Proc. XXXVII International School of Semiconducting Compounds, Jaszowiec 2008

Ti–Al–N MAX Phase, a Candidate for Ohmic Contacts to *n*-GaN

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Fabrication of a Ti_2AlN MAX phase for contact applications to GaN--based devices is reported. Sample characterisation was done by means of X-ray diffraction and secondary ion mass spectroscopy. Successful Ti_2AlN monocrystalline growth was observed on GaN and Al_2O_3 substrates by annealing sputter-deposited Ti, Al and TiN layers in Ar flow at 600°C. The phase was not seen to grow when the layers were deposited on Si (111) or when the first layer on the substrate was TiN. N-type GaN samples with Ti_2AlN layers showed ohmic behaviour with contact resistivities in the range 10^{-4} Ω cm^2.

PACS numbers: 61.05.cp, 68.49.Sf, 68.55.ag, 81.40.Ef

1. Introduction

In recent times there has been growing need for semiconductor devices that can operate at high power loads and in harsh environments. For these applications wide band gap semiconductors are well suited due to their high breakdown field and temperature tolerance. One such material receiving considerable attention is GaN. The problem is that however the material itself can operate in harsh conditions, the electric contacts leading the electric signal to and from a GaN-based device are not so resistant, especially to high temperature. The purpose of this work was to study a new material for such contact applications. Bearing in mind that the contact to *n*-GaN widely recognised as yielding the lowest resistivity consists of a Ti/Al bilayer [1], the approach of the experiment reported herein was to try to change such a simple contact into a Ti2AlN MAX phase in order to enhance its thermal stability and oxidation resistance.

The $M_{n+1}AX_n$ (n = 1, 2, 3) phases (known also as H or Hägg phases), first described by Novotny in 1970 [2], are solid-state ternary crystalline phases

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of unique metal–ceramic characteristics. They exhibit good thermal and electrical conductivity, high hardness, and machinability characteristic of metals alongside with oxidation resistance, damage tolerance, and thermal stability even at temperatures as high as 1000°C [3, 4] which are found in ceramics. These properties are due to the nanolaminate structure of the compounds [2, 3] consisting of: a transition metal (M), an element mostly from group IIIA or IVA (A) and carbon or nitrogen (X). Generally, monocrystalline MAX phase consists of MX monolayers intertwined with monoatomic A layers. The M–X bonds are strong covalent ionic bonds and as such give rise to the typical ceramic properties such as high thermal stability. The M–A bonds are metallic and lead to good electrical conductivity of the MAX phases. Figure 1 shows unit cells of three different MAX phases.

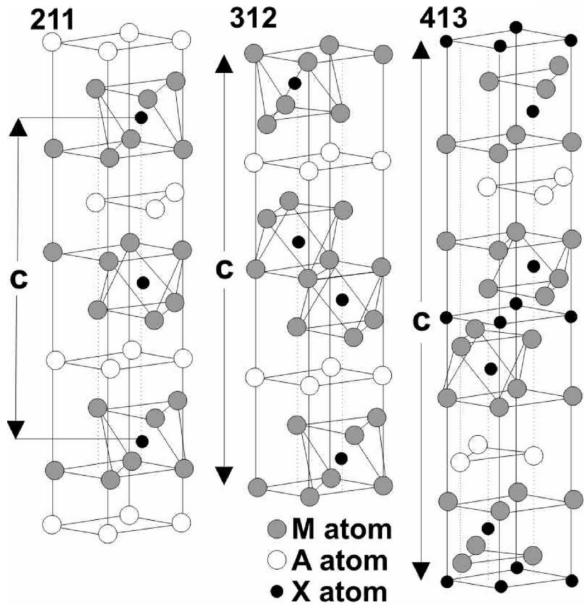

Fig. 1. Unit cells for M_2AX, M_3AX_2, and M_4AX_3 phases.

The main research interest in MAX phases focuses on the Ti_3SiC_2 and especially on its mechanical properties and damage tolerance [3]. Another MAX phase inducing considerable interest is Ti_2AlN. There are few studies made on other phases, especially concerning their electrical properties which leaves a large area yet unstudied.

2. Experimental details

2.1. Sample preparation

In the reported experiment two approaches to growing Ti_2AlN were used. The first one was to deposit Ti, Al and TiN layers in different sequences on gallium

nitride, sapphire and silicon (111) and to anneal them subsequently in argon flow at 600°C in order to form the MAX phase. The second approach was to deposit several Ti and Al bilayers on GaN with subsequent annealing in nitrogen flow at 600°C. The reason for using such substrates was to see whether monocrystalline Ti_2AlN growth conserving the main crystallographic directions of the substrate is possible. GaN has the wurzite structure and is oriented in the [0001] direction, Al_2O_3 can be described as well using the hexagonal indices, being oriented in the [0001] direction, and the Si (111) surface has an atom pattern similar to a wurzite (0001) surface. The substrates were prepared for deposition by cleaning and degreasing in boiling trichloroethylene, acetone and isopropanol, followed by rinsing in de-ionised water and blowing dry with nitrogen gas. The layers were deposited by magnetron sputtering in dc mode at room temperature using the Leybold Z550 sputtering system. Prior to deposition the system was evacuated to a vacuum of the order of 10^{-7} mbar. The layers were deposited from Al and Ti targets (99.99% and 99.999% purity, respectively) at 100 W power in an argon atmosphere and in argon mixed with nitrogen in the case of TiN layers. The argon pressures were: 6.5×10^{-3} mbar for Ti and Al layers and the nitrogen and argon pressures for TiN layers were 5×10^{-4} mbar and 4.7×10^{-3} mbar, respectively. The aluminium and titanium layers were of the thicknesses of 16 nm and the TiN layers were 20 nm thick. These thicknesses yield from composition stoichiometry. In order to have a Ti_2AlN stoichiometry it is needed to have twice as much titanium atoms than aluminium and nitrogen atoms in a unit of volume. Knowing the densities of Al, Ti, and TiN, the ratios of the thicknesses of these layers were calculated to be 1:1:1.25 for Al, Ti, and TiN, respectively.

After layer deposition, the samples underwent annealing at 600°C in argon or nitrogen atmospheres for 10 min or 3 h. For details, see Table.

TABLE

Samples used in this study.

No.	Substrate	Layers	Subsequent treatment
M01	Al_2O_3/GaN	Ti/Al/TiN/Ti/Al/TiN/Ti/Al/TiN	annealed 600°C, Ar, 3 h
M02	Al_2O_3/GaN	TiN/Al/Ti/TiN/Al/Ti/TiN/Al/Ti/TiN	annealed 600°C, Ar, 3 h
M03	Al_2O_3/GaN	Ti/TiN/Al/Ti/TiN/Al/Ti/TiN	annealed 600°C, Ar, 3 h
M04	Al_2O_3/GaN	TiN/Al/Ti/TiN/Al/Ti/TiN/Al/TiN	annealed 600°C, Ar, 3 h
M05	Al_2O_3/GaN	Ti/Al/Ti/Al/Ti/Al/Ti/Al	annealed 600°C, N_2, 10'
M08	Al_2O_3	Ti/Al/TiN	annealed 600°C, Ar, 3 h
M09	Si (111)	Ti/Al/TiN	annealed 600°C, Ar, 3 h
M10	Al_2O_3/GaN	Ti/Al/TiN	annealed 600°C, Ar, 3 h
M12	Al_2O_3/GaN	Ti/TiN	none

2.2. Characterisation methods

After deposition, the samples were characterised using secondary ion mass spectroscopy (SIMS) profiling in ultrahigh vacuum with a CAMECA IMS6F system and high resolution X-ray diffraction (HR XRD) with a Phillips X'Pert system using the Cu K_α line. The current–voltage characteristics were measured with a computer controlled Keithley 2400 source/meter and the ohmic contact characteristics were inferred from circular transmission line method [5]. The same tools were used for sample characterisation after annealing.

3. Results and discussion

The SIMS profiles taken after deposition show good separation of the individual layers with some interdiffusion at the interface to GaN. The situation after annealing shows significant interdiffusion of atoms in the layers (see Fig. 2).

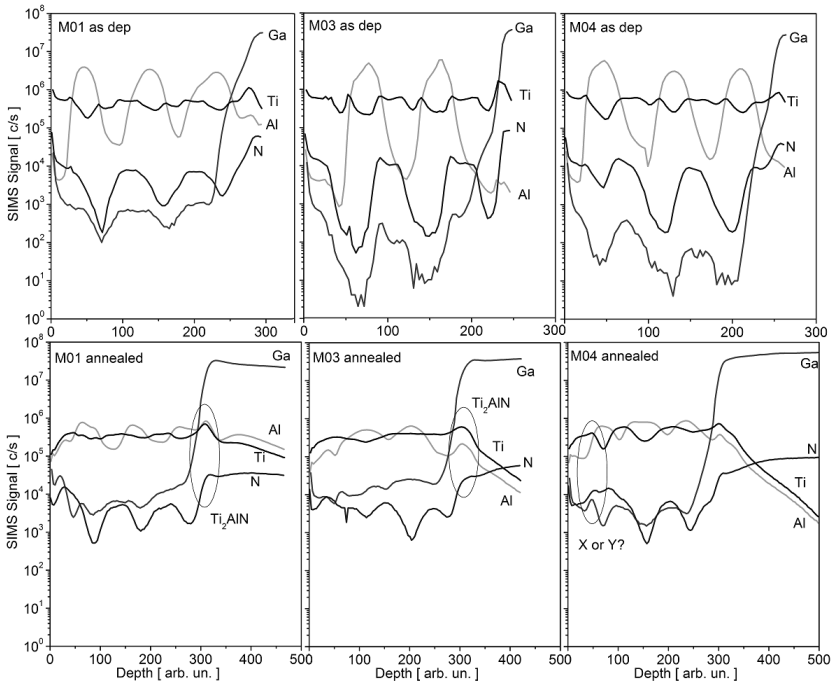

Fig. 2. SIMS profiles for as deposited and annealed M01, M03, and M04 samples.

The simultaneous peaks of titanium, aluminium and nitrogen at the interface to the substrate marked in Fig. 2 with an absence of a gallium peak, appear in the samples where the X-ray measurements showed lines identified as Ti_2AlN (0001) MAX phase (see Fig. 3). The same peaks appear in the samples shown in Fig. 3 and they are also observed by Höglund et al. [6] who used synchrotron radiation for their structural studies. It can be seen that the only peaks from Ti_2AlN observed have the same crystallographic (0001) orientation as the GaN

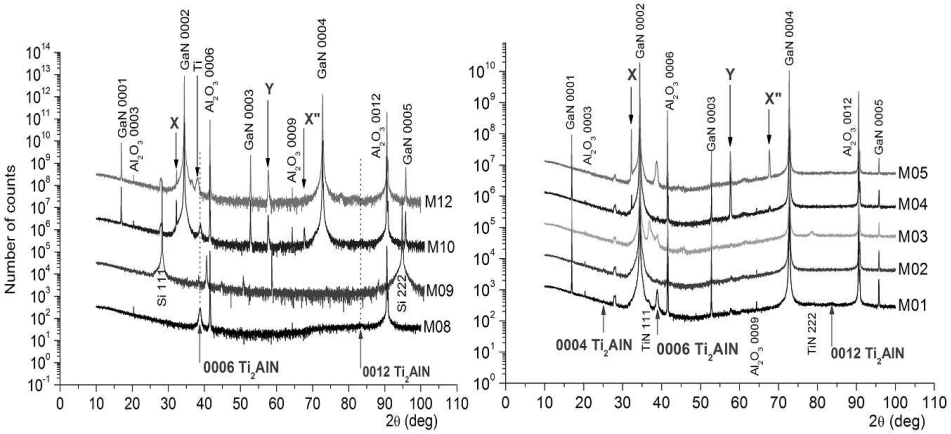

Fig. 3. X-ray diffractograms for as deposited M12 sample and annealed M01–M05, M08, M09, and M10 samples.

and Al_2O_3 substrates. This means that the MAX phase that forms after annealing is monocrystalline and follows the orientation of the substrate. The phase was observed to grow both on GaN and Al_2O_3 substrates which are (0001) oriented, but was not observed to grow on Si (111) which only has a similar surface pattern, although the orientation is different (see Fig. 3).

The Ti_2AlN peaks in the SIMS profile are significantly smaller for sample M04 for which the X-ray diffractometer does not show the Ti_2AlN (0001) lines. This may be due to TiN limiting interdiffusion between the substrate and the deposited layers and thus impeding the formation of the Ti_2AlN MAX phase.

Other two lines can also be observed, which are marked as X and Y in Fig. 3. X" is a second order of the X line. Y has different intensity behaviour than X (see M04 and M05 in Fig. 3) and as such is thought to be an other phase. The peaks appear both in as-deposited and annealed samples, however they do not appear on substrates other than GaN, which can lead to suspecting Ga outdiffusion. They also show no dependence on Al presence in the sample. That leads to think that the phases contain Ga and Ti. However, their identification was impossible. It was checked that they are not a Ti_2GaN MAX phase by comparing with a Ti_2GaN XRD spectrum with [7] and also by calculating the XRD spectrum for a unit cell of such a phase, with the cell parameters taken from [3]. In the SIMS profiles for M04 a peak of gallium, titanium and nitrogen is observed near the surface of the sample, that possibly may be the X or Y phase.

The current–voltage characteristics in Fig. 4 show a diode behaviour before annealing and an ohmic, or near ohmic behaviour after annealing. The circular transmission line method allowed to calculate the contact resistances for the cases where ohmic behaviour was observed, yielding $R_c = 6.96 \times 10^{-5}\ \Omega\ \mathrm{cm}^2$ and $R_c = 1.27 \times 10^{-4}\ \Omega\ \mathrm{cm}^2$ for M01 and M04, respectively.

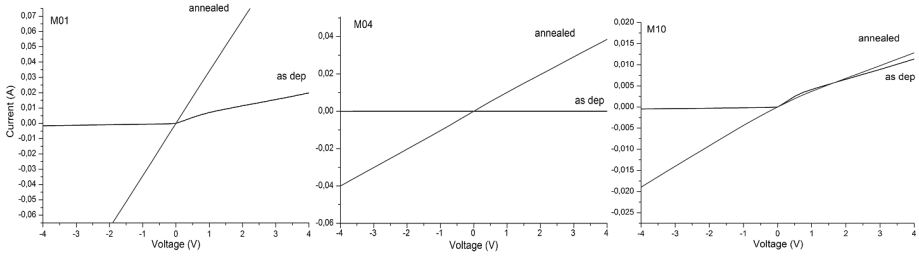

Fig. 4. Current–voltage characteristics for as-deposited and annealed M01, M04, and M10 samples.

4. Conclusions

Monocrystalline Ti_2AlN MAX (0001) phase growth on n-GaN was observed alongside two other unidentified phases containing Ga and Ti. The Ti_2AlN phase grows at the interface of the deposited layers with the substrate and does not grow when the first layer on the substrate is TiN which impedes interdiffusion with the substrate.

Ohmic current–voltage characteristics were observed yielding contact resistances in the range 10^{-4} Ω cm^2. In the knowledge of the authors, this is the first time an $I-V$ characteristic of a Ti_2AlN MAX phase n-GaN contact has been measured.

It is important to stress out that the deposition process is not optimised and all samples were prepared at first attempt. Further research is planned in order to gain fuller control over the growth of Ti_2AlN MAX phase, including further characterisation with complementary methods, and studying high temperature influence on the structural properties of such materials.

Acknowledgments

This study was partially supported by the EC under the project "Materials for Robust Gallium Nitride" CP-IP 214610-2 MORGaN.

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