TiN/GaN Metal/Semiconductor Multilayers for Thermionic Energy Conversion

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ABSTRACT

TiN-GaN multilayers were grown for potential application as solid-state thermionic direct energy conversion devices using reactive pulsed laser deposition in an ammonia ambient. The crystallographic analysis of the multilayers by high-resolution x-ray diffraction and cross-sectional TEM revealed that, despite the difference in crystal structures of TiN and GaN, it was possible to grow thick uniaxially textured columnar-grained multilayers. In-plane electronic transport was assessed using Hall effect and Seebeck coefficient measurements. Thermal conductivity measurements have shown that by increasing the interface density, the cross-plane thermal conductivity of the multilayers can be reduced to 3.6 W/m-K, compared to 135 W/mK for bulk GaN and 38 W/mK for bulk TiN.

Keywords: thermionic energy conversion, reactive pulsed laser deposition, TiN, GaN.

INTRODUCTION

The prospects for a compact, solid-state thermal-to-electrical energy conversion device with efficiency above 20% for hot-side temperatures in the range of 300-700°C has motivated research in nanostructured thermoelectric (TE) materials for more than a decade. Such a device would find early application in vehicle waste heat recovery systems, steam-free powering for naval vessels, and terrestrial generators employing concentrated solar energy. Although recent laboratory-scale research on bulk and thin-film nanostructured materials based on PbTe show promise for enhanced efficiencies, the best such material does not yet meet the requirements for 20% device efficiency [1,2]. Recent theoretical investigations [3,4] have suggested that metal/semiconductor multilayer-based thermionic (TI) energy converters can achieve much higher efficiencies than conventional thermoelectric devices. Such multilayers with nanoscale periods employ metal/semiconductor barriers to enhance the asymmetry of the differential conductivity about the Fermi energy (i.e. high hot electron concentrations) [3]. For applications involving moderate to high hot-side temperatures (~300-700 C), the multilayers must be stable against corrosion, decomposition, and interdiffusion. The nitrides meet these criteria, and offer potential materials combinations for metal-semiconductor multilayers. Nitrides such as TiN, ZrN, VN, and TaN are metals whereas GaN, InN, ScN and their alloys are semiconductors. Furthermore, the electrical and thermal properties of the nitride multilayers and their interfaces can be tuned by alloying. In this work, we describe our efforts to evaluate the potential of TiN-GaN multilayers for direct thermal energy conversion.

EXPERIMENTAL DETAILS

The nitride films and multilayers were deposited on sapphire and MgO substrates in a high vacuum pulsed laser deposition system (PVD Products, Inc.) with a base pressure of 8×10^{-8} torr. The targets were a TiN disk of 2” diameter and a liquid gallium target contained in a stainless steel dish. A 248 nm KrF excimer laser (Lambda Physik 305i) was used to generate 25 ns pulses at 5 Hz with a pulse energy of 650 mJ and a fluence of 8 J/cm^2 at the target. The process gas was ammonia at a pressure of 20 mtorr and a flow rate of 55 sccm. To ensure uniform film deposition, the targets and the substrate were rotated and the laser beam was rastered over the target surface.

Prior to deposition, both sapphire and MgO substrates were ultrasonically cleaned in acetone and isopropanol and then rinsed in deionized water. The above process was repeated three times. Sapphire substrates were then chemically etched in a 3:1 solution of sulphuric acid: phosphoric acid (H_2SO_4:H_3PO_4) at a temperature of 100^{o}C for 15 minutes. After etching, the sapphire substrates were rinsed in DI water for 3 minutes. The substrates were mounted with indium on a Mo disk and loaded into the deposition chamber. Both of these substrates were then annealed in vacuum at 585^{o}C for 30 minutes to allow for surface reconstruction [5]. Using the TiN/GaN multilayers with different multilayer periods were grown on sapphire and MgO substrates.

RESULTS & DISCUSSION

X-ray diffraction results obtained from TiN/GaN multilayers grown on sapphire (0001) substrates confirmed the presence of uniaxial texture within the multilayers as shown in figure 1. The orientation relationship between the TiN layers, GaN layers and the sapphire substrate was determined using asymmetric θ-2θ scan and Φ-scan about GaN (10-12) peak and it was found to be TiN (111)[1-10] || GaN (0001)[11-20] || sapphire (0001)[11-20]. The lattice mismatch between a TiN (a=0.424 nm) film and a GaN film (a=0.319 nm, c=0.518 nm) grown in the crystallographic orientation state above is 8.55%.

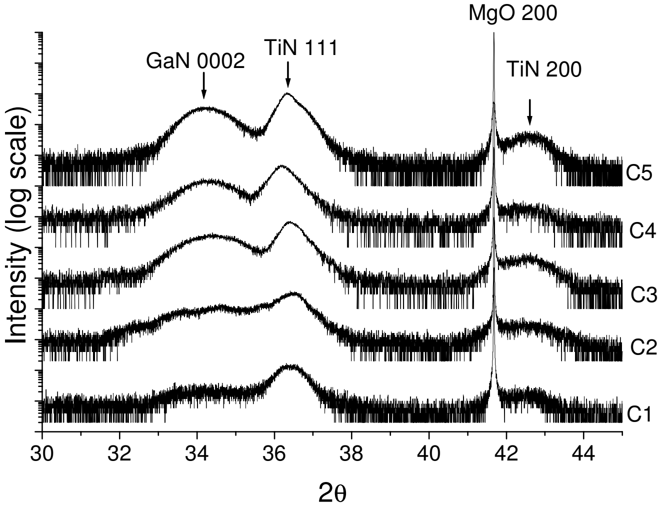

Figure 1: X-ray diffraction patterns obtained from five different TiN-GaN multilayers grown on sapphire with following periods, a) C1, λ=3.4 nm, b) C2, λ=6.8 nm, c) C3, λ=15.9 nm, d) C4, λ=19.1 nm and e) C5, λ=22.5 nm.

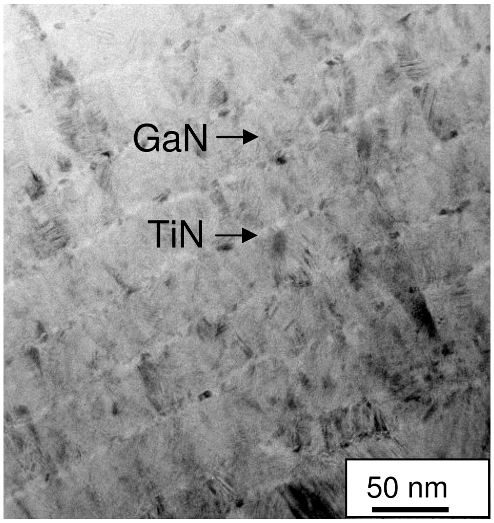

Figure 2: Cross-sectional TEM image of a TiN(5nm)-GaN(30nm) multilayer grown on a sapphire (0001) substrate.

The cross-sectional TEM image shown in figure 2 confirmed that, despite the differences in crystal structure and lattice parameter, the layered structure was preserved during growth. Similarly, TiN/GaN multilayers with thin layers of GaN sandwiched between TiN layers were grown on a cubic substrate (i.e. MgO) in an attempt to pseudomorphically stabilize the metastable rocksalt phase of GaN. Such pseudomorphic stabilization of the rocksalt phase has been achieved in the case of AlN, which exhibits a T-P phase diagram that is similar to that of GaN with wurtzite, zincblende and rocksalt phases[6]. X-ray diffraction patterns obtained from such short-period multilayers grown on MgO are shown in figure 3. Presence of evenly spaced satellite peaks and the absence of wurtzite GaN peak, confirms of the stabilization of rocksalt phase of GaN. This was seen only in the multilayers where the GaN layer thickness was less than 2nm. With the increase in GaN layer thickness, the wurtzite phase of GaN started stabilizing. The [010] zone axis electron diffraction pattern from one such multilayer grown on MgO with thick GaN layers is shown in figure 4. The electron diffraction pattern confirms the presence of the wurtzite phase of GaN.

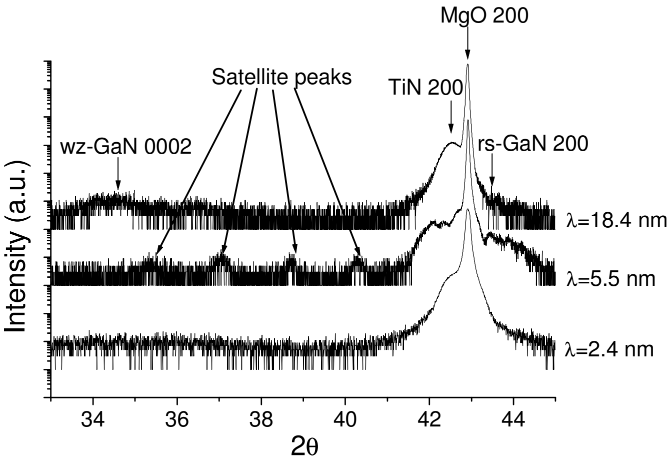

Figure 3: X-ray diffraction patterns obtained from TiN/GaN multilayers with short periods, grown on MgO substrates.

In-plane electrical characteristics were determined using Hall effect measurements. In-plane Hall mobility, carrier concentration and electrical conductivity of TiN/GaN multilayers grown on sapphire are shown in figure 5. In these samples the thickness of the TiN layer was varied from 0.5 nm to 5nm while the GaN layer thickness was kept constant at 10 nm. It can be inferred from the figure that with increasing TiN layer thickness, the electrical characteristics of the multilayers can be tuned from that of being a pure semiconductor to that of a metal. Similarly, the Seebeck coefficients of the multilayers vary from values characteristic of a degenerate semiconductor to those expected from a metal. The effective power factor "$S^2\sigma$" for these multilayers was calculated from the experimentally determined electrical conductivity and Seebeck coefficient values. The maximum value of in-plane power factor was found to be $1.5x10^{-3}$ W/m-K^2 for a TiN/GaN multilayer with a TiN layer thickness of 1 nm and a GaN layer thickness of 10 nm. The cross-plane power factor is expected to be much higher than the in-plane power factor due to the energy filtering effect.

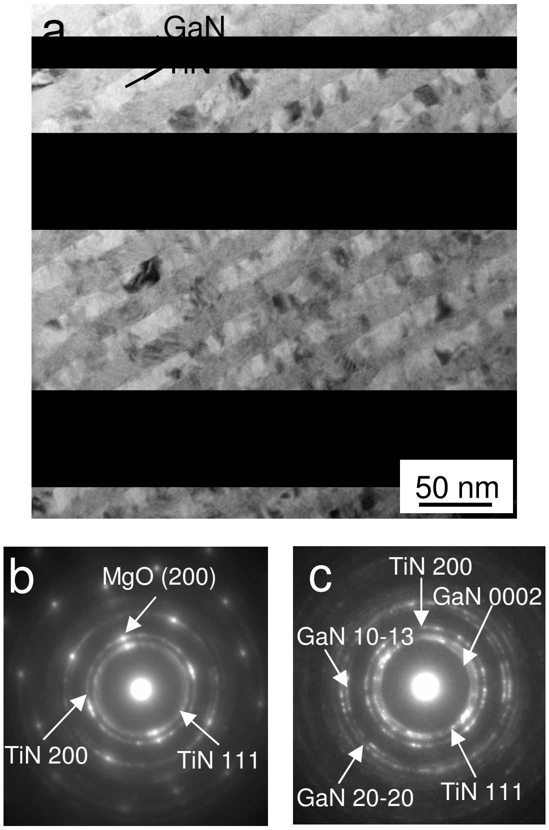

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Figure 4: (a) Cross-sectional TEM image of a TiN(10nm)-GaN(variable thickness) multilayer grown on MgO(100). (b) [010] zone axis diffraction pattern obtained from the MgO substrate and the multilayer. (c) Selected area diffraction pattern obtained from the multilayer only, showing presence of uniaxial texture.

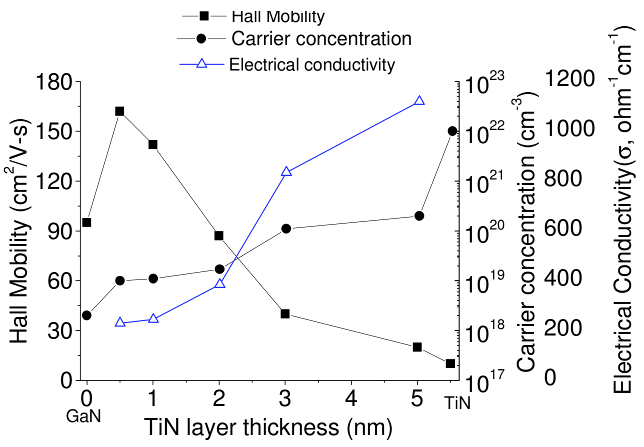

Figure 5: Left axis: In-plane Hall mobility, Right axis: In-plane electrical conductivity and carrier concentration as a function of TiN layer thickness. GaN layer thickness was kept constant at 10nm.

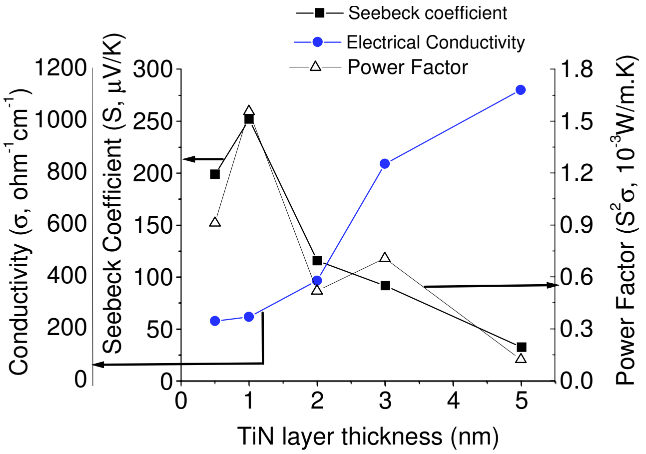

Figure 6: Left axis: In-plane electrical conductivity and Seebeck coefficient, Right axis: Calculated power factor as a function of TiN layer thickness. GaN layer thickness was kept constant at 10nm while the TiN layer thickness was changed.

Preliminary measurements of the room temperature cross-plane thermal conductivity of multilayers comprising of TiN(bulk κ=38 W/mK) and GaN(bulk κ=135 W/mK) layers on sapphire using time-domain photoreflectance show that short period multilayers have thermal conductivities as low as 3.6 W/m-K Measurements as a function of temperature are in progress. Further reduction in thermal conductivity is expected with solid-solution alloying of the metallic and semiconducting layers.

CONCLUSIONS

TiN/GaN multilayers with uniaxial texture were grown on cubic (MgO) and rhombohedral (sapphire) substrates using reactive PLD in an ammonia ambient. In-plane electrical measurements have shown that, depending on the relative thicknesses of the layers, the multilayer's electrical behavior can be tuned to yield semiconductor or semimetal like behavior. Thus, by varying the multilayer period, it is possible to obtain a multilayer with an optimum in-plane power factor($S^2\sigma$). The cross-plane thermal measurements revealed that by increasing the interface density, the thermal conductivity of these otherwise thermally conducting nitrides can be reduced drastically.

The TiN/GaN multilayers prepared in this study may represent the first crystalline metal/semiconductor multilayers with the nanoscale periods necessary to investigate thermal and electrical transport phenomena at characteristic length scales that are comparable to electron and phonon wavelengths. Preliminary x-ray scattering data suggests that rocksalt-structured metal-semiconductor superlattices are possible in this system for GaN layers thinner than 2 nm. Although measurements of in-plane electronic transport properties are promising, cross-plane thermal and electronic transport measurements will be necessary to test the solid-state thermionic concept for direct thermal energy conversion.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Rajeev Singh and Prof. Ali Shakouri (UCSC) for Seebeck coefficient measurement, and Kee Yon Koh and Prof. David Cahill (UIUC) for thermal conductivity measurements.. This work is funded by ONR/DoD through a MURI grant. A part of this work was carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-91-ER45439.

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