

XPS study of nanocomposites GaN/TiN prepared by means of the anaerobic imide route and aerosol-assisted vapor phase synthesis methods

¹Mariusz Drygaś, ²R. T. Paine, ^{1*}Jerzy F. Janik

¹AGH University of Science and Technology, Faculty of Fuels and Energy, Kraków, Poland

²University of New Mexico, Department of Chemistry, Albuquerque, NM 87131, USA

*Corresponding author: janikj@agh.edu.pl

Investigations of composites in GaN/TiN system may help in understanding complex phenomena observed at GaN/titanium metal interfaces as well as expand potential areas of their applications in modern electronics. In this report, we briefly describe the preparation of nanopowder composites of gallium nitride and titanium nitride, GaN/TiN, by two distinct synthetic methods: aerosol-assisted vapor phase synthesis (AAVS) and anaerobic precursor route. The products were characterized by spectroscopic and microscopic methods. Herein, discussed are mainly studies by X-ray photoelectron spectroscopy, XPS.

Presented at the Chemical Technology Congress TECHEM 5 held in Poznań, Poland, 11 – 15 September 2006.

INTRODUCTION

Group III¹³ nitrides have become a frequented ground for numerous precursor chemistry activities as the utilization of such materials in electronics and ceramics offers outstanding potentials¹. Gallium nitride, GaN, thanks to its significance in optoelectronics has notably been among the most studied compounds of this kind². GaN is a broad-band semiconductor designed for use in efficient light emitting or detecting devices in the blue/violet range³. The advantage of GaN over the classical semiconductors Si or Ge in manufacturing of high power transistors and switches is also of fundamental significance.

New material development often relies on controlling the material's thermal, mechanical, and surface characteristics by improving the properties through suitable composite make-ups. For instance, TiN/GaN composite layers have been shown to provide advantageous surfaces for growing free-standing, thick epitaxial GaN wafers for applications in optoelectronics, e.g., as supports in nitride blue-light emitters⁴.

TiN has hardness compared to that of diamond, high melting point at approx. 3000°C, remarkable chemical resistance, and advantageous adherence properties towards a wide range of materials⁵. High electrical conductivity exceeding that of titanium metal and low temperature superconductivity are additional examples of the nitride's technological properties⁶. The nitride's prospects for manufacturing Shottky's diodes and MOS transistor gates has also been reported⁷.

The composite powders of GaN/TiN could lead to enhanced mechanical, thermal, and structural properties relative to the pure nitrides and, therefore, to advantageous material modifications. Successful preparation of the homogeneous nanopowder composites from suitable mixed-metal chemical precursor systems may yield upon subsequent compacting/sintering useful materials forms of GaN/TiN for a range of exciting applications.

EXPERIMENTAL

Aerosol-assisted vapor phase synthesis (AAVS)

The Preparation of the composite powders was accomplished by the published aerosol-assisted synthesis⁸ which was also used to prepare powders of pure GaN⁹ and TiN¹⁰.

Aqueous solutions. Commercial Ga(NO₃)₃·xH₂O (Aldrich, x=2) and *in situ* prepared Ti(NO₃)₄¹¹ were used as water soluble metal precursors. A freshly made aqueous solution containing Ti⁴⁺ was mixed with a suitable amount of 0.12 M solution of Ga⁺³ to yield a solution with an atomic ratio of Ga⁺³/Ti⁺⁴=5/1. An aerosol mist of the solution was generated by using an ultrasound transducer and the aerosol was transported in a stream of N₂ carrier gas, 1 L/min., to a horizontal ceramic tube reactor maintained at 1000°C. An accompanying flow of nitriding NH₃ was introduced to the reactor at 3 L/min. The solution was aerosolized at a rate of approx. 30 mL/h yielding a brownish powder on the reactor's exit filter.

Methanol solutions. For aerosol formation, a freshly made methanol solution of titanium tetramethoxide Ti(OCH₃)₄ stabilized with HNO₃ (1.5 mL of conc. HNO₃ per 1000 mL of CH₃OH) was combined with a suitable proportion of Ga(NO₃)₃·xH₂O (x=2) to yield atomic ratio Ga/Ti=5/1. Freshly prepared solutions of this kind were transparent; however, their colloidal nature was evidenced by the Tyndall effect. In typical syntheses, the rate of aerosol generation was approx. 80 – 90 mL/h. A brown-tinted powder was recovered from the aerosol reactor after this stage.

To complete the nitridation process, the raw powders from the aqueous and methanol solution systems were additionally pyrolyzed in bulk at 1000°C, for 6 hours, under a NH₃ flow, 1 L/min. The final products were recovered as dark brown to black powders.

Anaerobic imide route

The imide route to nitrides was initially developed for making nanocrystalline powders of GaN¹² and AlN¹³ from the respective metal imide/amide via ammonolysis of {M[N(CH₃)₂]₃}₂, M=Ga, Al. Utilizing Schlenk technique and neutral gas atmosphere, an appropriate propor-

tion of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ (prepared according to Reference¹⁴) to yield atomic ratio $\text{Ga}/\text{Ti}=5/1$ was added with stirring to a diethyl ether solution of freshly prepared $\{\text{Ga}[\text{N}(\text{CH}_3)_2]_3\}_2$. After overnight stirring, volatiles were removed from the homogeneous solution and the resulting solid was subjected to ammonolysis in refluxing liquid ammonia for 4 hours. Upon pyrolysis of the mixed-metal solid precursor, 1000°C, 4 h, under a NH_3 flow, a yellow-brownish powder was obtained.

RESULTS AND DISCUSSION

The XRD patterns (not shown) indicate that the powders from all the reaction routes are composed of varying amounts of nanocrystalline hexagonal GaN and cubic TiN or cubic TiO_xN_y , and, from imide route, minor cubic GaN. The powders obtained via AAVS are somewhat depleted in gallium due to enhanced GaN-decomposition side reactions at 1000°C.

Figure 1 shows the XPS bands Ti 2p, N 1s, Ga 2p_{3/2}, and O 1s for the 1000°C-nitrided product from the AAVS aqueous solution system $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{Ti}(\text{NO}_3)_4/\text{H}_2\text{O}/\text{NH}_3$. The deconvolution of the N 1s band gives rise to three peaks. The peak at 397.2 eV can be attributed to N^3 in the nitride(s), GaN and TiN, while its low energy neighboring peak at 396.2 eV is in the region of chemical environments in titanium oxynitride¹⁰ which is corroborated by the corresponding Ti 2p_{3/2} peaks (see below). In this regard, the lattice constant for the observed cubic titanium-related phase, $a=4.23 \text{ \AA}$, is very close to the a -constant for microcrystalline TiN, $a=4.24 \text{ \AA}$, thus, supporting the formation of the latter. We recall here that the lattice constants for the stable cubic titanium oxynitrides, TiO_xN_y , that can be thought of as solid solutions of $c\text{-TiO}$ and $c\text{-TiN}$ vary between the value for TiO, $a=4.17 \text{ \AA}$, and for TiN, $a=4.24 \text{ \AA}$. The relatively low oxygen content in the composite, 1.6%, is consistent with a residual-only oxygen from synthesis further supporting the prevailing $c\text{-TiN}$ phase. Finally, the third N 1s peak at 398.8 eV can be assigned to $\text{N}\equiv\text{C}$ bonds linked to some minor surface-type contaminants.

The symmetrical Ga 2p_{3/2} band corresponds to a single peak at 1119.1 eV typical for GaN. The O 1s band is resolved into two peaks. The line at 530.4 eV is characteristic for metal-oxygen bonds and, in this case, can likely be related to Ti-O bonds in TiO_xN_y and/or surface passivating TiO_2 , which is supported both by the appearance of Ti 2p bands (see below) and XRD data. The second oxygen peak located at 532.1 eV corresponds to O-H bonding from the absorbed water during sample handling.

An important aspect of the chemistry leading to TiN is that Ti^{+4} in the intermediate TiO_2 , formed *in situ* from the decomposition of the applied titanium precursors, is formally reduced to Ti^{+3} in TiN. This reduction chemistry is conveniently detected by XPS through a significant broadening of the Ti 2p lines. The deconvolution of the complex Ti 2p band yields for each sample three major doublets (2p_{3/2} and 2p_{1/2} peak pairs) encompassing the set of three 2p_{3/2} peak components. The peak at 455.6 eV can be assigned to Ti-N bond environments in TiN.

The peak at 456.9 eV is in the range characteristic for TiO and/or TiO_xN_y , wherein titanium is in the formal Ti^{+2} oxidation state. The third and the most intense peak at 458.5 eV corresponds to TiO_2 . These results are consistent with the XRD results in the fact that both methods provide specific evidence for the occurrence of TiO_xN_y and/or TiN domains. Since XPS is a surface sensitive method, the unavoidable presence of passivating TiO_2 -layers on nanograin surfaces causes the observed relative enhancement of the peak at 458.5 eV.

As far as the AAVS methanol solution system is concerned (Figure 2), the XPS data are, qualitatively, similar to the discussed above for the aqueous solution case. The main differences include a relatively lower intensity of Ti 2p_{3/2} TiO_xN_y -related peak at 456.7 eV (better nitridation conditions due to carbothermal reduction/nitridation) and a higher intensity of N 1s $\text{N}\equiv\text{C}$ -related peak at 398.8 eV (abundant carbon in the methanol solution system).

Figure 3 shows the XPS bands for the 1000°C-product from the anaerobic imide route. Here, the N 1s band contains the same peaks as above but the peak at 398.6 eV for the likely $\text{N}\equiv\text{C}$ surface contaminants is relatively stronger. Similarly, Ga 2p_{3/2} and Ti 2p deconvoluted peaks support the presence of GaN and TiN while Ti 2p peak at 456.8 eV for titanium oxynitrides is, relatively, weak as one would expect in a product from the anaerobic route. In the O 1s band, the strong peak at 531.9 eV characteristic for O-H bonds, indicates a high propensity of the powder for adsorption of water in post-processing stages.

CONCLUSIONS

The XRD data show that the composites contain mostly nanocrystalline powders of $h\text{-GaN}$ and $c\text{-TiN}$ that, in the case of imide route, are admixed with minor $c\text{-GaN}$. The XPS study suggests that during nitridation *via* AAVS the oxygen displacement by nitrogen in the oxygen-bearing precursor systems takes place through the formation of the stable oxynitride intermediate, $c\text{-TiO}_x\text{N}_y$. Oxygen analyzed in the powder made *via* anaerobic imide route is likely to originate from the surface of Ti-O species. The Ti-O bonds detected by XPS in the AAVS 1000°C-pyrolyzed powders are mainly associated with passivating surface moieties either amorphous and/or in the amounts below detection limits of the powder XRD measurements.

ACKNOWLEDGEMENTS

Support of the AGH University of Science and Technology is acknowledged, Grant No. 11.11.210.62s

LITERATURE CITED

- (1) Morkoç H.: Mater. Sci. Eng. **1997**, B43, 137.
- (2) Han W., Zettl A.: Appl. Phys. Lett. **2002**, 80, 303.
- (3) Arakawa Y.: IEEE J. Sel. Top. Quant. **2002**, 8, 823.
- (4) Oshima Y., Eri T., Shibata M., Sunakawa H., Usui A.: phys. stat. sol. (a) **2002**, 194, 554.
- (5) Dubois L. H.: Polyhedron **1994**, 13, 1329.
- (6) Fix R. M., Gordon R. G., Hoffman D. M.: Chem. Mater. **1990**, 2, 235.

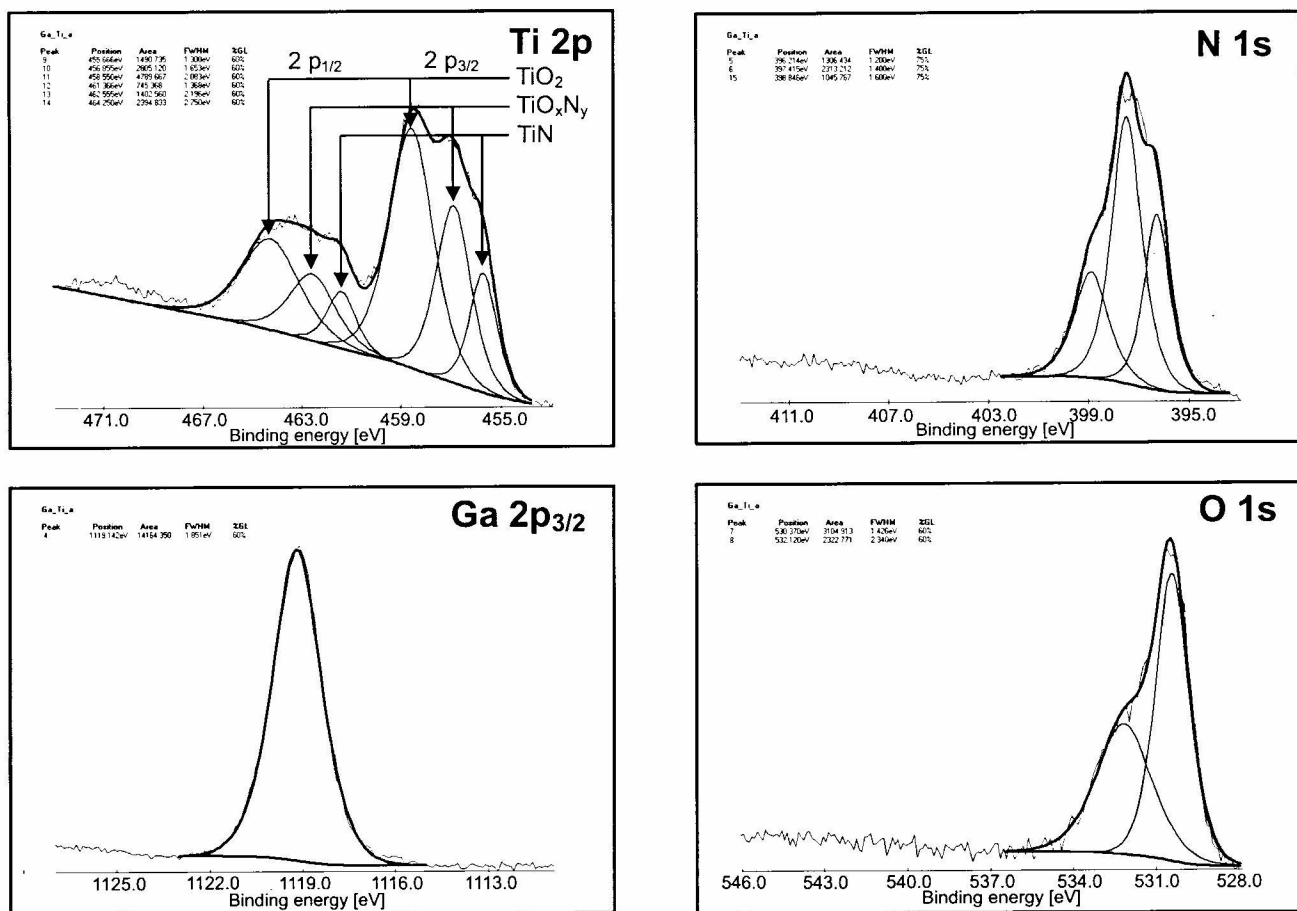


Figure 1. XPS spectra for the composite nanopowder derived from aqueous solution system $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{Ti}(\text{NO}_3)_4/\text{H}_2\text{O}/\text{NH}_3$ after nitriding pyrolysis at 1000°C (AAVS)

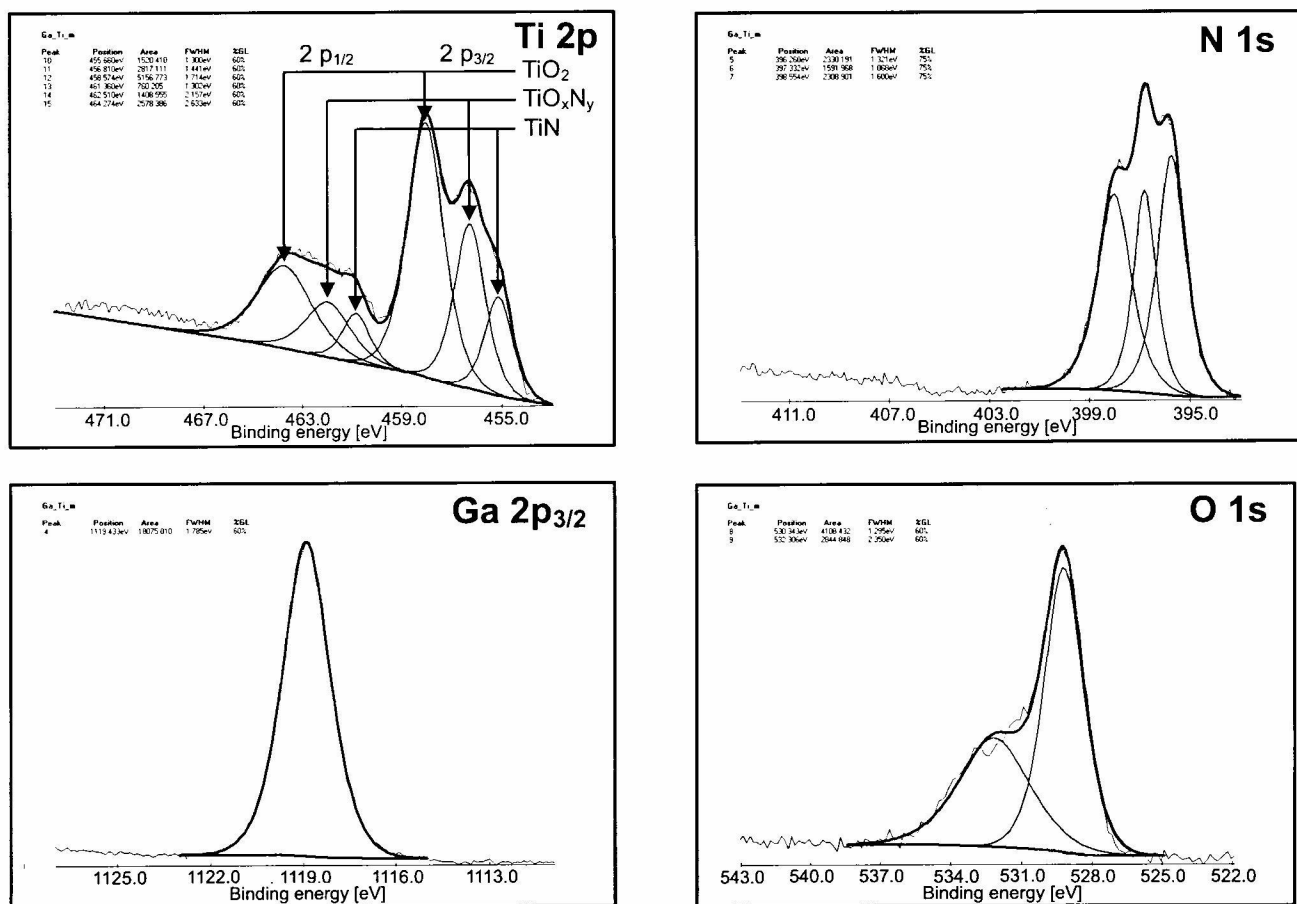


Figure 2. XPS spectra for the composite nanopowder derived from methanol solution system $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{Ti}(\text{OCH}_3)_4/\text{CH}_3\text{OH}/\text{NH}_3$ after nitriding pyrolysis at 1000°C (AAVS)

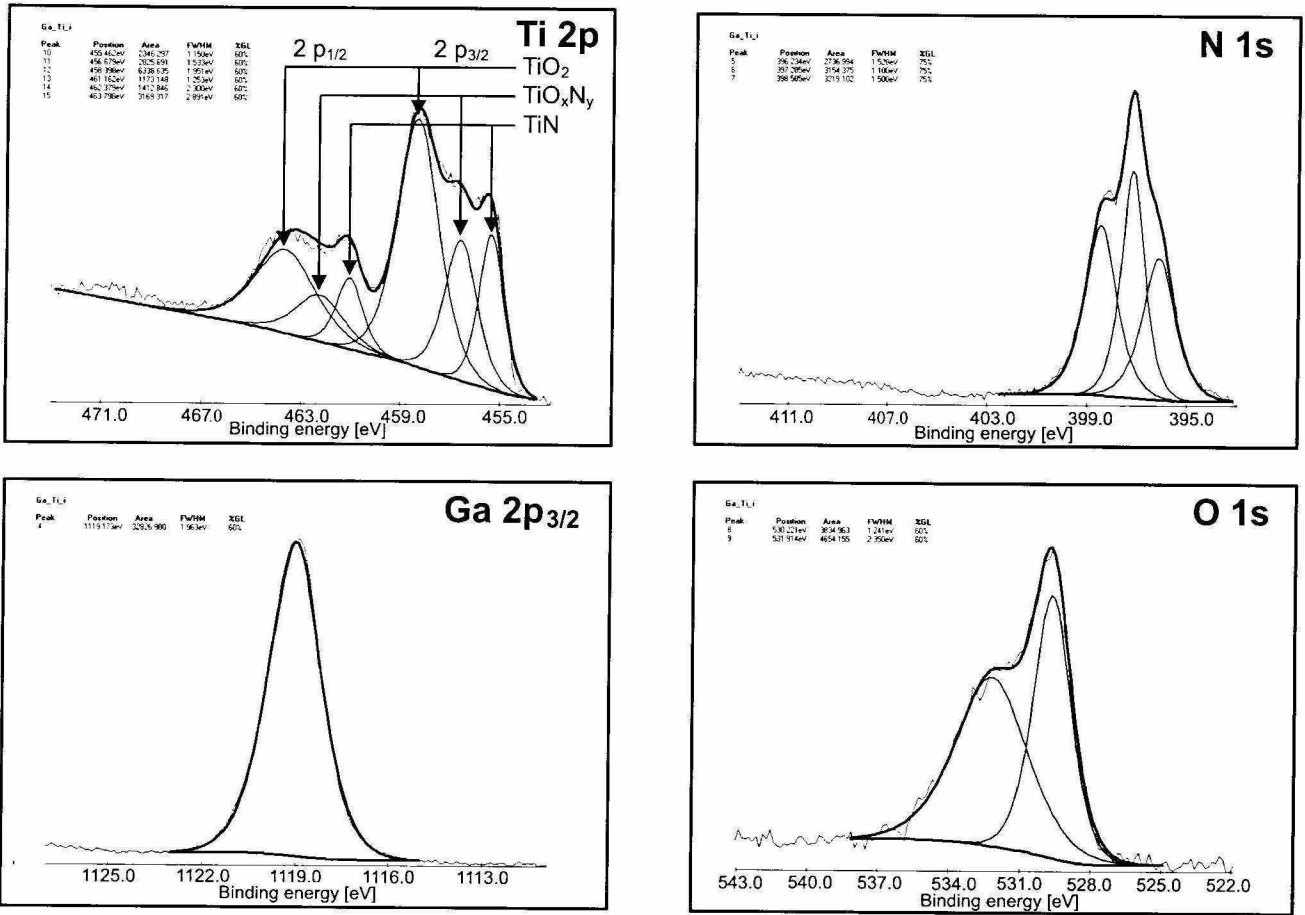


Figure 3. XPS spectra for the composite nanopowder obtained via from anaerobic imide route after nitrating pyrolysis at 1000°C.

- (7) Fix R. M., Gordon R. G., Hoffman D. M.: Chem. Mater. **1991**, 3, 1138.
- (8) Drygaś M., Czosnek C., Paine R. T., Janik J. F.: Mater. Res. Bull. **2005**, 40, 1136.
- (9) Wood G. L., Pruss E. A., Paine R. T.: Chem. Mater. **2001**, 13, 12.
- (10) Drygaś M., Czosnek C., Janik J. F., Paine R. T.: manuscript in preparation.
- (11) Jung C. H., Kim D. K.: J. Mater. Synth. Proces. **2002**, 10, 23.
- (12) Janik J. F., Wells R. L.: Chem. Mater., **1996**, 8, 2708.
- (13) Janik J. F., Wells R. L., Coffey J. L., St. John J. V., Pennington W. T., Schimeck G. L.: Chem. Mater. **1998**, 10, 1613.
- (14) Bradley B. C., Thomas I. M.: J. Chem. Soc. **1960**, 3857.