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Growth of TiN/GaN metal/semiconductor multilayers by reactive pulsed laser deposition

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TiN/GaN metal/semiconductor multilayers were grown by reactive pulsed laser deposition in an ammonia ambient on sapphire and MgO substrates for potential application in solid-state thermionic direct energy conversion devices. Crystallographic analysis of the multilayers by high-resolution x-ray diffraction and cross-sectional transmission electron microscopy revealed that, despite the difference in the crystal structures of rocksalt TiN and wurtzite GaN, it is possible to grow thick (micron scale) uniaxially textured columnar-grained multilayers with nanoscale periods and without agglomeration. X-ray scattering suggests that epitaxial growth of TiN/GaN multilayers on (100) MgO substrates stabilizes ultrathin (1–2 nm) GaN layers in the high-pressure rocksalt polymorph yielding (100) oriented rocksalt TiN/GaN superlattices. The challenges in growth and the chemical and morphological stability of lattice- and structure-mismatched multilayers are discussed on the basis of kinetic and thermodynamic factors. © 2006 American Institute of Physics.

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I. INTRODUCTION

Conventional thermoelectric materials are engineered by alloying and doping to maximize the materials figure-of-merit, $Z=S^2\sigma/k$,¹ where S is the Seebeck coefficient (V/K), σ is the electrical conductivity ($\Omega^{-1}\text{m}^{-1}$), and k is the thermal conductivity (W/m K). The numerator of Z (i.e., $S^2\sigma$), known as the “power factor,” is usually the highest for degenerate semiconductors, as these materials have both high conductivity and a large offset in the average energy of the conduction electrons with respect to the Fermi energy (proportional to S). Materials with high densities of states near the Fermi energy and high carrier mobilities, as might be achieved through quantum confinement, offer promise for improving the power factor.^{2,3} Recently, a radically different approach to enhancing the power factor through energy barrier filtering has been proposed by Mahan and Woods⁴ and Vashaee and Shakouri.⁵ By combining high electron concentrations, as in a metal, with semiconductor barriers that introduce the desired asymmetry in the conduction electron distribution relative to the Fermi energy, substantial improvements in the power factor may be expected. The high interface density in the direction of conduction should reduce the thermal conductivity,^{6–8} an effect that may prove to be at least as important as power factor enhancement is to improving Z .

Exploring the potential of this approach requires the development of metal/semiconductor multilayers or superlattices with nanoscale periods and Schottky barrier heights that are tunable to the range of several times $k_B T$. It is necessary that the metal and semiconductor phases do not react to form

a third phase. Furthermore, the driving force for interdiffusion should be small. Even if the metal-semiconductor couple is thermodynamically stable (i.e., tie lines connect the two phases in the equilibrium phase diagram), a multilayer of that metal and semiconductor will not be morphologically stable. In the simplest model based on capillarity, if the semiconductor wets the metal, the metal will not wet the semiconductor and vice versa.⁹ In practice, morphologically metastable multilayers of two disparate materials can be prepared at low homologous temperatures, yielding amorphous or nanocrystalline materials. At the other extreme, two materials with nearly identical crystal structures, bonding, and lattice parameters can be prepared in the form of coherent epitaxial superlattices [e.g., AlAs/GaAs (Ref. 10)]. The small values of excess interfacial free energy per unit interface area result in a small driving force for agglomeration. Attempts to fabricate epitaxial metal/semiconductor multilayers with continuous metal layers have failed in the past due to the relatively large excess interfacial free energy and the mismatch in excess surface free energies. Examples include silicide/Si (e.g., NiSi₂/Si),¹¹ B2 intermetallic/AlAs (e.g., NiAl/AlAs),^{12,13} and rare earth monophenide/GaAs (e.g., ErAs/GaAs).¹³

In this paper, the mutually stable combination of TiN (rocksalt structure) and GaN (wurtzite structure) is shown to be amenable to the deposition of textured polycrystalline metal/semiconductor multilayers with periods as small as 3.4 nm. The growth of these multilayers by reactive pulsed laser deposition (PLD) is described. Preliminary analysis of TiN/GaN multilayers with GaN layer thicknesses less than 2 nm indicates the formation of epitaxial superlattices in which the high-pressure rocksalt phase of GaN has been stabilized by lattice coherency with rocksalt TiN. The implica-

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tions of these results for the design of solid-state thermionic power generators operating at moderate hot-side temperatures (300–650 °C) are discussed.

II. EXPERIMENTAL METHODS

The TiN/GaN multilayers were grown on (0001) sapphire substrates using reactive pulsed laser deposition in a high vacuum deposition chamber (a modified NanoPLD™ system by PVD Products, Inc.), with a base pressure of 10^{-7} torr, in a flowing ammonia process gas ambient at a pressure of 20 mtorr. A 248 nm KrF excimer laser (Lambda Physik 305i) with a pulse width of 25 ns, pulsed frequency of 5 Hz, and target fluence of 8 J/cm^2 was incident at an angle of 45° onto the target. TiN layers were deposited from a TiN compound target while GaN was deposited from a liquid gallium target. The substrate was maintained at a temperature of 585 °C during deposition, as determined using an infrared pyrometer. To ensure uniform film deposition, the targets and the substrate were rotated during the deposition and the laser beam was rastered over the target surface.

Prior to deposition, the sapphire substrates were ultrasonically cleaned in acetone and isopropanol and then rinsed in de-ionized water followed by chemical etching in a 3:1 solution of sulfuric acid:phosphoric acid ($\text{H}_2\text{SO}_4\cdot\text{H}_3\text{PO}_4$) at a temperature of 100 °C for 15 min. After etching, the sapphire substrates were rinsed in de-ionized (DI) water for 3 min and then mounted with indium on a molybdenum disk. The substrates were then nitrided inside the deposition chamber at a temperature of 585 °C for 30 min to allow for AlN formation at the surface at a nitrogen pressure of 10 mtorr and a flow rate of 55 SCCM (SCCM denotes standard cubic centimeter per minute at STP). To systematically study the growth characteristics, interface roughness and texture in the TiN–GaN multilayers, five such multilayers with increasing periods (λ), henceforth referred to as ML1–ML5 in the order of increasing period thickness, were grown on sapphire substrates using the process described above. Additionally, a wider range of multilayers with different period thicknesses were grown using the same growth conditions on sapphire and MgO substrates.

III. RESULTS

The multilayer structure after growth was analyzed using cross-sectional transmission electron microscopy (TEM). TEM images of the samples confirmed the presence of a uniform, pinhole-free, layered structure. No sign of any interfacial reaction was seen, in agreement with the Ti–Ga–N ternary phase diagram¹⁴ that shows tie lines between stoichiometric (1:1) TiN and GaN. TEM cross-sectional images (Fig. 1) showed the presence of polycrystalline layers with columnar grains and a uniaxial texture that extends through the multilayer cross section. Electron diffraction patterns confirmed the presence of textured polycrystalline wurtzite GaN and rocksalt TiN.

X-ray diffraction scans obtained from the five multilayers (samples numbered ML1–ML5) grown on sapphire substrates are shown in Fig. 2; these data confirm the presence of a preferred uniaxial texture with $\{111\}$ TiN parallel to

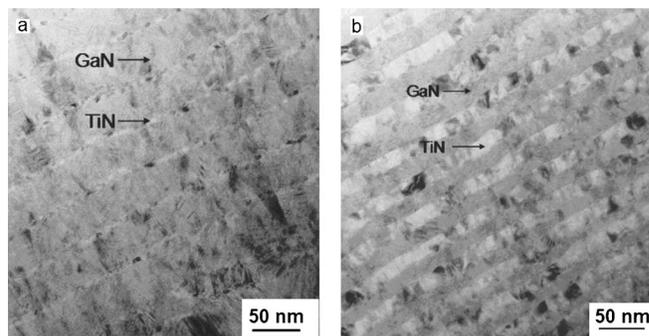


FIG. 1. Cross-sectional TEM images of (a) a TiN(5 nm)/GaN(30 nm) multilayer grown on a (0001) sapphire substrate and (b) a TiN(20 nm)/GaN (variable thickness) multilayer grown on a (100) MgO substrate.

$\{0001\}$ GaN, corresponding to parallel alignment of the triad symmetry elements in the point groups of the two crystal structures. Note that the lattice mismatch between a (111) oriented and relaxed TiN ($a=0.424 \text{ nm}$) film and a (0001) oriented and relaxed GaN film ($a=0.319 \text{ nm}$ and $c=0.518 \text{ nm}$) with the orientation relationship, $\text{TiN}(111) \times [1\bar{1}0] \parallel \text{GaN}(0001)[11\bar{2}0]$, is 6%.

The polycrystallinity of the multilayer introduces roughness at the TiN/GaN interfaces that was quantitatively assessed by grazing incidence x-ray reflectivity measurements. The measured x-ray reflectivity spectra were fit to model spectra using Philips WINGIXA™ software to obtain the root-mean-square interfacial roughness and the period thickness. The reflectivity spectrum for one of the samples, ML2, and the corresponding fit are shown in Fig. 3. The fitted roughness values for all of the multilayers are listed in Table I.

The elemental compositions of the multilayers as a function of depth were measured using Rutherford backscattered spectroscopy (RBS) at Thin Film Analysis Inc. (Santa Clara, CA) using a General Ionex Model 5110 with a 1 MV Tandem Accelerator. The RBS spectra were analyzed using DETECTOR™ software developed by MeV Technologies, Inc. The nitrogen content in all five multilayers was found to be approximately 50 at. % throughout the depth of the sample,

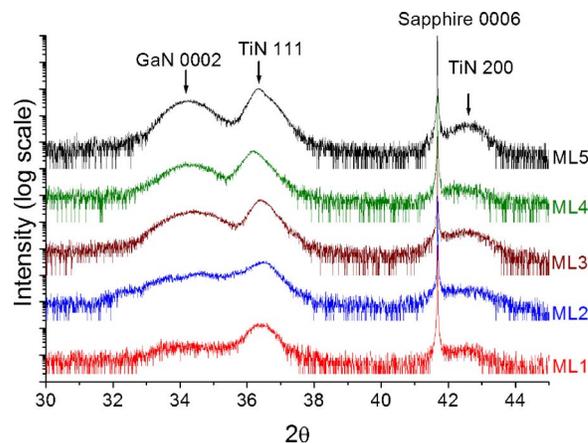


FIG. 2. (Color online) ω - 2θ symmetric θ - 2θ x-ray scans obtained from the TiN–GaN multilayers grown on sapphire with periods of, as measured by RBS, (a) ML1, $\lambda=3.4 \text{ nm}$, (b) ML2, $\lambda=6.8 \text{ nm}$, (c) ML3, $\lambda=15.9 \text{ nm}$, (d) ML4, $\lambda=19.1 \text{ nm}$, and (e) ML5, $\lambda=22.5 \text{ nm}$. The individual layer thicknesses are listed in Table I.

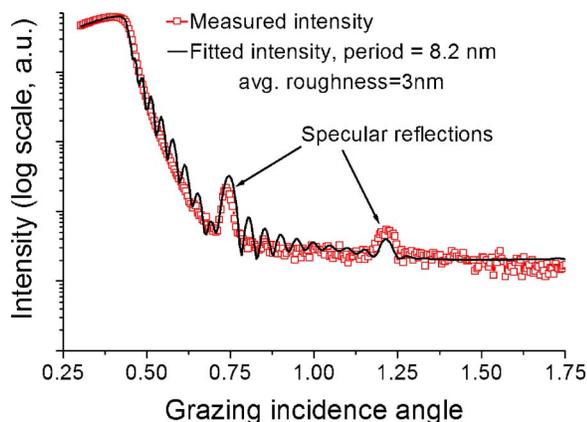


FIG. 3. (Color online) X-ray reflectivity spectra and the fitted data for sample ML2.

with the remainder being the sum of the Ti and Ga atomic concentrations, consistent with the expected 1:1 stoichiometry in the TiN and the GaN. The average nitrogen atomic concentration for each multilayer is listed in Table I. The period thicknesses of the multilayers were also calculated using RBS to corroborate the x-ray reflectivity measurements. The rocksalt TiN and wurtzite GaN areal atomic density per unit thickness were calculated from their respective atomic densities and were compared with the RBS measured areal atomic densities to determine the relative thicknesses of TiN and GaN in the multilayers. Then, the number of periods was used to determine the TiN and GaN layer thicknesses. The calculated period thicknesses are listed with the roughness values obtained from x-ray reflectivity measurement in Table I.

TiN–GaN multilayers with 1–2 nm thick GaN layers were also grown on (100) MgO substrates in an attempt to stabilize the high-pressure rocksalt phase of GaN so as to achieve a pure rocksalt-structured superlattice. The x-ray diffraction patterns of these samples (Fig. 4), with the absence of wurtzite GaN peaks and the presence of evenly spaced superlattice satellite peaks in the sample with 5.5 nm period, suggest the stabilization of the high-pressure

TABLE I. The period thicknesses and average interface roughnesses of TiN/GaN multilayers measured using RBS and XRR. The model fit to the XRR data for ML5 was not sufficiently good to extract a value for interface roughness.

Sample No.	Period thickness (TiN/GaN)	Nitrogen content (at. %)	No. of periods	Average interface roughness (nm)
ML1	(2 nm/1.4 nm), 3.4 nm period	51.3±0.8	115	5.2
ML2	(4.3 nm/2.5 nm), 6.8 nm period	51.3±1.2	56	3
ML3	(10 nm/5.9 nm), 15.9 nm period	50.3±0.3	17	4
ML4	(12.4 nm/6.7 nm), 19.1 nm period	48.6±1.24	23	4.4
ML5	(14.3 nm/8.2 nm), 22.5 nm period	51.6±8.4	13	

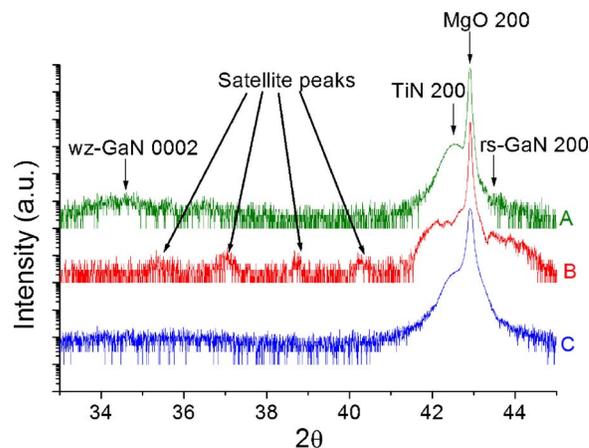


FIG. 4. (Color online) ω - 2θ x-ray scans obtained from three different period TiN–GaN multilayers grown on MgO(100) substrate and labeled as A, B, and C in the figure. The multilayer or superlattice period was determined by RBS measurements and is given as A=18.4 nm (with TiN=12.2 nm/GaN=6.2 nm), B=5.5 nm (with TiN=4.3 nm/GaN=1.2 nm), and C=2.4 nm (with TiN=1.4 nm/GaN=1.0 nm).

rocksalt GaN phase within the superlattice. Additionally, the x-ray phi scans done about asymmetric MgO 224 and rocksalt (TiN/GaN) 224 reflections, shown in Fig. 5, confirmed the orientation relationship to be TiN/GaN[110] \times (100) || MgO[110](100).

IV. DISCUSSION

Epitaxial growth of heterostructures of dissimilar materials can be rationalized by accounting for the roles of crystal structure relationships, interfacial energy minimization, morphological and phase stability, and dependence of surface diffusion kinetics on growth conditions. TiN/GaN, a candidate materials system for solid-state thermionic energy conversion, is a challenging materials system from the growth perspective.

A stoichiometric TiN thin film is thermodynamically stable in contact with stoichiometric GaN as described by the presence of tie lines between these two phases in an isother-

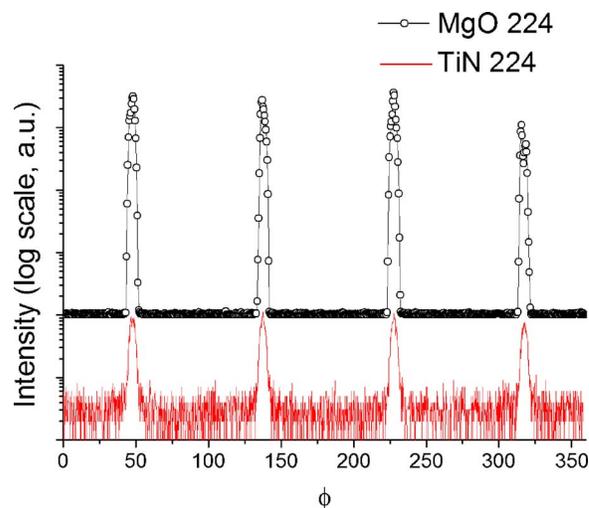


FIG. 5. (Color online) X-ray phi scans about MgO 224 and TiN 224 reflections of a 2.35 μm thick TiN(1.4 nm)/GaN(1 nm) multilayer grown on MgO. This sample is also listed as sample C in Fig. 4.

mal section of the Ti–Ga–N ternary phase diagram.¹⁴ Ti_2GaN and Ti_3GaN are possible ternary phases that can form at TiN/GaN interfaces if the composition of either of the two phases is not (1:1) stoichiometric. Obtaining a (1:1) stoichiometric TiN film is a challenge as growth of titanium nitride can lead to deposition of a series of compounds, namely, α -Ti(N) (hcp structured, $P6_3/mmc$), Ti_2N (rutile structured line compound, $P4_2/mnm$), and TiN (rocksalt structure, $Fm\bar{3}m$), listed in order of increasing nitrogen mole fraction as predicted by the Ti–N equilibrium binary phase diagram.¹⁵ The x-ray analysis of different TiN films grown from a Ti metallic target in the presence of nitrogen at approximately 600 °C revealed that the N_2 pressure plays a major role in texture evolution and stoichiometry in TiN. Only the growths done within a range of nitrogen gas pressures from 10 to 35 mtorr resulted in uniaxially textured films of primarily TiN with small peaks showing the presence of the Ti_2N phase. When the growth was done using a TiN compound target, it was found that in both nitrogen and ammonia ambients, uniaxially textured TiN films can be grown relatively easily in the pressure range of 10–35 mtorr with no signs of the presence of any secondary phase. Achieving (1:1) stoichiometry in TiN films is also important since the electrical conductivity of TiN film is maximized for this composition. Furthermore, any decrease in nitrogen content from this stoichiometry will decrease the TiN lattice parameter, thereby, increasing the lattice mismatch between TiN and GaN layers.¹⁶ Both TiN and GaN layers, grown at a temperature of 600 °C and an ammonia pressure of 20 mtorr, were (1:1) stoichiometric when analyzed using RBS, as shown in Table I. Lowering the growth temperature, as is desirable to suppress film agglomeration, leads to a reduction in the partial pressure of reactive nitrogen; at a temperature of 600 °C about 10% of the supplied ammonia is dissociated to release reactive nitrogen for GaN growth.¹⁷ Thus, a major challenge in growing such multilayers is to identify low-temperature growth conditions for growth of both stoichiometric (1:1) TiN and GaN. In order to overcome this challenge, TiN was grown from a TiN solid target with an ammonia process gas pressure of 20 mtorr while GaN was grown reactively from a liquid gallium target at the same ammonia pressure.

The hexagonal lattice of the equilibrium wurtzite polymorph of GaN promotes the growth of TiN in {111} orientation due to the compatible symmetry of wurtzite GaN and rocksalt TiN in this orientation. Even in this orientation, there is a 6% lattice mismatch between TiN and GaN, assuming the preferred orientation relationship is $TiN(111) \times [1\bar{1}0] \parallel GaN(0001)[11\bar{2}0]$. The surface energy of TiN(111) is about 140 meV/Å² (Ref. 18) while that for a GaN(0001) is about 123 meV/Å².¹⁹ The difference in crystal structures of TiN and GaN, the presence of 6% lattice mismatch in the plane of the interface, and the higher surface energy of the TiN(111) surface as compared to the GaN (0001) surface lead one to expect a three-dimensional (3D) Volmer-Weber type of growth of the TiN layer on the GaN layer. At moderate homologous temperatures, such a growth mode should preclude the formation of simply connected (pinhole-free)

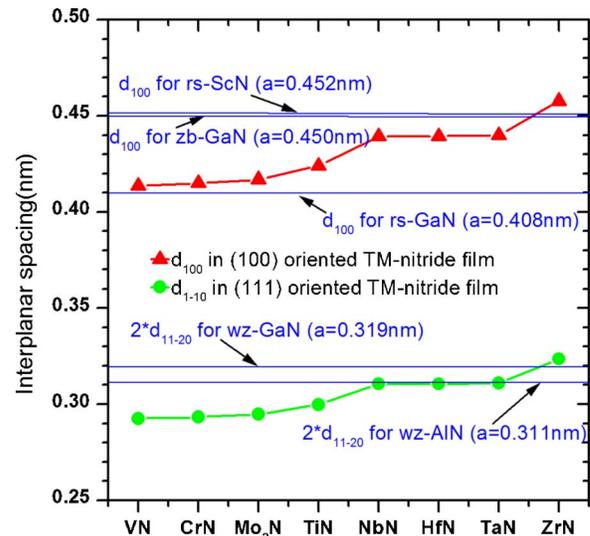


FIG. 6. (Color online) Comparison of interplanar spacings of (100) and (110) planes of transition metal nitrides with the interplanar spacings of corresponding parallel planes in rocksalt (rs), zinc blende (zb) and wurtzite (wz) structured III-V semiconducting nitrides (see Ref. 21).

films. Though the driving force for agglomeration is significant, a sufficiently high surface diffusivity of Ti or N adatoms on the GaN(0001) surface is required for the TiN phase to agglomerate. The homologous growth temperatures were evidently sufficiently low (~ 0.27 for TiN and ~ 0.31 for GaN) to kinetically suppress the formation of TiN islands on the GaN layer.

The electrical properties of III-V semiconducting and insulating nitrides such as GaN, InN, and AlN, and their solid solutions have been studied extensively in the last decade, while the metallic transition metal nitrides in thin-film form have not received that much attention. Nanoscale composites between materials with bulk electrical conductivities that differ by as much as six orders of magnitude (or more in the case of metallic nitrides in multilayers with AlN) are materials that are expected to have highly anisotropic electrical and thermal transport properties. From a materials growth perspective, the prospect of combining metals and semiconductors in epitaxial superlattices with nanoscale periods is fascinating. Figure 6 summarizes the structural compatibility of several metallic and semiconducting nitrides with their corresponding lattice parameters and the possibility of all rocksalt or {111} rocksalt/{0001} wurtzite epitaxy. Note that the TiN/GaN combination, the subject of these initial demonstrations of metal/semiconductor multilayers, is not the most favorable combination. Future studies of rocksalt ZrN/ScN (mismatch 1.7%), rocksalt TaN/wurtzite GaN (mismatch 4%), and rocksalt VN/rocksalt GaN ($a = 4.08$ nm)^{20,21} (mismatch 1.4%) are expected to generate epitaxial multilayers and superlattices with substantially improved structural quality.

It can be inferred from Fig. 6 that given the large number of hitherto unexplored transition metal nitrides, it should be possible to find a metallic nitride (binary compound or solid-solution alloy) that can be grown coherently in combination with rocksalt III-V semiconducting nitrides (e.g., ScN or the high-pressure polymorph of GaN) in epitaxial heterostruc-

tures or superlattices with arbitrary periods. The present work provides preliminary evidence of pseudomorphic stabilization of the rocksalt phase of GaN between TiN layers. The similar high-pressure rocksalt phase of AlN, an insulator, has been stabilized within TiN/AlN and VN/AlN superlattices,^{22,23} suggesting that a wide range of metal/semiconductor nitride multilayers will be demonstrated in the near future.

Similarly, the results of the present study suggest the possibility of identifying lattice matched or nearly lattice-matched combinations of metallic rocksalt phases and either zinc blende or wurtzite semiconducting nitrides that can be grown as epitaxial multilayers, albeit with defects inherent to the symmetry differences between the phases.

These metal-semiconductor multilayers may be well suited for applications such as materials for thermionic energy conversion devices due to the anisotropic nature of their electron and phonon transport. The presence of a high density of interfaces, the nanoscale interfacial roughness, and the difference in phonon density of states across the interface suggest that the cross-plane thermal conductivity will be substantially lower than bulk values. Similarly, the electron transport is also anisotropic with the cross-plane current expected to be thermionic in nature while the in-plane current will be primarily diffusive. The availability of a wide array of materials for metal-semiconductor multilayers and superlattices provides an opportunity to select the combination with desired barrier heights for filtering hot electrons in cross-plane thermionic transport.

V. SUMMARY

Nitrides are proposed as potential materials for fabricating metal-semiconductor multilayers for use as high temperature thermionic energy converters and the rationale behind choosing nitrides is presented. The first set of nitride metal/semiconductor multilayers, comprising TiN and GaN, has been grown using reactive pulsed laser deposition, and their crystallographic orientation, interfacial roughness, and stoichiometry have been studied using high resolution x-ray diffraction, x-ray reflectivity, and RBS. TEM studies showed that despite the difference in crystal structures and surface energies of TiN and GaN, these multilayers with nanoscale periods were morphologically stable to a thickness of at least 1 μm . This unexpected metastability may be attributed to the low homologous growth temperatures of both TiN and GaN. TiN/GaN multilayers grown on cubic MgO substrates yield

x-ray diffraction patterns suggesting pseudomorphic stabilization of the rocksalt phase of GaN. The wide range of electrical properties exhibited by nitrides with the experimental confirmation that lattice incompatible nitrides can be grown together and the additional possibility of stabilizing metastable nitride phases for improved epitaxy potentially enables the exploration of a wide range of metal-semiconductor heterostructure devices using nitrides.

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