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Epitaxial Nitride Thin Film and Heterostructures: From Hard Coating to Solid State Energy Conversion

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Abstract

Epitaxial nitride thin films and heterostructures are one of the most celebrated class of materials not only due to their utility in fundamental materials science and device physics studies, but also for their numerous industrial applications from hard coating technology to solid-state lighting. Transition metal nitrides such as TiN and others have been utilized for decades in hard coating and tribology applications. The last two decades have also seen the emergence and dominance of GaN for solid-state lighting and power electronic applications. Though TiN, and other wurtzite III-nitride semiconductor such as GaN remain the most important nitride coating materials for a range of applications, several other rocksalt nitride thin film and superlattice heterostructures such as ScN, CrN, and TiN/(Al,Sc)N metal/semiconductor superlattices have attracted significant interests in recent years for applications in thermoelectricity, plasmonics, solar energy conversion, and in high temperature electronic, optoelectronic, and plasmonic devices. In this chapter, we present an up-to-date summary of rocksalt nitride thin film and heterostructure coating materials for their applications in energy transport and conversion research fields. The suitability and usefulness of such nitride coating materials in the most recent scientific and engineering advances related to the energy transport and conversion research fields are highlighted.

Keywords: transition metal nitrides, epitaxy, superlattice, refractory electronics, thermoelectric, plasmonics

1. Introduction

Epitaxial nitride thin film and superlattice heterostructures are one of the most celebrated materials class, not only for their wide ranging industrial applications such as in corrosion resistant hard coating, light emitting diode (LED) and power electronic devices, but also for

their utility as model systems for fundamental materials science studies as well as device physics research. Transition metal nitrides (TMNs) such as TiN have long been used as a coating material in every day home appliances such as watches and others, while III-Nitride semiconductors such as AlN is used in many devices as a dielectric and piezoelectric material. The last 20–30 years have also seen the emergence of GaN as one of the most celebrated nitride semiconductors for its applications in LED and power-electronics/optoelectronics devices.

Such wide-ranging applications of nitride thin film and superlattice heterostructures are inherently related to their excellent properties, which are scarce in most other class of materials. Some of these interesting properties are

- a. *Diversity in electronic properties:* nitrides comprise materials having a full spectrum of electronic properties (from highly conductive metals to excellent dielectric or insulators). For example, TMNs such as TiN, ZrN and others are highly conductive metals with their electrical conductivity as high as traditional noble metals such as Cu, Ag, Au and others in some cases. AlN, BN and others are insulators with large bandgap (>5 eV) and highly resistive, which makes them essential parts in many devices as dielectric layers. GaN, InN, ScN and others are excellent semiconductors with bandgap ranging from few 100 s of meV to several eV. Because of such great diversity in electrical properties nitride have attracted many industrial applications.
- b. *High melting temperature:* nitrides usually possess extremely high melting temperature in ~ 2000 – 3000°C temperature range, which make them suitable for several high-temperature electronic, optoelectronic and plasmonic applications. For example, TiN has a melting temperature of about 2600°C , while the same for GaN is $\sim 2500^\circ\text{C}$.
- c. *Corrosion resistant and high mechanical hardness:* nitride thin film and multilayer heterostructures are well-known to be corrosion resistant and mechanically hard materials with hardness at room temperature ranging more than ~ 25 GPa for thin film to ~ 40 GPa or more for multilayers. Such high hardness and corrosion resistant properties of are extremely useful for many applications such as cutting tools, bearings and in tribology, especially for harsh conditions.
- d. *Potential for large acoustic impedance mismatch:* due to the mass difference of metal atoms forming mono-nitrides, the nitride family of materials offer tremendous opportunity to create large acoustic impedance mismatch. Acoustic impedance mismatch in a heterostructure material creates phonon bandgap, which help in reducing thermal conductivity necessary for several applications such as thermoelectricity. For example, the acoustic impedance mismatch between HfN and ScN resulting from the mass difference between Hf (178.49 u) and Sc (44.95 u) atoms, results in a significantly lower cross-plane thermal conductivity in HfN/ScN multilayers compared to the individual thin films.
- e. *Low homologous growth temperature:* deposition temperature of nitrides is typically much smaller in comparison to their melting temperatures, which assist in uniform thin film and superlattice heterostructure growth with standard deposition methods such as magnetron sputtering, molecular beam epitaxy, chemical vapor deposition and others.

Given such excellent set of physical properties, it is not surprising that nitrides are researched and developed for decades, and many industrial products are available in commercial market having nitride materials as components.

However, more recently, a large number of new properties and functionalities that were previously neglected and were relatively unexplored have emerged with nitrides. TMN semiconductor ScN, and its solid state alloys ($\text{Al}_{1-x}\text{Sc}_x\text{N}$ and others) [1] and superlattices ((Hf, Zr)N/ScN and TiN/(Al, Sc)N) [2] have emerged as attractive materials for solid state energy transport and conversion research fields with applications ranging from thermoelectricity, plasmonics, and solar thermo-photovoltaics. Though several books, books chapter and research articles have addressed the broader implications of nitrides in materials science and solid-state physics, a detailed discussion on the most recent advances of TMNs thin film and superlattice heterostructures on energy transport and conversion research fields are lacking. In this chapter, we will discuss the recent progress and development on the epitaxial nitride thin film and superlattice heterostructures for applications in solid state energy conversion and transport.

2. Nitride thin film and heterostructure growth

Traditionally nitride thin film and superlattice heterostructures are deposited by a variety of deposition techniques such as molecular beam epitaxy (MBE), chemical vapor deposition (CVD), magnetron sputtering, arc discharge method and others. Each of these deposition methods have their own advantages, and both research and development in academia and industries employ deposition techniques suitable for specific applications. For example, corrosion resistant hard coating technology, which has traditionally been the most prevalent application space for nitrides usually employ magnetron sputtering and arc discharge methods. The use of sputtering and arc discharge for hard coating applications are justified as several of such materials such as TiN, $\text{Ti}_{1-x}\text{Al}_x\text{N}$ and others are TMNs having metallic characteristics, and controlling electronic defects are not of great concern. Instead the sputtering and arc discharge methods allow industries large volume scalability, which may not be possible with some of the other methods.

LED and other optoelectronic industries, however, prefer several types of CVD methods due to their high through-puts and industrial scalability. Use of CVD are also necessary due to the requirement of controlling defects in epitaxial nitrides, and selective doping of the materials to *n*-type or *p*-type. For example, GaN based LED and power electronic devices are generally deposited via. Metal organic chemical vapor deposition (MOCVD) technique in industries.

Research and development of nitrides, however, employ almost all available techniques including ultra-high vacuum MBE, magnetron sputtering and others. As unwanted impurities such as oxygen, carbon, halogens, and others could significantly alter the electronic properties of semiconducting nitrides, device research with nitride thin film and heterostructures usually require ultra-high vacuum-based methods. A detailed discussion on each of these deposition techniques are beyond the scope of this book chapter, however, readers could refer to [2] for further details.

3. Historical perspective: TiN as hard coating and GaN as solid-state lighting materials

3.1. Hard coating materials

Hard coating industries are one of the early adopters of nitride thin film and heterostructures. Since tribology applications require materials that are mechanically hard, chemically stable at elevated temperatures with low wear rate and coefficient of frictions over wide working conditions, TMNs such as TiN found immediate attention and applications. Titanium nitride (TiN) is a leading coating material and is used 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 (**Figure 1**). However, the hardness of TiN is relatively low ($\sim 20\text{--}24$ GPa) and the oxidation resistance of TiN in air is limited to temperatures below 700°C , beyond which TiN forms TiO_2 and nitrogen bubbles, which significantly limits its application range [3, 4]. To overcome these limitations, several ternary nitrides thin film coating material have been developed starting from 1980s by solid state alloying TiN with other metals such as aluminum (Al), vanadium (V), molybdenum (Mo), zirconium (Zr), etc. (see **Table 1**).

Titanium-aluminum-nitride ($\text{Ti}_{1-x}\text{Al}_x\text{N}$) is the most celebrated among these ternary nitrides, as it overcomes several limitations of TiN as a coating material. Aluminum atoms exhibit higher mobility compared to titanium atoms, therefore, exposure of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ in air or in oxygen environment results in the formation of thin aluminum oxide layer on $\text{Ti}_{1-x}\text{Al}_x\text{N}$ surfaces at elevated temperatures [3]. Aluminum oxide layer acts as a barrier for further oxygen diffusion inside the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ thin film, thus preventing further oxidation of the nitride film. Such oxidation resistant properties of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ makes it an effective tooling material at elevated temperatures, where TiN fail to operate. Apart from the oxidation resistant behavior, $\text{Ti}_{1-x}\text{Al}_x\text{N}$ also exhibits enhanced hardness (~ 35 GPa) in comparison to TiN (~ 24 GPa) necessary for tribology applications. $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coated cutting tools have also shown excellent wear resistance in machining sticky metals such as aluminum alloys and austenite stainless steel, and widely used in other industries.

Apart from $\text{Ti}_{1-x}\text{Al}_x\text{N}$, several other ternary nitrides have found applications in tribology applications such as titanium-vanadium-nitride ($\text{Ti}_{1-x}\text{V}_x\text{N}$), titanium-molybdenum-nitride

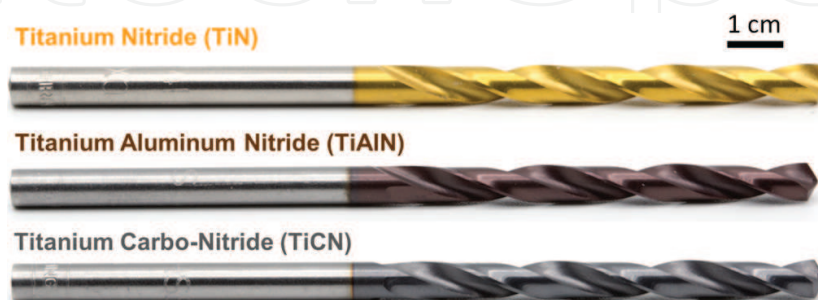


Figure 1. Nitride coating materials used in hard coating applications (adapted from Advanced Coating Service, Rochester, NY, USA).

Material	Deposition technique	Hardness (GPa)	Challenges
TiN	Magnetron sputtering	~24	Oxidation above ~700°C
	Arc discharge method	~25	
$Ti_{1-x}Al_xN$	Magnetron co-sputtering	~24	High temperature stability and AlN cubic-to-wurtzite phase transformation
	Cathodic arc vapor deposition	~27	
	Multiple arc vapor deposition	~35	
$Ti_{1-x}V_xN$	Magnetron sputtering	~28	Lower hardness values
	Cathodic arc ion plating	~26	
	Arc ion plating	~24	
$Ti_{1-x}Mo_xN$	Magnetron sputtering	~30	Low solubility of Mo in TiN
TiN/NbN	Magnetron sputtering	~48	Porosity at column boundary weakens the multilayer
TiN/VN	Magnetron sputtering	~54	–
TiN/CrN	Magnetron sputtering	~37	Poor oxidation resistance and interdiffusion at interface above 700°C
TiN/AlN	Pulsed laser deposition	~30	Extremely low AlN layer thickness
TiN/ $Al_{1-x}Sc_xN$	Magnetron sputtering	~46	–

Significant challenges of each of these coating materials are also highlighted.

Table 1. Hardness of various TMN coating materials are presented along with the deposition methods.

($Ti_{1-x}Mo_xN$), etc. [4]. $Ti_{1-x}V_xN$ is a technologically important thin film coating and it is used in a diverse range of areas such as the packaging industry, transparent barrier coatings, micro-electronics and others. Magnetron sputtered $Ti_{1-x}V_xN$ thin films have high hardness (~28 GPa) and excellent thermal stability [4]. Similarly, $Ti_{1-x}Mo_xN$ is also an effective alternative ternary thin film coating material and is used in industries improve the mechanical properties of TiN. $Ti_{1-x}Mo_xN$ have a lower friction coefficient and wear rates compared to TiN thin film. The hardness of $Ti_{1-x}Mo_xN$ is significantly high at ~30 GPa [4].

Apart from these ternary nitride coating materials, recent study on quaternary titanium-aluminum-scandium-nitride ($Ti_{1-x-y}Al_xSc_yN$) has shown significantly higher hardness of ~46 GPa at room temperature [5]. Experimental results showed that incorporation of a small amount of scandium nitride (ScN) inside $Ti_{1-x}Al_xN$ matrix improved the crystal quality and the hardness of the alloy thin film. The exact mechanism of the hardness enhancement, however, still remains to be addressed in details.

Thin-film multilayers and superlattices are also a potential configuration that realize extraordinarily hard materials with long lifetime at high operating temperatures. Koehler had proposed in the 1970s that the interfaces in multilayers should act as high energy barriers for dislocation motion, thereby increasing hardness [6]. Based on that suggestion, several nitrides

multilayer system (e.g., TiN/NbN, TiN/VN, and TiN/CrN) have been developed in 1990s and 2000s that showed improved hardness compared to TiN and $\text{Ti}_{1-x}\text{Al}_x\text{N}$ thin films (see **Table 1**). However, all of the nitride multilayers mentioned above are miscible at temperatures exceeding 800°C , which significantly limits their usefulness in cutting tool applications, where the surface temperature can reach as high as 1000°C during the cutting process. Cubic (rocksalt)-TiN/AlN superlattices were developed to overcome the miscibility problem since TiN/AlN superlattices are immiscible up to $\sim 1000^\circ\text{C}$. TiN/AlN superlattices also exhibit excellent oxidation resistance, relatively high hardness compared to TiN, and they are already used commercially as a coating material.

However, TiN/AlN superlattice coatings have a significant drawback. The hardness of TiN/AlN superlattices is around 33–35 GPa when the thickness of the AlN layers is less than 2–3 nm but decreases sharply to 23–24 GPa as the AlN layer thickness is increased [5]. This large reduction in hardness is attributed to the transition from the epitaxially stabilized metastable cubic-AlN phase to the stable wurtzite-AlN phase when the AlN layer thickness exceeds the critical thickness of 2–3 nm [7]. The formation of wurtzite-AlN breaks the epitaxial relationship with cubic-TiN leading to polycrystalline grain growth and a significant hardness reduction. The same cubic-AlN to wurtzite-AlN transition is also the cause for deteriorating hardness in industrial $\text{Ti}_{1-x}\text{Al}_x\text{N}$ tool coatings at times.

Saha et al. have successfully addressed this challenge by developing nominally single crystalline cubic-TiN/(Al, Sc)N epitaxial superlattices on MgO substrates, where the (Al, Sc)N is in metastable cubic (rocksalt) phase for more than 120 nm thickness [5]. The lattice-matched superlattices showed increased hardness as a function of the decreasing period thickness proposed by Koehler [6] and for a period thickness of 3 nm, a maximum hardness of 42 GPa was achieved at room temperature. Further analysis related to the temperature dependent hardness evolution and other mechanical properties are needed for TiN/(Al, Sc)N superlattices before its full potential for industrial applications can be realized. Therefore, nitrides are a reliable coating material for more than four-to-five decades, and significant research and development is currently underway with nitrides for their applications as coating materials.

3.2. Solid state lighting materials

While the coating industry continues to develop and utilize nitrides, the last two-to-three decades have seen the emergence of semiconducting GaN for solid state lighting applications and dominated the research and industrial materials development space. GaN have been attractive for blue emission from 1950s owing to its direct gap of 3.4 eV. However, high quality GaN growth on common substrates like Si and Sapphire was a significant challenge. Large lattice-mismatch of GaN with several common substrates rendered poor quality thin films, therefore, sub-standard electronic and optical properties. Moreover, development of *p*-type GaN necessary for LED and other electronic and optoelectronic devices were also significantly difficult.

Significant breakthroughs were achieved in 1970s when using newly developed molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) techniques,

researchers started to grow high quality GaN films. The most significant of these efforts could be attributed to the work of Amano et al. where they deposited high quality GaN thin films by using a polycrystalline AlN as a buffer layer [8]. Similarly, Nakamura et al. at Nichi Chemical Company deposited high quality GaN films by using a low temperature GaN buffer layer with low background of *n*-type doping [9]. Development of low temperature GaN as a buffer layer proved to be an attractive and industry wide approach for mass production of GaN based light emitting devices.

Apart from the materials quality issue, another important challenge in early years was on how to develop *p*-type GaN thin films. Though the idea of *p*-type doping of GaN through the incorporation of Mg was known, most experimental efforts to achieve *p*-type GaN were unsuccessful. Amano et al. managed to develop *p*-type GaN by electron beam irradiation [10]. However, the electron beam irradiation technique was an inefficient method and required a lot of time for hole-doping. Efforts to develop *p*-type GaN with Mg incorporation via chemical vapor deposition methods were also unsuccessful initially. Important breakthrough was made when modeling work showed that Mg bonds with hydrogen (H) thus forming Mg-H complex during the CVD growth process, which prevent the hole-doping activity of Mg and render development of *p*-type GaN difficult. Nakamura et al. addressed this important challenge by annealing Mg-doped GaN in N₂ environment, where Mg frees up from the Mg-H complex and enable *p*-type GaN [11].

The development of high quality GaN thin film growth technique and of *p*-type GaN lead to the ultimate discovery of blue LEDs, which has significantly changed our society. Akasaki, Amano and Nakamura were awarded the 2014 Noble Prize in Physics for their pioneering work on GaN LED development. GaN today is the workhorse for producing blue emission and along with a suitable dye, most commercially available LED light sources employ GaN. Significant efforts are also currently underway to develop GaN based electronic and optoelectronic devices for power-electronic applications.

4. Recent advances in energy transport and conversion

4.1. Thermoelectrics

Thermoelectric materials convert waste heat energy directly into electrical power and are attractive for harvesting energy in automobiles, power plants, and for deep space exploration. Such materials could also be used as a Peltier cooler in microelectronic chips and devices, where unwarranted heat generation (hot spots in integrated circuits (IC)) limit device efficiencies. Devices made from thermoelectric elements are environmentally friendly and they do not have any movable parts except for a fan in most cases. The efficiency of a thermoelectric material is represented by its dimensionless *figure-of-merit*, $ZT = (S^2 \sigma T) / (\kappa_e + \kappa_p)$, where *S* is the Seebeck coefficient, σ is the electrical conductivity, κ_e and κ_p are the electronic and lattice contributions to the thermal conductivity, respectively, and *T* is the absolute temperature. The higher the thermoelectric *figure-of-merit* (*ZT*) of a material, the more efficient the energy

conversion is. To be competitive with conventional power-generator and refrigeration technology, thermoelectric materials need to exhibit a ZT of about 3–4 over a wide temperature range. However, extensive research in the last decade has only improved the ZT to ~ 2 at high operating temperatures [12]. Designing high-efficiency thermoelectric materials having $ZT > 2$ is particularly challenging due to the mutually conflicting design parameters. While the individual thermoelectric materials must exhibit high ZT values at the required temperature ranges of interest, practical thermoelectric devices require both n -type (electron conducting) and p -type (hole-conducting) materials with high ZT s, as well as effective methods to integrate them with metals having low contact resistances. Such restrictions naturally impose additional challenges in terms of material selection and device fabrication techniques.

Traditionally nitrides are regarded as poor thermoelectric materials, primarily because of their higher thermal conductivity. For example, GaN has a room temperature thermal conductivity in excess of 100 W/m-K, which is about two orders of magnitude higher compared to the most celebrated thermoelectric materials like Bi_2Te_3 , having a thermal conductivity of ~ 1 W/m-K at room temperature [2]. Other traditional III-nitride semiconductors (AlN, etc.) also have high thermal conductivity, which significantly limits their suitability in thermoelectricity. Apart from the high thermal conductivity, most commonly known nitrides also do not possess electronic properties that are commensurate for high ZT , such as (a) asymmetric distributions of density of states near the Fermi energy, (b) suitable carrier density (electron or hole) of $\sim 10^{19}/\text{cm}^3$ and others, which has limited the exploration of nitrides as thermoelectric materials for a long time.

This situation has changed significantly in recent years with the emergence of scandium nitride (ScN) as a rocksalt (cubic) semiconducting material. ScN is a promising group III (B)-nitride semiconductor with an indirect bandgap and octahedral coordination [2]. Like most other transition metal nitrides (TMNs), ScN is structurally and chemically stable, mechanically hard (23 GPa), corrosion resistant, and possesses high melting temperatures in excess of 2873 K. Due to its rocksalt (cubic) crystal structure, ScN also offers a materials platform for engineering the band structure of alloys with the III–V nitride semiconductors (AlN, GaN, and InN, which adopt the wurtzite crystal structure without ScN) for applications where integration of the semiconductor with cubic(rocksalt) metals is required.

Although controversies persisted about the nature of its electronic structure during the 1990s and early 2000s, recent experimental results and theoretical modeling have demonstrated conclusively that ScN has an indirect bandgap of 0.9–1.2 eV and a direct gap of 2.2 eV. Kerdsonpanya et al. have demonstrated an extremely large power factor of $2.5 \times 10^{-3} \text{ W/m-K}^2$ in ScN thin films grown on Al_2O_3 substrates [13]. While later research by Burmistrova et al. have improved the power factor values to $\sim (3.3\text{--}3.5) \times 10^{-3} \text{ W/m-K}^2$ at 600–850 K in sputter deposited n -type ScN thin films grown on MgO substrates [14]. These power factors at 600–850 K temperature ranges are higher than those of Bi_2Te_3 and its alloys at 400 K, as well as the best high-temperature thermoelectric materials such as La_3Te_4 at 600 K and compare well with undoped crystalline SiGe in the same temperature range. The origin of such large power factors can be explained by the changes in ScN's electronic structure with respect to the presence of point defects and impurities (such as Sc and N vacancies, and doping effects of O and C on N-sites, and Ca and

Ti on Sc sites on ScN's electronic structure). For sputter deposited ScN grown on MgO substrate, Burmistrova et al. have showed that as-deposited ScN thin films exhibit a large *n*-type carrier concentration of $(1-6) \times 10^{20} \text{ cm}^{-3}$ due to the presence of oxygen as unwanted dopant impurities incorporated during deposition [14]. Several other studies have also reported the presence of carbon (C) and fluorine (F) as impurities inside sputter-deposited ScN thin films, which could potentially be electronically active [15].

The high electrical mobility of $\sim 100 \text{ cm}^2/\text{Vs}$ at room temperature and $\sim 3 \times 10^{20} \text{ cm}^{-3}$ carrier concentration creates a favorable condition for high thermoelectric power factors in ScN, evidenced by the measured Seebeck coefficient of $-156 \mu\text{V/K}$, and an electrical conductivity of $\sim 1300 \text{ S/cm}$ at 840 K [13] (**Figure 2**). Modeling analysis have showed that unwanted impurities such as oxygen incorporation during growth process dope the material heavily *n*-type and shift the Fermi level from inside the bandgap to inside the conduction band. Though the thermal conductivity of ScN thin films ($\sim 14 \text{ W/m-K}$) are not as high as many other traditional III-nitrides, it is still higher than the values suitable for achieving high ZT. The best obtained ZT values for ScN is 0.18 at 800 K temperature.

Significant efforts have been made in recent years to reduce the thermal conductivity of ScN with the development of ScCrN and ScNbN solid-solution alloys, which exhibit reduced thermal conductivities due to increased alloy scattering [16, 17]. However, like the challenges encountered in most other thermoelectric materials systems, the reduction in thermal conductivity must be attained without reducing the power factor, for achieving higher *figure-of-merit* (ZT). In this regard, incorporation of nanoparticles, phase separation, a small amount of heavy element inclusion, and other approaches may be explored. For example, incorporation of rare-earth metallic nanoparticles such as ErAs inside GaAs and InGaAlAs matrix have already demonstrated enhanced thermoelectric performance in such semiconductors [12]. Similarly, heavy metallic nitrides such as ZrN, HfN or WN could be incorporated inside ScN matrix, and the thermoelectric properties could be explored.

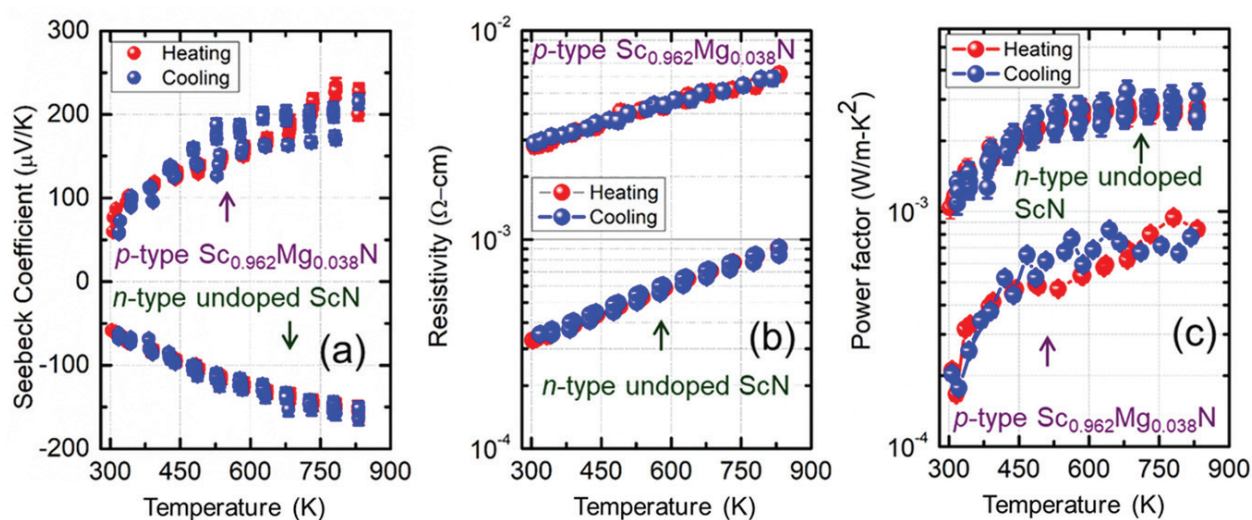


Figure 2. Temperature dependence of (a) Seebeck coefficient, (b) resistivity and (c) power factor of n and p-type of ScN. Reprinted with permission from Saha et al. [15]. Copyright 2018 American Physical Society.

While the large power factor in the as-deposited *n*-type ScN is attractive for thermoelectricity, practical devices also require a highly efficient *p*-type material. Reducing the carrier concentration in ScN, and eventually turning it into a *p*-type semiconductor was also important for a host of other applications. Saha *et al.* have demonstrated *p*-type $\text{Sc}_{1-x}\text{Mn}_x\text{N}$ and $\text{Sc}_{1-x}\text{Mg}_x\text{N}$ thin film alloys by solid-state alloying of ScN with Mn_xN_y and Mg_xN_y , respectively [2]. The *p*-type $\text{Sc}_x\text{Mg}_{1-x}\text{N}$ thin film alloys were found to be (a) substitutional solid solutions without any detectable Mg_xN_y precipitation, phase segregation, or secondary phase formation; (b) exhibited a maximum hole-concentration of $2.2 \times 10^{20} \text{ cm}^{-3}$ and hole mobility of $21 \text{ cm}^2/\text{Vs}$; (c) did not show any defect states inside the direct gap of ScN, thus retaining its basic electronic structure; and (d) exhibited impurity scattering by Mg addition that dominated hole conduction at high temperatures. The *p*-type $\text{Sc}_x\text{Mg}_{1-x}\text{N}$ thin film alloys also exhibit very high Seebeck coefficients, in excess of $200 \mu\text{V/K}$. However, due to the reduced mobility, the electrical conductivities are an order of magnitude lower, which results in a lower power factor values.

Apart from ScN, chromium nitride (CrN) has shown great promise for thermoelectric applications. Thermal conductivity of CrN is much smaller compared to ScN thin film, and as a result it may be possible to engineer CrN for high thermoelectric *figure-of-merits* (ZT). Similarly YN and several other rare-earth nitrides such as GdN, ErN, etc. exhibit semiconducting properties. Due to their higher atomic mass, such materials should exhibit lower thermal conductivity, and could be explored for thermoelectric applications.

4.2. Plasmonics

Traditionally noble metals such as Au and Ag are regarded as the best plasmonic materials in the visible spectral range both for research as well as for limited number of industrial applications. However, noble metal-based plasmonic components have materials properties that significantly limit realization of practical plasmonic devices [18]. Some of the severe materials challenges with noble metals are (a) incompatibility with standard complementary metal oxide semiconductor (CMOS) fabrication processes, (b) noble metals are morphologically not stable at high temperatures $>500^\circ\text{C}$, (c) the real part of the dielectric permittivity (ϵ') for noble metals are too large for several applications, (d) because of their high surface energies noble metals are difficult to fabricate in thin film or ultrathin film form, and (e) it is difficult to engineer optical properties of noble metals through materials engineering. Due to such materials challenges real life applications of plasmonics as a research field with noble metals have been extremely limited to only a handful of applications.

Transition metal nitrides and their epitaxial metal/semiconductor superlattices have enormous promise and potential in the plasmonics research field as they overcome several of the shortcomings of noble metals [18]. Optical characterizations have showed, that TiN and ZrN are excellent plasmonic materials in the visible spectral range (500–900 nm) [19]. The real part of the dielectric permittivity (ϵ') of TiN and ZrN (**Figure 3**) are smaller compared to noble metals (such as Au and Ag films) due to their relatively lower carrier concentrations. For several practical applications such as in devices for transformation optics, or in hyperbolic metamaterials, lower values of ϵ' are a necessity and the nitrides have already attracted significant interest in that pursuit. The imaginary parts of the dielectric permittivity (ϵ'') of

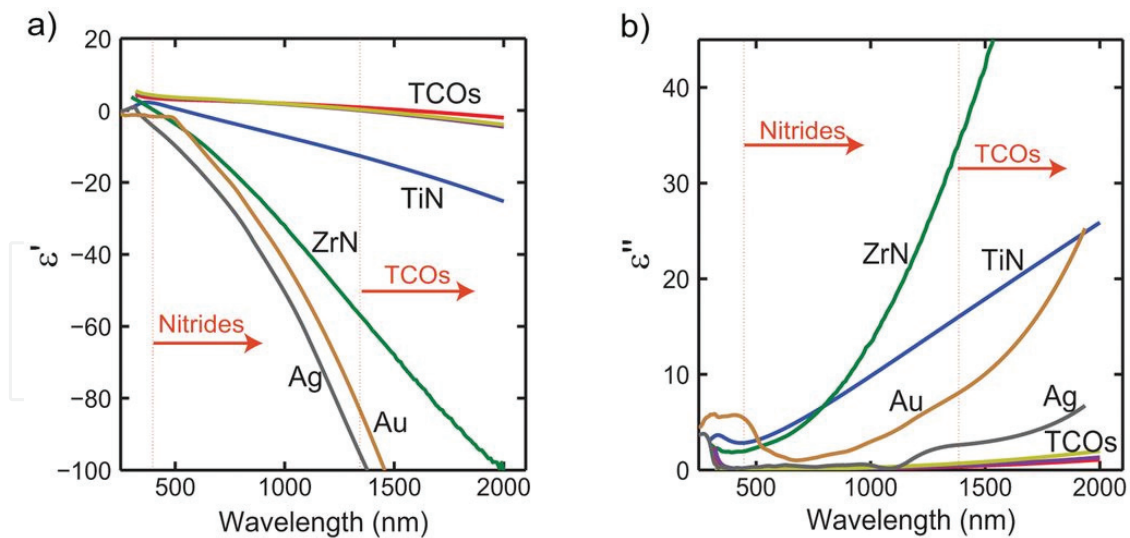


Figure 3. (a) Real (ϵ') and (b) imaginary (ϵ'') parts of the dielectric permittivity of TMNs such as TiN, ZrN and TCOs (AZO, GZO and ITO) are plotted along with those of gold and silver. The arrows show the wavelength ranges in which nitrides and TCOs are respectively metallic. Reproduced with permission from Naik et al. [19]. Copyright 2011 Optical Society of America.

the nitrides (**Figure 3**) however, are larger compared to noble metals due to increased inter-band transitions, which is a limitation.

Detailed studies on the plasmonic 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 nitrides (e.g. TiN, ZrN and others) in comparison to Au and Ag. Vigorous research activity is currently underway to convert the wonderful optical properties of nitrides into device applications.

4.3. Solar selective coating technology

Solar selective coatings are spectrally selective layers which has high absorptance in visible region and high reflectance (or low thermal emittance) in IR region of solar spectrum. These spectrally selective coatings are used to efficiently capture sunlight as heat in solar thermal converters, which has variety of applications such as solar water heating, solar thermal electricity generation, solar thermoelectric generator, solar thermophotovoltaics, etc. Though solar thermal conversion has been used for water heating purposes for several years, currently this technology is gaining significant attention in electricity production as it has achieved overall efficiency >30% and more suitable technology for large scale electricity production. In addition, solar thermal technology has efficient ways to store heat energy so that it can be used to generate power in overcast conditions and also at night.

Conversion of solar radiation into useful heat energy is dependent on the optical properties of the solar selective materials such as α , the solar absorptance (fraction of the solar energy absorbed by a surface) and ϵ , the thermal emittance (fraction of radiant energy emitted from the surface with respect to energy radiated by a blackbody at same temperature). Ideally a

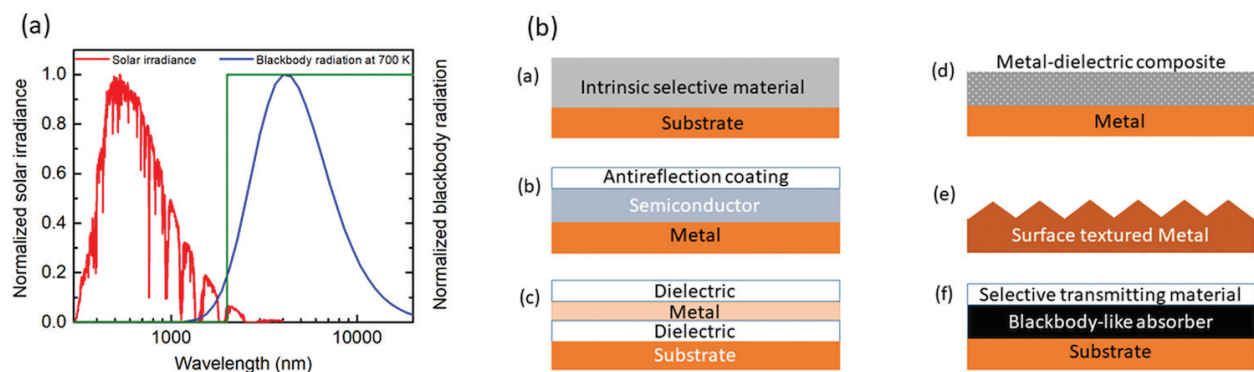


Figure 4. (a) Spectral reflectance for an ideal solar selective surface (green line) compared with solar spectrum (red line) and black body radiation (blue line) and (b) schematic diagram of different type of solar selective coating.

selective surface must have α close to 1 in the wavelength range of 0.3–2 μm of the solar emission spectrum, which covers the 95% of the solar energy and ε close to 0 beyond 2 μm (**Figure 4a**).

However, in practice most material surfaces do not meet these requirements perfectly. Therefore, the research has been focused on materials in order to maximize α at the same time reducing ε as lower values. Since solar thermal electricity production requires high operating temperatures in excess of 500°C, in addition to these optical properties the solar selective materials must be stable at such operating temperature. Several types of spectrally selective coatings have been developed based on the following concepts (**Figure 4b**): (a) intrinsic absorber, (b) metal-semiconductor tandem, (c) multilayer absorbers, (d) multi-dielectric composite, (e) textured surface, and (f) selectively solar-transmitting coating on a blackbody-like absorber, etc.

Intrinsic absorbers such as W, Mo doped-MoO₃, ZrB₂, etc. inherently have spectral selectivity induced by dielectric dispersion as a function of wavelength. Though such materials are easy to fabricate, their spectral selectivity is less than ideal and require some kind of structural and compositional modification to achieve near-ideal spectral selectivity. Therefore, combination of design concepts such as metal-semiconductor tandem, multilayer absorbers, metal-dielectric composites, etc. are most widely studied. In metal-dielectric composites, cermet (metal nanoparticles dispersed in dielectric matrix) such as Mo-Al₂O₃, W-AlN, Mo-AlN, Mo-SiO₂, W-Al₂O₃, Cr-Cr₂O₃, etc. have been investigated as selective coatings for high temperature applications. These composite coatings exhibit excellent solar selectivity and are thermally stable in vacuum. Hence they are already commercialized by many manufactures such as Luz International Ltd., USA, Siemens (formerly Solel), Germany, Archimede Solar Energy, Italy and Schott, Germany [20]. Major concerns with these cermet based coatings is their thermal stability in air above 400°C. Beyond this temperature the optical properties, emittance in particular, starts degrading due to oxidation and/or diffusion of metal particles.

TMNs possess a good combination of chemical, mechanical properties, and are extremely stable at high-temperatures. Until last decade the optical properties of the TMNs were rarely studied. Initial studies on optical properties of TiAlN and TiAlON have exhibited high absorption coefficient and low reflectance in visible region [21, 22]. Further studies on TiN based compounds

showed that the refractive index, absorptance or reflectance, can be tuned from that of metallic to dielectric characteristic by varying the composition and/or by incorporating O, N, C and Si. This can be attributed to changes in the electronic structure and bonding nature (i.e., metallic to covalent) with the change in stoichiometry of TiN based compounds and incorporation of elements such as Al or O, respectively [20]. In addition, these TMNs can act as diffusion barrier for metals, which may diffuse into the absorbers or oxidize at high operating temperatures (above 400 °C). Consequently, preventing the degradation of optical properties of the coatings [23]. These properties give TMNs an edge over cermets for high temperature (i.e., above 500°C) solar selective applications.

Taking advantage of these properties, several groups have developed TMN based tandem (metal/dielectric) solar selective coatings. For instance, Barshilia et al. fabricated TiAlN/TiAlON/Si₃N₄ solar selective tandem absorbers on copper substrate demonstrating high solar selectivity 0.95/0.06 and thermal stability up to 525°C in air (50 h) and 800°C in vacuum [23]. In this case, TiAlN (metallic in nature) acts as a main absorber, TiAlON (with low metallic content) acts as a semi-absorber and Si₃N₄ as an antireflection coating. The tandem absorber was fabricated such that the refractive index (in visible region) gradually increases from the coating surface to substrate. Such graded refractive index ensures that reflectance is minimized in visible region and absorptance is increased. Following this many other transition metals-based nitride, oxynitride, carbonitrides coatings have been developed in order to improve solar selectivity and thermal stability further, which are listed in **Table 2**. Detailed review on various combination of TMNs based solar selective coatings, their optical properties and growth methods can be found in Ref. [20].

4.4. Hot-electron collection for solar water splitting

Solar water splitting is a well-known photocatalytic process used to produce molecular hydrogen, which is an attractive source of energy as it can be stored, transported and consumed as a fuel on demand. The photocatalytic reaction is driven by the electrons and holes generated in a semiconductor in response to the absorbed photons. Efficiency of such a solar-to-fuel conversion

Absorber	α	ε	Thermal stability (°C)	
			Air	Vacuum
TiAlN/TiAlON/Si ₃ N ₄	0.93–0.94	0.15–0.17	550	600
NbAlN/NbAlON/Si ₃ N ₄	0.93–0.95	0.07	500 (2 h)	600 (2 h)
TiAlN/CrAlON/Si ₃ N ₄	0.94–0.95	0.05–0.07	500 (2 h)	800 (2 h)
HfMoN/HfON/Al ₂ O ₃	0.94–0.95	0.13–0.14	475 (34 h)	600 (450 h)
TiAlC/TiAlCN/TiAlSiCN/TiAlSiCO/TiAlSiO	0.96	0.07	500 (2 h)	900 (2 h)
			325 (400 h)	650 (100 h)
NbTiON/SiON	0.95	0.07	–	500 (40 h)
Mo/ZrSiN/ZrSiON/SiO ₂	0.94	0.12	–	500 (500 h)

Table 2. TMNs based metallic/dielectric tandem absorber along with their absorptance, emittance and thermal stability at different ambiances.

is limited by the (a) short-range of light response of the semiconductor catalysts (used as photoelectrode) dictated by their bandgap and (b) smaller diffusion length of the photo-generated carriers than the photon absorption depth resulting in carrier recombination, instead of contributing in solar-to-fuel conversion. In order to overcome these limitations several strategies have been developed such as (a) doping/alloying of the semiconductor to tune its band structure, (b) fabrication of heterostructures to efficiently separate charge carrier at the junctions, (c) decreasing the particle size of the catalysts to efficiently collect carriers before they could recombine and (d) synthesize faceted nanostructures that are catalytically more active.

Tian and Tatsuma developed a new strategy to use plasmonic metal nanoparticles to enhance the photocurrent, and thereby improve solar-to-fuel conversion efficiency [24]. While traditionally plasmonics are used to confine light into nanoscale volume to provide intense electromagnetic localization and improved light scattering, in this work the plasmon decay was used to generate energetic electrons (hot electrons) and metal-semiconductor interface for charge separation. Using such phenomena in Au-TiO₂ photoelectrode, the authors demonstrated an improvement in incident photon to current conversion efficiency (IPCE) by more than 20× in the presence of suitable donors. Advantage of using plasmonic photoelectrode over that of semiconductor is that photons with energy lesser than bandgap can also be absorbed through plasmon resonance, hence, has a broadband photo-response. In Au-TiO₂ case, photon absorption and carrier generation for TiO₂ takes place at UV region (≈380 nm) and that for Au at its plasmon band (≈520 nm). This will result in enhanced photocatalytic efficiency.

Several plasmonic based photocatalysis systems have been developed in terms of metal-semiconductor combinations and their structural configurations such as Au (nanorod)/TiO₂-Co-borate (oxygen evolution catalyst) grown electrochemically using anodized alumina template [25], Au/CeO [26], Au decorated 3D structured ZnO [27], etc. However, in such plasmonic structures, the extraction of hot electron (generated due to plasmon decay) from metal nanoparticle is limited by the Schottky barrier. The electrons with energy higher than the potential barrier (ϕ_B) can only be collected at electrode. This limitation is imposed by the larger difference between work function and electron affinity of largely used noble metal (i.e., Au and Ag) and semiconductors (TiO₂ and ZnO), respectively.

In order to overcome the limitation imposed by large Schottky barrier, Naldoni et al., developed a novel photoanode using TiN based plasmonic nanoparticle decorated on TiO₂ nanoroads [28]. With TiN(nanoparticle)/TiO₂, they have demonstrated twice as many hot electrons as Au nanoparticle injection into TiO₂, i.e., 25% increase in photocurrent in comparison to Au/TiO₂. The observed enhancement in performance has been attributed to the broadband absorption (500–1200) of cubic TiN as well as lower work function of TiN ($\phi_M \approx 4$ eV) in comparison to Au ($\phi_M \approx 5.2$ eV) (see **Figure 5**). This work has opened up a new avenue for several other metallic TMNs similar to TiN and ZrN, which found to exhibit Au-competitive optical properties.

4.5. Refractory electronics and plasmonics

TMNs are well known refractory materials that are chemically, structurally, and morphologically stable at high temperature. Further, the TMNs are electronically diverse with insulators,

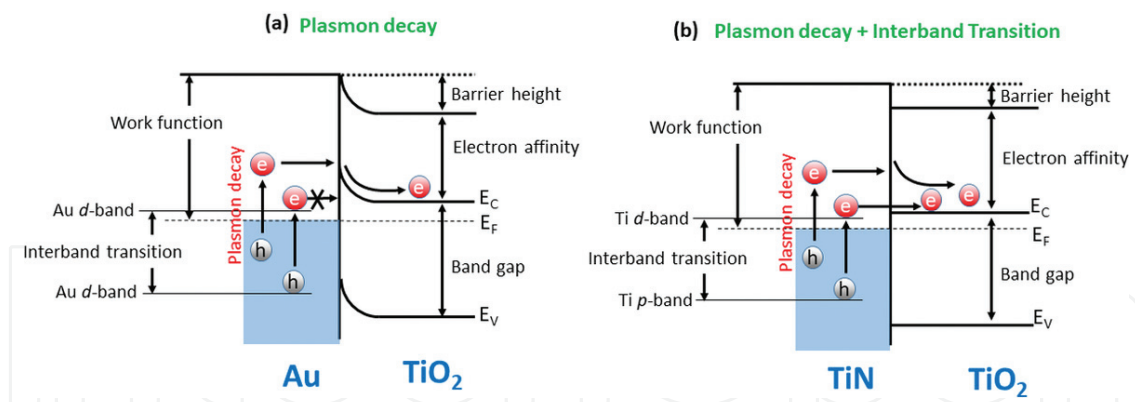


Figure 5. Schematic representation of plasmon induced hot electron collection in (a) Au-TiO₂ photoelectrode and (b) TiN/TiO₂ photoelectrode.

semiconductors, metals, and their heterostructures offering novel electronic and optoelectronic properties that are not present in other material systems. For high-temperature and high-power applications materials must have high melting point, large breakdown voltage, ability to dope preferentially *n*- and *p*-type and ability to form stable metal/semiconductor or metal/dielectric contacts (interface) for high temperature operations. Diverse properties of TMNs makes it a suitable candidate for such applications. Previously, stable epitaxial and low resistive contacts for high temperature applications with traditional metals was difficult due to their high surface energy and lack of crystal structure compatibility leading to misfit dislocations and defect states. However, recent efforts to grow epitaxial TMNs have shown that wide range of binary and ternaries such as $\text{Ti}_x\text{Me}_{1-x}\text{N}$ and $\text{Ta}_x\text{Me}_{1-x}\text{N}$ ($\text{Me} = \text{Ti, Zr, Hf, Nb, Ta, Mo, W}$) with stable cubic rocksalt structure [29, 30]. With ternary alloying of TMNs, tunable lattice parameter (0.416–0.469 nm) and electronic properties such as bandgap, conductivity, work function (3.7–5.1 eV), etc. can be achieved [31]. This flexibility of TMNs in lattice parameter (also, close to III–N) and work function has made them attractive for electronic device application such as diffusion barriers [32], metallization and lattice matched growth templet for wide bandgap semiconductors [33], which are used in high power devices. Apart from these passive components, TMNs are also finding application in nanoelectromechanical systems (NEMS) such as TiN cantilever-type nanoelectromechanical switch fabricated using CMOS process [34]. The fabricated switches exhibited excellent performance and TMNs gives robustness to such devices at harsh environment such as radiation and high temperature.

Until recent years, realization of electronic devices with TMNs as active a component was not possible due to the fact that most known TMNs are metallic and non-availability of suitable semiconducting TMNs. However, recent research works revealed that ScN (indirect bandgap 0.9 eV) and rocksalt- $\text{Al}_x\text{Sc}_{1-x}\text{N}$ (direct bandgap 2.2–3.7 eV) are semiconductors and can be doped preferentially both *n*- and *p*-type [15]. This has opened up a new direction for the development of new refractory electronic devices fully based on TMNs. Future research on the epitaxial growth of rocksalt nitride semiconductors heterostructures will be useful for the exploring device properties such as intersubband absorption and emission, confinement of electrons in metallic wells, photodiodes, photo-conductors, and terahertz devices.

Refractory optics and plasmonics with TMNs is yet another emerging and immensely promising research direction. Traditional plasmonic materials i.e., noble metals have highly limited absorption band width because of its resonant nature of plasmon excitation and high reflection in non-resonant frequencies. In addition, noble metals have low melting point, hence, poor thermal stability at high temperature and easily diffuses into surroundings. On the other hand, refractory metals such as W, Mo and others exhibit plasmon resonance in IR region with relatively high losses. Whereas TMN nitrides with their high melting temperatures and Au-competitive optical properties could replace current polycrystalline refractory metals for high-temperature applications. Making use of these superior properties, Li et al. developed a TiN-SiO₂-TiN broad band solar absorber, which can absorb 95% of light over the range of 400–800 nm with 240 nm thick device [35]. Similarly, Ishii et al. fabricated TiN-ZnO-TiN structure, which showed superior performance in comparison to gold in visible region [36]. Both these devices were chemically robust, stable at high temperature and can be used in several emerging technologies such as solar-thermophotovoltaics (STPV), heat-assisted magnetic recording (HAMR).

5. Transition metal nitride metal/semiconductor heterostructures

Transition metal nitrides have been utilized in recent years to develop the first epitaxial, nominally single crystalline TiN/(Al,Sc)N metal/semiconductor superlattices on MgO substrates. Rocksalt Al_{1-x}Sc_xN thin alloy films were developed with high AlN mole-fractions and critical thickness on TiN/MgO substrates by solid-state alloying of ScN and AlN. The lattice-matched TiN/(Al,Sc)N metal/semiconductor superlattices exhibit atomically sharp interfaces, structurally stable at high temperatures ($\sim 950^\circ\text{C}$), and amenable to doping, alloying and quantum size effects.

These novel (Ti,W)N/(Al,Sc)N metamaterials (**Figure 6**) have already exhibited lower thermal conductivity (~ 1.7 W/mK at room temperatures) suitable for their thermoelectric applications. Coherent phonon thermal transport phenomenon was also demonstrated recently in these materials. Saha et al. have demonstrated hyperbolic dispersion of photonic iso-frequency surfaces in these materials and enhanced photonic densities of states. Significant

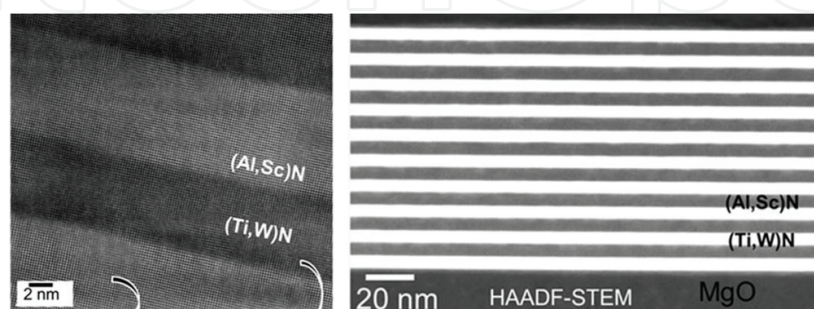


Figure 6. HRTEM and HAADF-STEM image of the superlattices (Ti,W)N/(Al,Sc)N. Reproduced with permission from Saha et al. [37]. Copyright 2016 American Physical Society.

research is currently underway to unlock several aspects of their physical properties to develop practical devices.

6. Conclusions

TMNs have been the most important materials for industrial applications such as hard coatings, corrosion and wear resistant coatings for many decades owing to their high mechanical strength, thermal stability and chemical inertness. There has been significant progress in the understanding of process-structure-properties relationship of TMNs over the years. Now it is possible to fabricate wide variety of alloys and composites of TMNs with diverse and engineerable properties which were not available earlier. This has resulted in new device applications of TMNs such as solar selective absorbers, refractory plasmonics, photocatalysis, etc. Further, the development of stable epitaxial TMNs, heterostructures and superlattices has opened up new directions for refractory electronic device applications. Particularly, recent development of semiconducting rocksalt ScN and $\text{Al}_x\text{Sc}_{1-x}\text{N}$ and their high n - and p -type dopability has further widened the scope for new device applications such as active components in thermoelectrics, electronic and optoelectronic devices. Future research on the epitaxial growth of rocksalt nitride semiconductor heterostructures will be useful for many emerging and novel industrial applications. 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, photo-conductors and terahertz devices.

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