrograph of a TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice (a) asdeposited, (b) annealed at  $950\,^\circ C$  for 24 h, and (c) annealed at 950 °C for 120h, clearly demonstrate significant bulk diffusion with an increase in temperature. Due to the heavy atomic difand inter-mixing, fusion the superlattice becomes an alloy 24h of annealing at 950°C. The HRTEM-EDS maps [(d), (e), and (f)] show the spatial distribution of various atoms as a function of annealing time. Reproduced with permission from Schroeder et al., J. Mater. Sci. 50(8), 3200-3206 (2015). Copyright 2015

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wurtzite structural phase transformation had also showed<sup>158</sup> similar 12 diffraction spots because of twin wurtzite grains separated by a 30° twin-boundary. Subsequent HRTEM analysis on the annealed sample confirmed the phase transformation in the  $Al_{0.72}Sc_{0.28}N$  layers. Since  $Al_{0.72}Sc_{0.28}N$  adopts the metastable rocksalt phase inside the superlattices,<sup>54</sup> thermal annealing provides the required energy to achieve the structural phase transformation.

Contrary to ZrN/ScN and similar multilayers, however, significant inter diffusion of Ti, Al and Sc atoms were also observed in the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices, starting at an early stage in the annealing process and continuing with the progression of annealing time. For annealing time of more than 120 h, HRTEM images<sup>57</sup> showed that the superlattices become random alloys (also shown in Fig. 12). The TEM-EDX maps demonstrated anisotropy in diffusion rates with Sc atoms diffusing inside TiN layers at a much faster rate. This mismatch in diffusion rates resulted in uniform Sc atom distribution inside the entire superlattice structure after annealing for 120 h. The thermal stability analysis, therefore, demonstrated that the nitride multilayers and superlattices should be suitable for high-temperature applications up to 900 °C.

#### X. PHYSICAL PROPERTIES OF THE METAL/ SEMICONDUCTOR MULTILAYERS AND SUPERLATTICES

#### A. Thermal transport: Applications to thermoelectrics

Thermal transport properties of the TMN thin films, multilayers, and superlattices are extremely important not only for designing efficient thermoelectric and thermionic materials and devices with higher power conversion efficiencies<sup>33–36</sup> but also for most electronic, optoelectronic, plasmonic and high-temperature applications.<sup>159,160</sup> As the thermal management and hot-spot cooling in semiconductor integrated circuit (IC) technologies are becoming extremely

important<sup>161–163</sup> in data storage and computing devices, TMN based materials and heterostructures could offer viable solutions. Thermal conductivity of the TMNs varies significantly (see Table I), and the development of heterostructure and superlattices has added to the broad range of thermal conductivity that can be engineered. Significant research efforts<sup>34,53,56,74,75,111,164,165</sup> have been dedicated over the last several years to measure the thermal conductivities of TMN thin films, alloys, and superlattices to understand the microscopic heat conduction mechanism, to calculate the phonon dispersion spectra of the materials and superlattices, and to develop mesoscopic theories for the explanation of the thermal transport properties.

First-principles based density functional perturbation theory<sup>166,167</sup> (DFPT) was adapted to calculate the phonon spectrum of the TMN metals<sup>53,56,74,168,169</sup> (ZrN, HfN, and TiN), semiconductors<sup>53,56,74,75,168</sup> (ScN, YN, and Al<sub>0.75</sub>Sc<sub>0.25</sub>N), and metal/semiconductor multilayers<sup>164,165</sup> (ZrN/ScN and HfN/ScN). As the DFPT calculations are extremely time consuming, the phonon spectrum of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N and Ti<sub>0.70</sub>W<sub>0.30</sub>N/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices has not been calculated as yet. Rather, analytical models related to alloy scattering<sup>53,56</sup> have been employed to explain important aspects of the heat conduction mechanism in such epitaxial superlattices.

The vibrational spectra of the metals (presented for HfN in Fig. 13, which is typical for other TMN metals) show acoustic and optical phonon modes arising due to the vibration of metal-atoms (such as Zr, Hf, Ti, and others) and nitrogen (N) atoms, respectively. The phonon modes are generally separated by an energy gap in the dispersion spectrum. The separation energy between the phonon modes is different for different nitride metals and is proportional to the mass difference between the transition metal and nitrogen atoms. For example,<sup>74</sup> in HfN the acoustic and optical phonon modes were separated by ~300 cm<sup>-1</sup> (see Fig. 13), since Hf atoms vibrate with much lower frequencies compared to nitrogen atoms. Apart from the energy gap, the



FIG. 13. First-principles density functional theory based analysis of the vibrational spectra of HfN (a), ScN (b), and HfN/ScN (c) multilayer. A clear energy gap between the acoustic and optical phonon modes is seen in HfN that arises due to the difference in mass of the Hf and N atoms. In the case of ScN, the longitudinal optic (LO) and transverse optic (TO) phonon modes are split due to its polar nature. For the ZrN/ScN multilayers, the mid-frequency range phonon modes show flat dispersions along the cross-plane growth directions suggesting their lower group velocities. (d) Boltzmann-transport theory based analysis of the thermal conductivity shows that compared to the individual nitride materials, superlattices should have  $10 \times -15 \times$  lower lattice thermal conductivities. Reproduced with permission from J. Appl. Phys. **107**, 033715 (2010), copyright 2010 AIP Publishing LLC and reproduced with permission from J. Appl. Phys. **109**, 083717 (2011). Copyright 2011 AIP Publishing LLC.

vibrational spectra of the metals behave in expected ways, except for some anomalies.

In case of the semiconductors<sup>56,74,75,168</sup> (ScN, YN, and Al<sub>0.75</sub>Sc<sub>0.25</sub>N), no such gap in the energies between the acoustic and optical phonon modes was observed (presented for ScN in Fig. 13, which is typical of other TMN semiconductors). The reasons for such a continuous dispersion spectrum could be related to the fact that Sc (or Al) and nitrogen atoms have much smaller mass difference compared to the mass difference between Hf (or Zr) and nitrogen atoms. An additional reasoning could also be related to the fact that ScN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N semiconductors have polar chemical bonds, which results in the splitting of longitudinal optic (LO)-transverse optic (TO) phonon modes. In the case of ScN, the LO-TO splitting results in a frequency difference<sup>74</sup> of  $\sim$ 420 cm<sup>-1</sup> (see Fig. 13). Apart from these LO-TO splittings, the phonon spectra of ScN and Al<sub>0.75</sub>Sc<sub>0.25</sub>N also exhibit some minor anomalies.<sup>168</sup>

The phonon dispersion spectrum of ZrN/ScN and HfN/ ScN multilayers [calculated with a supercell constructed with one unit-cell of ZrN (or HfN) and one unit-cell of ScN] have been calculated,<sup>164,165</sup> and the results show that along

the  $\Gamma$ -Z transport direction, the velocities of the transverse acoustic (TA) phonon modes are reduced considerably compared to the individual nitride materials. The mid-frequency range  $(300-420 \text{ cm}^{-1} \text{ for ZrN and } 200-420 \text{ cm}^{-1} \text{ for HfN})$ phonon bands are flattened in the dispersion spectra of multilayers, which demonstrates a reduction of the phonon velocities due to the localization of the vibrational modes (see Fig. 13). Such localization of the mid-frequency range phonon modes is a direct consequence of the mismatches in the densities of the phonon-states observed among the nitride metal and semiconductors. Subsequent Boltzmann Transport Theory (BT) based analysis also showed that the mismatch in phonon densities of states resulted in very small transmission probabilities for the mid-frequency range phonons in ScN to HfN (or ZrN), significantly reducing the thermal conductivity of the multilayers along the cross-plane direction. The BT analysis has predicted  $^{164,165}$  that the ZrN/ScN and HfN/ScN multilayers should have  $\sim 10 \times$  to  $\sim 15 \times$  lower thermal conductivities in comparison to the individual nitride thin films (Fig. 13).

Thermal conductivity of the TMN, multilayers, and the superlattices have been measured with a time-domain

thermoreflectance (TDTR) measurement technique.<sup>170,171</sup> A summary of the room temperature thermal conductivity, and associated electronic contribution to the total thermal conductivity for the thin films and alloys are presented in Table. II. TDTR measurements showed that the total thermal conductivity of ScN and Al<sub>0.72</sub>Sc<sub>0.28</sub>N thin films are 10.6 W/m K and 4.5 W/m K, respectively<sup>34,53,56,106</sup> at room temperature, while the thermal conductivity of the metallic nitrides<sup>34,53,56</sup> TiN, ZrN, and HfN are 63 W/m K, 47 W/m K, and 37 W/m K, respectively. Thermal conductivities of the semiconductors were dominated primarily by phonon contributions. However, for the TMN metals, electronic contributions play a significant role in the overall thermal conductivity. For example,<sup>56</sup> about 76% of the total thermal conductivity is contributed by the electronic component in the case of TiN at room temperature. Thermal conductivities of several alloy films (such as  $Zr_{0.65}Sc_{0.35}N$ ,  $Zr_{0.7}W_{0.3}N$ ,  $Zr_{0.36}W_{0.10}Sc_{0.54}N$ , Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N, and Ti<sub>0.35</sub>W<sub>0.15</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N) were also measured to determine the extent of thermal conductivity reduction due to alloy scattering, as well as to explore the possibility of overcome the alloy limits of thermal conductivity.

Thermal conductivity of the ZrN/ScN multilayers and the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N, and Ti<sub>0.7</sub>W<sub>0.3</sub>N/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices have been measured as a function of the period thicknesses.<sup>34,53,56</sup> Results show that the thermal conductivity at room temperature decreased with an increase in the number of interfaces (or decrease in the period thickness, while keeping the total thickness constant) for medium-to-long multilayer and superlattice period thicknesses (from 4 nm to 240 nm). Such decrease in thermal conductivity suggests that interface scattering plays a dominant role in the thermal transport when the period thicknesses are larger than 4 nm. In ZrN/ScN multilayers,<sup>34</sup> for example, thermal conductivity was reduced from ~10 W/m K to ~5 W/m K for a reduction of the period thickness from 40 nm to 4 nm. In the case of

TABLE II. Thin film composition, thicknesses, measured room-temperature in-plane electrical conductivity, measured room-temperature cross-plane thermal conductivity, and calculated lattice contributions to overall thermal conductivity using the Weidemann–Franz law are presented for nitride materials (Refs. 34, 53, 56, 106, and 107).

Film composition	Film thickness (nm)	In-plane electrical conductivity (S/m)	Measured cross-plane thermal conductivity (W/m K)	Estimated lattice contribution to the thermal conductivity (W/m K)
TiN	240	$1.5  imes 10^7$	63	17
ZrN	1450	$3.7  imes 10^6$	47	19.5
HfN	807	$3.1 \times 10^{6}$	37	
ScN	306	$1.3 \times 10^5$	10.6	10.6
Al <sub>0.72</sub> Sc <sub>0.28</sub> N	240		4.5	4.5
Zr <sub>0.65</sub> Sc <sub>0.35</sub> N	297	$1.4 \times 10^{6}$	15.6	5
Zr <sub>0.7</sub> W <sub>0.3</sub> N	600	$3.6 \times 10^5$	3.75	1.04
Zr <sub>0.36</sub> W <sub>0.10</sub> Sc <sub>0.54</sub> N	600	$9.1 \times 10^4$	2.1	1.43
Ti <sub>0.7</sub> W <sub>0.3</sub> N	240		6.4	4.3
Ti <sub>0.5</sub> Al <sub>0.36</sub> Sc <sub>0.14</sub> N	240		23	16
Ti <sub>0.35</sub> W <sub>0.15</sub> Al <sub>0.36</sub> Sc <sub>0.14</sub> N	240		3.2	2.4

TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices,<sup>56</sup> thermal conductivity decreased by about 54% for a decrease in the period thickness from 240 nm to 4 nm. Each interface in the multilayers and superlattice could be considered to contribute a finite boundary resistance that adds in series to reduce the thermal conductivity with the increase in number of interfaces.

Thermal conductivity for period thickness smaller than 4 nm, however, increased with the reduction of the period thicknesses (or with the increasing number of interfaces). Such behavior of thermal conductivity is opposite to the classical nature of phonon transport and suggestive of a different phonon transport mechanism involving its wave-nature.<sup>56</sup> Experimental results suggested that phonon wave interference<sup>53,56</sup> at short superlattice periods results in formation of coherent phonon wave modes that propagate without scattering from the interfaces and increase the thermal conductivity with decreasing period thicknesses. Such descriptions of the coherent phonon dominated heat transport mechanism have been addressed<sup>172–174</sup> in recent years, which are consistent with experimental observations for short-period epitaxial TMN superlattices.

Achieving high thermoelectric figure-of-merit (ZT) requires low thermal conductivity, preferably less than 1 W/m K at the operating temperature. While nitride superlattices have already shown substantially lower thermal conductivity in comparison to individual TMN films, further reduction of the thermal conductivity in superlattices are necessary. Along with the incoherent boundary scattering, alloy scattering in the metallic nitrides have also been used as an additional scattering mechanism for reducing thermal conductivity. Tungsten nitride (W<sub>2</sub>N) has been alloyed with ZrN and TiN, respectively, to grow (Zr,W)N and (Ti,W)N alloys films, (Zr,W)N/ ScN multilayers, and (Ti,W)N/(Al,Sc)N superlattices. TDTR measurements show that additional alloy scattering from heavy tungsten (W) atoms help further reduce the thermal conductivity in both materials systems. For (Ti,W)N/(Al,Sc)N superlattices, thermal conductivity was found to be smaller than the equivalent Ti<sub>0.35</sub>W<sub>0.15</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloys, thus overcoming the alloy limits of thermal conductivity (see Fig. 14). The Ti<sub>0.7</sub>W<sub>0.3</sub>N/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices with a period thickness of 2-4 nm also showed the lowest thermal conductivity of 1.7 W/m K at room temperature, which is thus far the smallest thermal conductivity value for nitride metal/semiconductor superlattices.

Temperature dependent thermal conductivity measurements showed that ZrN/ScN multilayers<sup>34</sup> and Ti<sub>0.7</sub>W<sub>0.3</sub>N/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices<sup>53</sup> exhibit increase in thermal conductivity with an increase in temperatures (300 K-550 K). With the help of temperature-dependent electrical measurements, it was demonstrated that such increase in the thermal conductivity with increasing temperature was associated with an increase in electrical conductivity of Ti<sub>0.7</sub>W<sub>0.3</sub>N with temperature and an associated increase in electronic portion of thermal conductivity. For TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices,<sup>56</sup> however, thermal conductivity decreased with increasing temperature due to anharmonic Umklapp scattering, which also suggest dominance of wave nature of phonon transport in the epitaxial superlattices.

In summary, significant progress has been made to understand the basic thermal transport characteristics in



FIG. 14. (a) Room temperature thermal conductivity of TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N metal/semiconductor superlattices are presented as a function of period thickness. Thermal conductivity decreased with the reduction of the period thickness (or increasing interface density). For short-period superlattices (less than 4 nm period thickness), thermal conductivity increased with increasing interface densities suggesting dominance of phonon wave effects in thermal transport. Reproduced with permission from J. Appl. Phys. **121**, 015109 (2017). Copyright 2017 AIP Publishing LLC. (b) Thermal conductivity of  $Zr_{1-x}W_xN/ScN$  multi-layers as a function of the  $W_xN_y$  mole-fractions inside the  $Zr_{1-x}W_xN$  layers. Heavy W atoms help increase alloy scattering, thereby, decreasing the thermal conductivity of  $Zr_{1-x}W_xN$  layers, and hence, that of the multilayers. Reproduced with permission from J. Appl. Phys. **105**, 024909, (2009). Copyright 2009 AIP Publishing LLC.

TMNs, in metal/semiconductor multilayers and superlattices. Experimentally, the cross-plane thermal conductivities of engineered nitride superlattices are already approaching values appropriate for thermoelectric applications. Nitride superlattice metamaterials may also find several other industrial applications, such as in thermal management in IC circuits, hot-spot cooling and others. Further work on important mechanism of heat transport such as (a) electron-phonon coupling and (b) detailed understanding of the effects of coherent phonon modes on thermal transport will require additional research.

# B. Optical properties: Applications to plasmonics and hyperbolic metamaterial

TMNs and epitaxial metal/semiconductor superlattices have already made impact in the fields of plasmonics and optical-metamaterials.<sup>39,175,176</sup> Noble metals such as Au and Ag are traditionally regarded as the best plasmonic materials in the visible spectral range. However, noble metal-based plasmonic components have materials properties that limit realization of practical plasmonic devices.<sup>175</sup> Some of the materials challenges<sup>175</sup> with noble metals are (a) noble metals are morphologically not stable at high temperatures (>500 °C), (b) they are incompatible with standard complementary metal oxide semiconductor (CMOS) fabrication processes, (c)  $\epsilon'$  for noble metals are too large for several applications, (d) they are difficult to fabricate in thin film or ultra-thin film form, and (e) it is difficult to engineer optical properties of noble metals though materials engineering.

TMNs have enormous promise and potential in the plasmonics research field as they overcome some of the shortcomings of noble metals. Ellipsometry measurements have showed<sup>34,175</sup> that TiN and ZrN are excellent plasmonic materials in the visible spectral range (500–900 nm). The real part of the dielectric permittivity ( $\epsilon'$ ) of TiN and ZrN (see Fig. 15) are much smaller compared to noble metals (such as Au and Ag films) due to their relatively low carrier concentrations. For several practical applications<sup>175,176</sup> such as in devices for transformation optics, or in hyperbolic metamaterials, lower values of  $\epsilon'$  are a necessity and the TMNs have already attracted significant interest in that pursuit. The imaginary parts of the dielectric permittivity ( $\epsilon''$ ) of the TMNs (see Fig. 15), however, are larger compared to noble metals due to increased inter-band transitions.<sup>177</sup>

Detailed studies on the plasmatic properties of TMNs (TiN and ZrN), such as surface plasmon polariton (SPP) propagation length, SPP mode size, second harmonic generation, absorption and emission, have already demonstrated superior plasmonic qualities of TMNs (e.g., TiN) in comparison to Au and Ag.<sup>178–180</sup> TMNs are also proposed as next generations of refractory plasmonic materials<sup>181</sup> for their high temperature applications in solar-thermophotovoltaics (STPV), heat-assisted magnetic recording (HAMR). More recently, TiN based metamaterial absorbers<sup>182</sup> were also shown to possess superior performance for high temperature applications.

TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N metal/semiconductor superlattice heterostructures have already exhibited excellent hyperbolic metamaterial properties in the visible spectral range, with the hyperbolic dispersion of the iso-frequency surface ranging from  $\sim 500 \,\text{nm}$  to the near-IR spectral regions<sup>42,43</sup> (see Fig. 15). Both the type-I and type-II hyperbolic dispersions (which are usually not common in noble metal-based HMMs) were observed in these nitride superlattices. Hyperbolic dispersion in metamaterials have significant implications in their optical properties, since such dispersions leads to open iso-frequency surfaces in momentum space, leading to large enhancement in densities of photonic states, negative refraction, hyperlens, and many other exotic optical phenomena.<sup>40,45,46</sup> Naik *et al.*<sup>43</sup> have shown that the densities of photonic states in TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices are significantly higher in comparison to the nitride thin films because of their hyperbolic dispersion. TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N metal/semiconductor superlattices were also used to show<sup>183</sup>



FIG. 15. (a) Real  $(\varepsilon')$  and (b) imaginary  $(\varepsilon'')$  parts of the dielectric permittivity of TMNs such as TiN, TaN, HfN, and ZrN. ZrN, HfN, and TiN show negative real permittivity characteristic of a metal starting ~500 nm spectral range. Reproduced with permission from Naik et al., Opt. Mater. Express 1, 1090–1099 (2011). Copyright 2011 Optical Society of America (Ref. 236). (c) The anisotropic dielectric permittivity of TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice as a function of wavelength (calculated with effective medium theory). The spectrum shows above 480 nm but below 720 nm,  $\epsilon'_{\parallel}$  is positive but  $\epsilon'_{\perp}$  is negative, which gives rise to type-I HMM dispersion. The sign of the permittivity reverses in the higher wavelength regions to give type-II dispersion. (d) The imaginary part of the dielectric permittivity along the in-plane and out-of-plane direction. Reproduced with permission from Saha et al., Phys. Rev. B 90, 125420 (2014). Copyright 2014 American Physical Society.

enhancement of collection in single-photon emission from nitrogen vacancy centers in nanodiamond and reduction of excited state lifetimes, which could impact future CMOS compatible integrated quantum sources. In summary, TMN and their epitaxial heterostructures have shown enormous promise for various plasmonic and optical metamaterial applications.

#### C. Mechanical hardness of the superlattices: Applications to hard coatings

TMN and their metallic heterostructures have been studied for decades to develop corrosion resistant hard coating.184-186 TiN, (Ti,Al)N, and some other nitrides have already found extensive industrial applications for edge retention, and corrosion resistance on machine tooling, such as drill bits and milling cutters, often improving tool lifetime by a factor of three or more.<sup>187,188</sup> Apart from the nitride thin films themselves, superlattices were also proposed as potential configuration that may help realize extraordinarily hard materials with long lifetime at high operating temperatures. Koehler<sup>189</sup> proposed in a seminal work in 1970s that the interfaces in superlattices should act as high-energy barriers for dislocation motion, thereby, increasing hardness. Several multilayers based on TMNs (such as TiN/VN, TiN/ AlN, and others) have been developed over the years that show improved hardness compared to the individual materials.<sup>186,188</sup> Apart from the requirement of high hardness; one principal challenge of coating technology is also to improve the stability of the materials at high operating temperatures, since many of the TMNs oxidize at elevated temperatures. For example, TiN oxidizes<sup>190</sup> at ~550 °C, and (Ti,Al)N at slightly higher temperatures. In the case of TiN/AlN polycrystalline multilayers,<sup>191,192</sup> the hardness of the multilayers are relatively higher in the 33–35 GPa, when AlN is epitaxially stabilized in rocksalt phase with layer a thickness of 2–3 nm. However, increase in the AlN layer thicknesses greater than a few nanometer leads to sharp decrease in the hardness values to 23–26 GPa, which is associated with the AlN's phase transformation from rocksalt-to-wurtzite structure.

TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices are stable at high temperatures (950 °C, for 24 h). Therefore, these superlattices could offer lasting solutions to the coating industries for various applications. To explore that hypothesis, the hardness of the superlattice films and alloys were measured using nanoindentation techniques at room temperature. Results<sup>35</sup> show that with a decrease in the period thickness, the hardness of the superlattices increased by a factor of  $2\times$ , which was explained with a confined layer slip model<sup>193</sup> of hardness enhancement (see Fig. 16). For the thinnest period superlattice (3 nm) the measured hardness was 42 GPa, which in about  $2 \times$  higher than the hardness of sputter-deposited TiN thin films (23 GPa) and  $\sim 1.5 \times$  higher than the hardness of rocksalt-Ti<sub>0.72</sub>Sc<sub>0.28</sub>N alloys. Surprisingly, however, the study also showed that the hardness of the equivalent alloy of the superlattice i.e., Ti<sub>0.5</sub>Al<sub>0.36</sub>Sc<sub>0.14</sub>N alloys is 46 GPa, higher than the superlattice with smallest period thickness. The elastic modulus of the alloy was also higher at 410 GPa compared to the elastic modulus of the superlattices  $(350 \pm 30 \,\text{GPa})$ . Though the physical origins of the high hardness in the alloy remains to be determined in detail, the



FIG. 16. Hardness of the TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices and nitride thin films (shown as horizontal lines) grown on [001]-MgO substrates is presented as a function of the period thickness. Reproduced with permission from Appl. Phys. Lett. **105**, 151904 (2014). Copyright 2014 AIP Publishing LLC.

crystal quality of the alloys was found to be better than that of the superlattices when the full-width-at-half-maxima (FWHM) of the rocking curve was chosen as a metric. The alloy and superlattice hardness results are extremely promising given the simplicity of deposition technique, and their high temperature stability.

#### D. Electrical transport: Towards thermionic emission

Historically, the motivation for the development of metal/semiconductor superlattice heterostructures has been catalyzed by the prospect of controlling current flow across multiple Schottky barriers in a superlattice, and thereby, realizing electronic and optoelectronic devices that are not possible to achieve with either normal metals or with semiconductors. Vashaee et al.<sup>25</sup> have theoretically proposed that the Schottky barriers at the metal/semiconductor interfaces should filter out low-energy electrons through thermionic emissions, thereby improving the thermoelectric figure-of-merit (ZT) at high temperatures. Moreover, electron quantization in thin metals films could also lead to several quantum electronic devices such as resonant tunneling diodes, metallic quantum wells, and others.<sup>30,194–197</sup> Crossplane electrical transport measurements in superlattices are, therefore, extremely important. However, unlike the heat (phonon) and light (phonon) transport measurements, electrical measurements along the cross-plane direction in a metal/semiconductor superlattice are challenging. Controlling the electronic defects that affect the bandstructure of the superlattices, as well as extrinsic effects such as fabrication induced leakages poses significant challenges. Zebarjadi<sup>149</sup> and Saha et al.<sup>198</sup> have made significant progress over the last few years; yet a substantial amount of work still remains to be addressed.

A combination of theoretical modeling analyses based on Boltzmann Transport Theory and experimental measurements by Zebarjadi *et al.*<sup>149</sup> have shown that the crossplane electrical current in ZrN/ScN multilayers demonstrate an exponential dependence with increases in temperatures (presented in Fig. 17), consistent with Schottky barriers at the metal/semiconductor interfaces. The effective barrier height of ZrN/ScN multilayer was measured to be 0.28 eV, which is consistent with theoretical estimates.<sup>75</sup> Thermal imaging analysis along with the Seebeck transient voltage measurements have shown that the room temperature Seebeck coefficient of the multilayer is ~820  $\mu V/K$ , which is very close to the modeling result of 800  $\mu V/K$ . However, in spite of such initial encouraging results, reproducible electrical measurements in multilayers need to be performed.

Two main obstacles for the difficulty in cross-plane electrical measurements of the multilayers and superlattices have been identified: (a) High carrier concentration in the semiconducting component, ScN of  $(1-5) \times 10^{20}$  cm<sup>-3</sup> would result in very small depletion widths (of the order of a few nanometers) that will make the Schottky barriers transparent for electron flow through the field emission (tunneling). (b) Metallic shunt path either due to surface leakage arising from the device fabrication process, or due to internal dislocation path leakage due to mismatches in the lattice constants of the nitrides with that of the substrates.

Reduction of the carrier concentration of ScN through hole doping (alloying ScN with  $Mg_xN_y$  or  $Mn_xN_y$ ) has successfully solved the first issue to an appreciable extent.<sup>110,111,119</sup> Electrical measurements showed that the *n*-type carrier concentration in Sc<sub>1-x</sub>Mg<sub>x</sub>N alloys could be reduced to as low as  $2 \times 10^{18}$  cm<sup>-3</sup> before the Sc<sub>1-x</sub>Mg<sub>x</sub>N thin film turns into a *p*-type semiconductor. Depletion width calculations suggest that a carrier concentration of  $2 \times 10^{18}$  cm<sup>-3</sup> would lead to a depletion of width of about 10 nm, which should be sufficient for observation of the thermionic emission phenomena. Development<sup>42,54</sup> of defect free epitaxial, nominally single crystalline TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices should also overcome the internal shunts through dislocations.

Cross-plane electrical transport properties of nominally single crystal TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattices with compensated Al<sub>0.72</sub>Sc<sub>0.28</sub>N layers are indeed necessary for conclusive demonstrations of thermionic emission in metal/ semiconductor superlattices, but the progress made in last several years suggest that such measurements are realizable.

#### **XI. FUTURE CHALLENGES**

Translating the fundamental development of the metal/ semiconductor superlattice heterostructures into practical devices will be a monumental challenge. While there is still a long road to travel before the TMN thin films and superlattice heterostructures impact technological application spaces, the developments presented herein provides a platform for other researchers to explore the materials, understand and innovate basic science, and demonstrate devices with improved efficiencies. Here, we discuss a very small list of scientific challenges and future research directions that can be addressed in the near future.



FIG. 17. Cross-plane electrical conductivity measured as a function temperature for ZrN/ScN multilayer, which demonstrates thermionic transport behavior. The simulation was performed with Boltzmann transport modeling based analysis. The effective barrier height extracted from the experimental data was 0.28 eV. Reprinted with permission from Zebarjadi *et al.*, J. Electron. Mater. **38**, 960–963 (2009). Copyright 2009 Springer International Publishing AG.

## A. Development of rocksalt III-nitride semiconductors and metal/semiconductor superlattices

Development of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N alloys has marked a significant step in the subsequent realization of the epitaxial, nominally single crystalline TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N metal/semiconductor superlattices. However, rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N is not the only promising rocksalt semiconducting alloy that can be integrated in epitaxial heterostructures. Solid-solution alloys of ScN with two other wurtzite nitride semiconductors (GaN and InN) should also be perfectly suitable for future superlattice heterostructure materials. Both GaN and InN are stable in the wurtzite crystal structure at ambient conditions. However, like AlN, they also exhibit the high-pressure rock-salt crystal structure<sup>62,199,200</sup> with lattice constants of 4.08 Å and 4.63 Å, respectively. Therefore, rocksalt-Ga<sub>x</sub>Sc<sub>1-x</sub>N, and rocksalt-In<sub>x</sub>Sc<sub>1-x</sub>N should be developed and studied. As the optical bandgap<sup>62,199,200</sup> of *c*-GaN and *c*-InN are smaller in comparison with *c*-AlN, the proposed alloys with variable ScN mole fractions should allow tunability of their bandgap, electronic and optical properties, and should be useful for engineering Schottky barrier height from few milli-electron-Volts.-to-several electron-Volts. Such broad tunability of Schottky barrier height will be exciting not just for thermoelectricity, but for various types of electronic and optoelectronic devices such as in terahertz generators, sensors and others. In the future, rocksalt ScN, and rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N, Ga<sub>x</sub>Sc<sub>1-x</sub>N and In<sub>x</sub>Sc<sub>1-x</sub>N alloys may become a semiconducting materials system of III-nitrides that has technological applications as broad as those of the zincblende arsenides and phosphides and the wurtzite nitrides.

Similarly, though TiN was the choice of metal to integrate with  $Al_xSc_{1-x}N$  for the development of the metal/semiconductor superlattices thus far, TiN by no means the only choice for a rocksalt metal. Eight other TMNs along with their lattice constants are highlighted in Fig. 18. Difference in work functions of each of these TMN metals could be exploited in controlling the Schottky barrier height in heterostructures and for designing metamaterials with desirable properties.

Rare-earth mononitrides<sup>201–203</sup> (REN) (see Fig. 18) are also an extremely attractive yet largely unexplored materials family for the development of rocksalt semiconductors as well as epitaxial metal/semiconductor superlattice heterostructures. Unlike the TMNs, very little is known about the electronic, plasmonic and materials properties of the RENs. Several challenges<sup>204,205</sup> related to their abundance, chemical stability under ambient conditions, choice of proper substrates for thin film growth and protective coatings remain to be studied. However, along with their rocksalt crystal structure and diverse electronic properties, RENs (such as GdN, EuN) also offer magnetism as an extra degree of freedom  $^{206}$ currently missing in TMNs. Therefore, in the future, rareearth-based metal/semiconductor mononitride heterostructures could be developed for spintronic applications. Hybrid heterostructures with transition metal and rare-earth metal nitrides could also usher in new functionalities for novel device concepts and applications.



#### **Rocksalt Metal/Semiconductor Heterostructures and Superlattices**

FIG. 18. Experimentally measured direct bandgap of rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N alloys are presented as a function of their lattice constants. Similar to the rocksalt-Al<sub>x</sub>Sc1-xN alloys, rocksalt- $Ga_xSc_{1\text{-}x}N$  and  $In_xSc_{1\text{-}x}N$  alloys can be developed. The lattice constants of rocksalt metals are presented in the same figure, which showed that the metals have lattice constants that are commensurate for lattice matched metal/semiconductor superlattice growth with the rocksalt semiconducting alloys. Transition metals and rareearth elements are shown separately to emphasize that epitaxial nitride metal/ semiconductor superlattice growth may be possible.

# B. Thermionic emission, Schottky barrier height, and defect induced interface states

Engineering thermionic emission of electrons over the Schottky barriers in metal/semiconductor superlattice heterostructures requires most immediate attention. Controlled Schottky barriers with height from few milli-eV to severaleV would not only help achieve higher thermoelectric *figureof-merit (ZT)* in metal/semiconductor superlattices but it will also result in many other electronic and optoelectronic devices. In Sec. X, it was noted that (a) large carrier concentrations in the semiconducting layers and (b) lack of efficient device fabrication techniques, for reproducible electrical measurements without surface, and dislocation leakage were the major obstacles.

Since the origin of such large carrier concentration is identified, and the carrier concentration of the semiconductors (ScN) has been reduced with hole doping, a major obstacle in the pursuit for thermionic emission have been addressed. Device fabrication challenges, however, still remain. Zebarjadi *et al.*<sup>149</sup> have previously used reactive dry etching with  $Cl_2$  and  $BCl_4$  gases for the fabrication of crosssectional multilayer device pillars. However, that etching technique requires further process and material optimization for reproducible electrical measurements. Wet chemical etching techniques, unfortunately, have not been developed yet for the TMNs and superlattices. Such wet etching techniques will be necessary and beneficial for large-scale device fabrications.

In pursuit of tuning the Schottky barrier height in metal/ semiconductor superlattice heterostructures, fundamental questions about band-alignment at interfaces should be addressed. For an ideal metal/semiconductor interface without any interface states, the Schottky barrier height may be estimated by the Schottky-Mott rule,<sup>237,238</sup> which uses the superposition principle of electrostatic potential and states that the Schottky barrier height  $(\phi_{B,n})$  at a metal/*n*-type semiconductor interface is given by  $\phi_{B,n} = \phi_M - \chi$ , where  $\phi_M$  and  $\chi$  are the work function of the metal and electron affinity of the semiconductor, respectively. For a metal/ptype semiconductor interface, the Schottky barrier height  $(\phi_{B,p})$  is expressed as  $(\phi_{B,p}) = \chi + E_{g.} - \phi_M$ , where  $\chi$  and  $E_{g}$  are the electron affinity and the bandgap of the semiconductor, respectively, and  $\phi_M$  is the work function of the metal. While this simple yet elegant rule is a powerful tool for the determination of Schottky barrier height of noninteracting metal/semiconductor interfaces assembled without charge or atomic relaxation, interfacial chemistry and dipole formation at the metal/semiconductor interfaces results in deviation between experimentally observed barrier values and predicted values. Previous studies on metal/semiconductor interfaces have employed elemental polycrystalline metals (such as Au, Cu, Ni, and others) having large number of dangling bonds and corresponding surface states, while semiconductors (such as Si, GaAs, GaSb, and others) possess large covalency, favoring Fermi level pinning within the bandgap of the semiconductors. Mead and Spitzer<sup>207</sup> showed that the Schottky barrier heights of most group IV and III-V semiconductors with elemental metals are weakly dependent on the metal work functions, and with Fermi energies that are usually pinned at one-third of the bandgap when the energies are measured from the bottom of the valence band edge. Subsequent research for over five decades has shown that formation of the Schottky barrier height at metal/ semiconductor interface is an extremely complex phenomenon, and the barrier height depends on many different physical and chemical aspects of not just the individual metals and semiconductors, but also on the nature and chemistry of the interface formation. For example, interfacial charge transfer and dipole formation plays a significant role in the determination of Schottky barrier height, and despite research for over six decade no such analytical model exists which could predict the Schottky barrier height across the spectrum of metal/semiconductor interface. Although a detailed discussion of the various factors that determine the Schottky barrier height is beyond the scope of this review article, readers are encouraged to refer to a recent review article by Tung,<sup>239</sup> where details about the physics and chemistry of Schottky barrier height are discussed.

With the development of epitaxial, lattice-matched TiN/ Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice heterostructures, the metal/semiconductor interfaces are lattice matched, suggesting few dangling bonds and associated interface states. Moreover, TiN (like other TMNs) is highly ionic, and both ScN and rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N also have high degrees of iconicity that could prevent Fermi level pinning. Therefore, it is expected that the nitride superlattice heterostructures could allow greater tunability of the barrier heights. Changes in composition of superlattice would also change the work function of the metals and electron affinity of the semiconductors, thereby, allowing the tunability of the Schottky barrier height.

Estimates of defect induced interface state<sup>208,209</sup> ( $D_{it}$ ) density and their energy position with respect to the bandgap are also extremely important, not only to control the crossplane electrical transport properties but also for many optoelectronic devices (presented in Fig. 19). A measure of the  $D_{it}$  could also be served as a metric for the hetero-interface quality. In the most technologically important Si/SiO<sub>2</sub> interfaces, the  $D_{it}$  numbers usually range from 10<sup>10</sup> to  $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$  primarily due to the dangling bonds. Recent research on III-V semiconductors has also established that high  $D_{it}$  limits the possibility of achieving steeper subthreshold swing in tunneling field effect transistors.<sup>210</sup> Therefore, measurement of the  $D_{it}$  in nitride superlattices and their positions with respect to the Fermi level and bandedges should be important.

#### C. Reduction of optical losses in nitride metals

Optical losses in TMNs remain its biggest challenge for practical device applications. For example, in the 500–800 nm spectral range, noble metals such as Au and Ag have  $\epsilon''$  in the 0.5–1 range, while in the same spectral range the  $\epsilon''$  of TiN and ZrN are much larger<sup>178</sup> at 3–7. The physical loss mechanisms<sup>177</sup> in plasmonic materials can be associated with several factors such as (a) intraband transitions or Drude absorptions that usually affect the optical properties in the near-to-mid IR spectral ranges, (b) interband transitions



FIG. 19. Schematic band diagram of a metal/semiconductor interface. The n-type Schottky barrier height (denoted by the  $\phi_{BN}$ ) can be obtained by subtracting the electron affinity of the semiconductor ( $\chi$ ) from the work function of the metal ( $\phi_M$ ) when there is no Fermi level pinning. Three different current transport mechanisms are shown: (a) thermionic emission—when electrons have energies higher than that of the Schottky barrier height, they travel over the top of the barrier at the interfaces, (b) thermionic field emission—when thermally excited electrons tunnel through the depletion region in the semiconductors, and (c) field emission—when electrons at the Fermi level tunnel through the semiconducting layer. Defect-induced interface states (D<sub>it</sub>) that arise primarily due to dangling bonds and other interfacial in-homogeneities are shown.

that affect the plasmonic properties mostly in the visible spectral range, and (c) grain boundary, dislocation, alloy, and impurity scattering. Careful observation of the electronic band structure<sup>68,74,211,212</sup> shows that the TMN metals suffer from the interband transitions in the visible spectral range that result in higher optical losses. It is also important to note that such inter-band transitions and associated optical losses are also present in noble metals such as in Au and Ag albeit with lesser effects.<sup>177,178</sup> Therefore, for the practical applications, effective strategies must be developed to reduce the optical losses in TMNs.

Growth of high quality epitaxial material with lower defect densities would help reduce the optical losses across the spectral range. However, reducing the optical losses associated with interband and intraband transitions is challenging.<sup>213</sup> Traditionally, little progress has been made both on theoretical understandings and on experimental developments to address the optical losses in materials. Khurgin *et al.*<sup>214</sup> have theoretically proposed recently that both the intraband and interband losses in plasmonic materials could be reduced significantly, and the interband transitions can be completely suppressed for special spectral ranges by altering the bandstructrure of a material or through artificial structuring.

Metals usually have completely filled valence bands and partially filled conduction bands with the Fermi energy inside the conduction bands, which results in higher carrier concentrations and large electrical conductivities. Careful observations would also reveal that the conduction bands in a metal usually overlap with one another, and the densities of conduction band states disperse continuously from the Fermi energy to several electrons-volts above the bandedge. In such a scenario, both the intraband and interband transitions are allowed for a wide range of energies, leading to optical losses in plasmonic materials (see Fig. 20). However, Khurgin *et al.*<sup>214</sup> suggest if the conduction bands above the Fermi energy could be split in energy, and if the width of the bands can be reduced by a significant amount, then a special situation would arise where for some specific energy ranges the interband transitions would be completely forbidden due to the lack of allowed states. Such forbidden interband transitions could result in practically zero optical losses for that particular frequency range.

Though the idea of splitting the conduction band in a metal is simple and intriguing, practical demonstration of such band splitting on the orders of electron-volts as well as reduction of the width of the bands is extremely challenging. For example, strain engineering<sup>215–217</sup> is known to be a well-established technique in semiconductors that splits both valence and conduction band-edges in Si, GaAs and other semiconductors. However, the extent of such splitting are usually very small (in milli-electron-Volts) for reasonable amounts of strain in most semiconductors. Therefore, though both tensile and compressional epitaxial strains could be applied in TMNs (such as in TiN and ZrN) with suitable choice of substrates, the splitting of the bands may not be sufficient to reduce interband transitions.

Conduction band splitting in semiconductors, however, has been demonstrated with the incorporation of small amounts of iso-electronic doping with atoms of larger electronegativity and bigger sizes in comparison with the host elements.<sup>218–221</sup> The physical mechanism of such splitting has been explained by the band anti-crossing model, which suggests that incorporation of larger electronegative atoms creates localized states near the conduction band-edge of the host materials. The localized states interact with the bands resulting in the splitting of the conduction bands. For example, in GaAs,<sup>219</sup> small incorporation of N<sub>2</sub> on the As atomic site, splits the conduction band by several 100 mV and reduces the bandgap of the host matrix.

A detailed description of the band anti-crossing model, and experimental results are fascinating.<sup>219</sup> TMNs such as TiN and ZrN could be alloyed with a small amount of highly electronegative but isoelectronic elements (such as Hf, La, or Ac) that could potentially result in defect states near the conduction bands, and split the bands reducing optical losses. The carrier concentration and mobility still need to be maintained for good plasmonic properties.

#### D. What carries heat in metal/semiconductor heterostructures—Electrons or phonons? Electronphonon coupling mechanism in the thermal transport of metal/non-metal heterostructures

Though various aspects of heat conduction<sup>34,53,56,164</sup> (such as boundary and alloy scattering, phonon-zone folding, phonon densities of states mismatch and others) have been studied and addressed in this article, the detailed roles of electron-phonon coupling, as well as quantitative details on coherent phonon modes on the thermal transport in a metal/ semiconductor superlattice heterostructure require further investigation. Detailed understanding of both of these



FIG. 20. Absorption of electromagnetic waves in metals in presented. Figure (a) represents the electron band diagram of a conventional metal with filled valence bands and partially filled conduction bands. Free electrons inside the lowest conduction band absorb low-energy electromagnetic waves such as  $\hbar\omega_1$  and  $\hbar\omega_2$  that result in intraband transitions. Interband transitions results from the band-to-band transitions with high-energy electromagnetic waves  $\hbar\omega_3$ . As a result, metals show optical losses in the entire spectral regions. Figure (b) show if the conduction band of the metal is split into two with a gap, then for certain energies ( $\hbar\omega$ ) band-to-band electronic transitions are forbidden. The range of the electromagnetic energy that do not results in the ban-to-band transitions can be increased by large splitting of the conduction bands as well as by reducing the width of the bands. Reproduced with permission from Appl. Phys. Lett. **96**, 181102 (2010). Copyright 2010 AIP Publishing LLC.

mechanisms is important for the nitride superlattices and for the description of thermal transport in all types of heterostructures.

Electrons are the dominant heat carriers in metals, while lattice vibrations or phonons carry heat in semiconductors and dielectric materials.<sup>222</sup> Traditionally, the Wiedemann-Franz's law<sup>222,223</sup> is used in metals to determine the electronic contributions to the total thermal conductivity from the electrical transport measurements. In the metallic nitrides, such as in TiN and ZrN, results showed that the electronic contribution to the total thermal conductivity was ~73% and ~60%, respectively. ScN and rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N semiconductors, however, are highly resistive; and electrons do not contribute appreciably to the total thermal conductivity.

While Wiedemann-Franz's law by and large explain the electronic contribution to the thermal conductivity in isotropic materials, thermal transport along the cross-plane or growth directions in a metal/semiconductor superlattice heterostructure presents an intriguing question of what carries the heat, electrons or phonons? Estimates of the interface thermal conductance (*ITC*) in TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N superlattice heterostructure,<sup>56</sup> and several other metal/non-metal interfaces<sup>224,225</sup> show that phonon contributions alone [calculated through<sup>226–228</sup> the Acoustic Mismatch Model (AMM) and Diffused Mismatch Model (DMM)] are not enough to

describe the experimental *ITC* values across a wide temperature range. These results suggest that there must be extra channels of heat transport, not accounted for in the



FIG. 21. Schematic descriptions of two types of electron-phonon coupling mechanisms in a metal/non-metal interface. (a) Electrons in metal couple directly with phonons in semiconductor at the interfaces, which are expected to increase the interface thermal conductance (ITC) over the phonon-phonon ITC. Several metal/non-metal systems including  $\text{TiN}/\text{Al}_{0.72}\text{Sc}_{0.28}\text{N}$  show higher ITC values in experiments than the phonon-phonon ITC calculated with transport models. (b) Electrons in metals first couple with the phonons inside the metals, subsequently phonons in metals couple with the phonons in semiconductors. It is expected that this mechanism will reduce the ITC values over the phonon-phonon ITCs.

traditional theoretical models. Several researchers<sup>36,37,224,225,229,230</sup> have suggested that electron-phonon coupling in the metal/non-metal interface between materials is a possible mechanism that would add a parallel channel for thermal energy propagation, thereby, explaining the larger ITC.

Two different models (presented in Fig. 21) for electronphonon coupling in metal/non-metal interfaces have been proposed:<sup>229</sup> (a) Electrons in the metal couple directly with the phonons of the non-metal at the interface and (b) Electrons in the metal couple with the phonons in the metal, and these phonons subsequently couple with the phonons of the non-metal at the interfaces. The thermal resistance associated with the electron-phonon coupling within the metallic layer is expected to add a heat resistance for cross-plane transport, and should lower the ITC at the metal/non-metal interfaces in case (b). Such a process may explain heat transport for interfaces where the experimental ITC are smaller than the theoretical estimates. Direct electron-phonon coupling at the metal/nonmetal interface is expected to increase the ITC over the phonon-phonon conductance observed calculated with various theoretical models in some other interfaces.

While the theoretical mechanism of electron-phonon coupling at metal/non-metal heterostructures are intriguing, very few experimental analysis to date have been performed that could directly validate such mechanisms.<sup>37</sup> One of the important challenges in the experimental demonstration of the electron-phonon coupling mechanisms is due to the fact that most of the metal/non-metal interfaces that exist in literature and studied thus far are highly defected with misfit dislocations, intermixing of atoms, grain boundaries and rough interfaces. All such crystal defects are known to affect the thermal conductivity and *ITC*, which could overshadow the electron-phonon coupling effects. Varying in the thicknesses of the metal and non-metal layers is also not possible in most of the metal/non-metal interface systems without affecting the interface quality.

TMN based metal/non-metal heterostructure and superlattices overcome the material challenges for the growth of defect and dislocation-free epitaxial heterostructures with sharp interfaces and very little intermixing.<sup>42,53,56</sup> Moreover, the layer thickness of the metal and non-metals (semiconductors) can also be varied without affecting the interface properties. Therefore, a detailed thermal transport analysis could be performed as a function of the layer thicknesses of the metal and semiconducting layers, which would hold valuable information about the nature of the electron-phonon coupling mechanism not only in these materials but also for the general description of electron-phonon coupling in materials. Thermal conductivity and ITC measurements with variable temperatures will also be helpful, as electron-phonon coupling are strong function of temperature. The validation of the coupling mechanisms will be a significant step forward in understanding heat transport in nanoscale heterostructures, and should help design the next generations of devices, where thermal transport will play an increasingly important role.

# E. Refractory electronics and plasmonics with transition metal nitrides

Refractory materials in materials science and solid-state chemistry are defined as materials that are chemically, structurally, and morphologically stable at high temperatures<sup>231</sup> (~2000 °C). For refractory electronic applications,  $^{232-234}$  a semiconductor in general has to satisfy several conditions such as (a) large bandgap, (b) high melting temperature, (c) large breakdown voltage, (d) ability to easily dope both n and *p*-type, and (e) ability to integrate with metals for stable contacts at high operating temperatures. TMNs are, therefore, ideal for refractory applications. Moreover, the TMNs are electronically diverse with insulators, semiconductors, metals, and their heterostructures offer novel electronic and optoelectronic properties that are not present in other material systems. A comparison of physical properties of rocksalt nitride semiconductors (ScN and Al<sub>x</sub>Sc<sub>1-x</sub>N) with other conventional high temperature semiconductors such as GaN, SiC, and diamond (presented in Table III) show two important advantages of the

TABLE III. Comparison of ScN and rocksalt- $Al_xSc_{1-x}N$  with other refractory semiconducting materials.

Properties	ScN	$c - Al_x Sc_{1-x} N x = 0$ to 0.72	Si	4H-SiC	Diamond	GaN
Bandgap $(E_g)$ eV	2.2 (D) 0.9 (ID)	2.2 - 3.7 (D) Unknown (ID)	1.1	3.26	5.5	3.4
Dielectric constant $(\epsilon_r)$	12.3	12.3 - 6.6	11.8	9.66	5.5	9
Thermal conductivity (W/m K)	10.6	4.5 ( <i>x</i> =0.72)	150	320	2000	130
Electron mobility (cm <sup>2</sup> /V s)	106	106 - 5	1400	1000	2200	900
Hole mobility (cm <sup>2</sup> /V-S)	30		600	115	1600	150
Melting temperature (°C)	2600		1390	2800	>2200	1800
Breakdown voltage (MV/cm)			0.3	3.2	10	5
Electronic maximum operating temperature (°C)			150	700	1000	>750
Physical stability	Good	Good	Good	Excellent	Good	Good
Key technical issues and limitations	Not enough research	Not enough research	Not suitable for harsh environments	Ohmic contact to <i>p</i> -type material and material quality	<i>n</i> -type doping, materials quality	Materials quality, reproducibility, and Ohmic contacts.

TMN semiconductors with respect to other refractory electronic materials.

- 1. High bandgap materials such as diamond are extremely difficulty to dope preferentially *n*-type or *p*-type, which is a limitation for diamond based refractory electronics. In comparison, ScN and rocksalt-Al<sub>x</sub>Sc<sub>1-x</sub>N (presumably) can be easily doped with both carrier types.<sup>110,111</sup>
- 2. Formation of stable epitaxial metallic contacts with low resistivity, and stable interface properties are extremely difficult to achieve in traditional refractory semiconductors because of their high surface energies, lack of crystal compatibility, and defects states. Stable epitaxial contacts of nitride semiconductors with other nitride metals have been established in this article in details.

Future research on the rocksalt nitride semiconductors and metal/semiconductor superlattice heterostructures at elevated temperatures will be useful for many emerging and novel industrial applications as well. Nitride superlattice heterostructures offer an excellent test bed for the exploration of refractory electronic and optoelectronic device properties such as intersubband absorption and emission, confinement of electrons in metallic wells, photodiodes, photoconductors, and terahertz devices. Detailed studies on the role of superlattice minibands on electrical transport at high temperature will also add tremendous functionalities in heterostructure-based devices.

Refractory optics and plasmonics<sup>181,182</sup> with TMNs is yet another emerging and immensely promising research direction. TMN nitrides with their high melting temperatures, and diverse electronic properties could replace current polycrystalline refractory metals (such as W, Mo, and others) wherever epitaxial integrity and materials quality are of importance. Several emerging technologies such as solarthermophotovoltaics (STPV), heat-assisted magnetic recording (HAMR) are expected to have TMN components.

#### XII. IMPACT ON THE HETEROSTRUCTURE RESEARCH FIELD

Development of epitaxial, nominally single crystalline metal/semiconductor superlattice heterostructures adds a new dimension to the heterogeneous materials integration research field and has potential to conjoin the epitaxial semiconductor/semiconductor superlattice heterostructure as a key element in enhanced performance solid-state devices. While it is early to summarize the impact of the TMN materials or superlattice material systems on its larger research field, here we highlight some significant advances to date.

#### A. Scandium nitride (ScN): Emergence of a rocksalt nitride semiconductor

For decades, scandium nitride (ScN) was widely perceived to be a semimetal, and was over-shadowed by more promising, interesting, and industrially useful III-V wurtzite nitride semiconductors such as GaN, AlN, and InN. However, recent research has revealed that ScN is a promising indirect bandgap rocksalt semiconductor that can be doped preferentially both *n*-type and *p*-type. ScN is also an

#### B. Novel rocksalt nitride semiconductors

for metal/semiconductor superlattices.

Rocksalt ScN and its solid-state alloys, rocksalt- $Al_xSc_{1-x}N$ , rocksalt- $Ga_xSc_{1-x}N$ , and rocksalt- $In_xSc_{1-x}N$ , are emerging as a novel class of semiconducting materials with tunable structural, electronic, optoelectronic, and thermal properties. Similar to the wurtzite III-V nitrides, and the zincblende arsenides and phosphides, rocksalt nitride semiconductors have the potential to enable new classes of devices, particularly, in epitaxial combinations with metallic rocksalt mononitrides.

#### C. Lattice matched epitaxial single crystalline metal/ semiconductor superlattices

Epitaxial, nominally single-crystalline TiN/(Al,Sc)N metal/semiconductor superlattice heterostructures are the first metal/semiconductor superlattices and promise a new era in superlattice physics and device applications. Importantly, the research performed over the last several years has also demonstrated the potential and possibility for development of several other epitaxial metal/semiconductor superlattice systems with variable Schottky barrier heights and transport properties.

#### D. Dislocation pipe diffusion

Despite the theoretical prediction of dislocation pipe diffusion in the 1950s, direct lattice-resolved microscopic observation of dislocation pipe diffusion has not been achieved until the recent demonstration in rocksalt nitride metal/semiconductor miltilayers. The demonstration of the dislocation pipe diffusion in HfN/ScN multilayers marks a great progress in dislocation and diffusion research fields. Dislocation pipe formation and diffusion are prevalent not only in nitride metal/semiconductor multilayers but also in several industrially relevant metals and semiconducting systems. Nitride metal/semiconductor multilayers, therefore, offered a vehicle for understanding the microscopic origin and details of such diffusion process.

# E. Epitaxial TMN plasmonic and hyperbolic metamaterials

TiN, ZrN, and other TMN metals have already demonstrated excellent plasmonic properties in the visible spectral ranges and promise to serve as alternative for more traditional plasmonic materials such as gold (Au) and silver (Ag) for some practical applications. While early in its developmental stage, epitaxial nitride hyperbolic metamaterials could also provide new physics and device functionalities useful for a whole variety of applications.

#### **XIII. CONCLUSION**

In conclusion, development of epitaxial, rocksalt metal/ semiconductor  $(TiN/Al_{0.72}Sc_{0.28}N)$  superlattices marks an important step in heterostructure research field. The simple fact that metals and semiconductors can now be integrated at the atomic-scale with remarkable precision is a significant step forward. Though significant challenges related to the materials and device physics remains to be addressed, six decades of research have finally yielded an epitaxial, nominally single crystalline, lattice-matched metal/semiconductor superlattice system (TiN/Al<sub>0.72</sub>Sc<sub>0.28</sub>N). This is a new material platform for testing of transport physics and design of novel devices.

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