MICROSTRUCTURE AND THERMAL STABILITY OF TRANSITION METAL NITRIDES AND BORIDES ON GaN

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ABSTRACT

Microstructure and thermal stability of ZrN/ZrB_2 bilayer deposited on GaN have been studied using transmission electron microscopy methods (TEM) and secondary ion mass spectrometry (SIMS). It has been demonstrated that annealing of the contact structure at 1100^0C in N_2 atmosphere does not lead to any observable metal/ semiconductor interaction. In contrast, a failure of the integrity of ZrN/ZrB_2 metallization at 800^0C, when the heat treatment is performed in O_2 ambient has been observed.

INTRODUCTION

One of the most challenging problems in the fabrication of GaN-based devices is the development of thermally stable metallization. This is especially important because material properties of GaN make it the most suitable, from among other III-V compound semiconductors, for high-temperature and high-power electronics. The subject of reliable metallization for GaN is extensively studied, and there have been reports on the thermal stability of a variety of metal/GaN contacts. However, in most of these studies pure metal contacts such as Al, W, Ni, Pd, and Pt with stability limited to 700^0C have been used [1-5]. On the other hand, the majority of thermally stable contacts systems, implemented with Si and GaAs-based devices rely on refractory transition metal nitrides and borides. These materials are distinguished for their exceptional combination of properties like low resistivity, high melting point, hardness and resistance to corrosion. Such characteristics might also be essential in preventing the decomposition of GaN during thermal processing steps such as formation of ohmic contacts or post-implantation annealing.

We have previously reported an approach for improving the reliability of metallization to n-GaN by using TiN diffusion barrier [6]. Excellent stability of TiN in contact to GaN up to annealing temperature of 900^0C has been demonstrated. In the present study, in search for metallization systems with further improved resistance to high-temperature treatment we investigate ZrN/ZrB_2 bilayers. The presence of nitrogen in the film adjacent to GaN is a key factor in preventing the decomposition of the semiconductor. Taking into account recent reports concerning the impact of annealing ambient on electrical properties of metal/GaN contacts [7], we compare the microstructure and thermal stability of contacts heat treated in both nitrogen and oxygen atmosphere.

EXPERIMENTAL PROCEDURE

GaN epilayers grown *via* organometallic vapor phase epitaxy on sapphire have been used in this study. Zr-based layers, nominally 100 nm thick, were prepared by DC sputtering in Ar discharge, from ZrB_2 or ZrN targets, without breaking the vacuum. Heat treatments up to 1200^0C were performed in a rapid thermal annealing system, under flowing N_2 or O_2.

The microstructure of the metal/semiconductor system was investigated by cross-sectional transmission electron microscopy (XTEM). Composition profiles were evaluated using secondary ion mass spectroscopy (SIMS) and compared with the results of selected area electron diffraction (SAED) analysis. TEM studies were performed with JEOL 2000EX microscope. SIMS depth profiling was carried out with Cameca 6f instrument using cesium primary ion beam. As the mode of operation of a particular capping layer may critically depend upon its crystalline structure, special attention was paid to the recrystallization processes.

RESULTS

The microstructure and mechanical properties of capping films are highly dependent on the surface morphology of GaN. Films deposited on rough surface peeled immediately after sample coating, while films deposited on smooth surface exhibited excellent adhesion to the substrate.

The evolution of the microstructure of GaN/ZrN/ZrB_2 system under heat treatment is presented in a series of TEM micrographs, shown in Fig.1.(a)-(d). The as-deposited ZrN layer, adjacent to the semiconductor substrate, is partially crystalline while ZrB_2 film is totally amorphous. Upon annealing a progressive recrystallization of Zr-based metallization occurred. Two metallization films became polycrystalline during annealing under N_2 flow for 5min at 800^oC. The analysis of SAED ring patterns recorded for these two layers confirmed that the lower and upper layers consisted of ZrN and ZrB_2, respectively. Similar results were obtained for the contact subjected to annealing under N_2 flow for 30s at 1000^oC. It is worth to mention that the studies of the microstructure of these two bilayers (Fig.1(c) and Fig.1(d)) did not reveal any indication of interaction between ZrN and ZrB_2. Sharp, abrupt interfaces are visible on micrographs of these structures. Also the metallization/GaN interface remains unchanged. The results of more detailed TEM studies of ZrN and ZrB_2 films heat treated at 1100^0C in N_2, presented in Fig. 2, show that two Zr-based films considerably differ in microstructure. ZrN layer shows a columnar arrangement of grains of a size comparable with the thickness of the whole film. In contrast, ZrB_2 layer is fine-grained.

The crystalline structure of the metallization annealed under O_2 flow at 800^oC, shown in Fig.1(b), is completely different. Here, the bottom polycrystalline layer, of a thickness of 100nm, is covered by about 80nm thick amorphous film. SAED pattern of the polycrystalline layer revealed mainly the presence of ZrN. However, our SIMS data, as will be discussed in the following section, indicated that there was also boron present in this layer. In addition, closer inspection of the TEM micrograph of this layer shows the presence of very faint and not well defined interface in the middle of this layer. This can indicate that in fact this layer was formed from the two initial layers. The origin and the

composition of the amorphous layer are not very clear. SAED of the amorphous layer contained three, very broad diffraction rings. It was found that their radii correlated within the experimental errors with the three smallest inter-planar spacing for ZrB_2 hexagonal phase. This can indicate presence of amorphous ZrB_2 within this layer.

SIMS results obtained for as-deposited and heat treated GaN/ZrN/ZrB_2 structures are shown in Fig.3. The profiles of ZrN^- and ZrB^-complexes show no evidence of interaction both between the layers and substrate at 950^0C. The tails of ZrB and ZrN signals extending to the semiconductor originate from the surface roughening caused by the sputtering process. With increasing temperature, the two films seem to interact with each other, however no reaction with the semiconductor is observed even at 1100^0C. In contrast, heating at 800^0C in oxygen ambient leads to interdiffusion of the structure constituents.

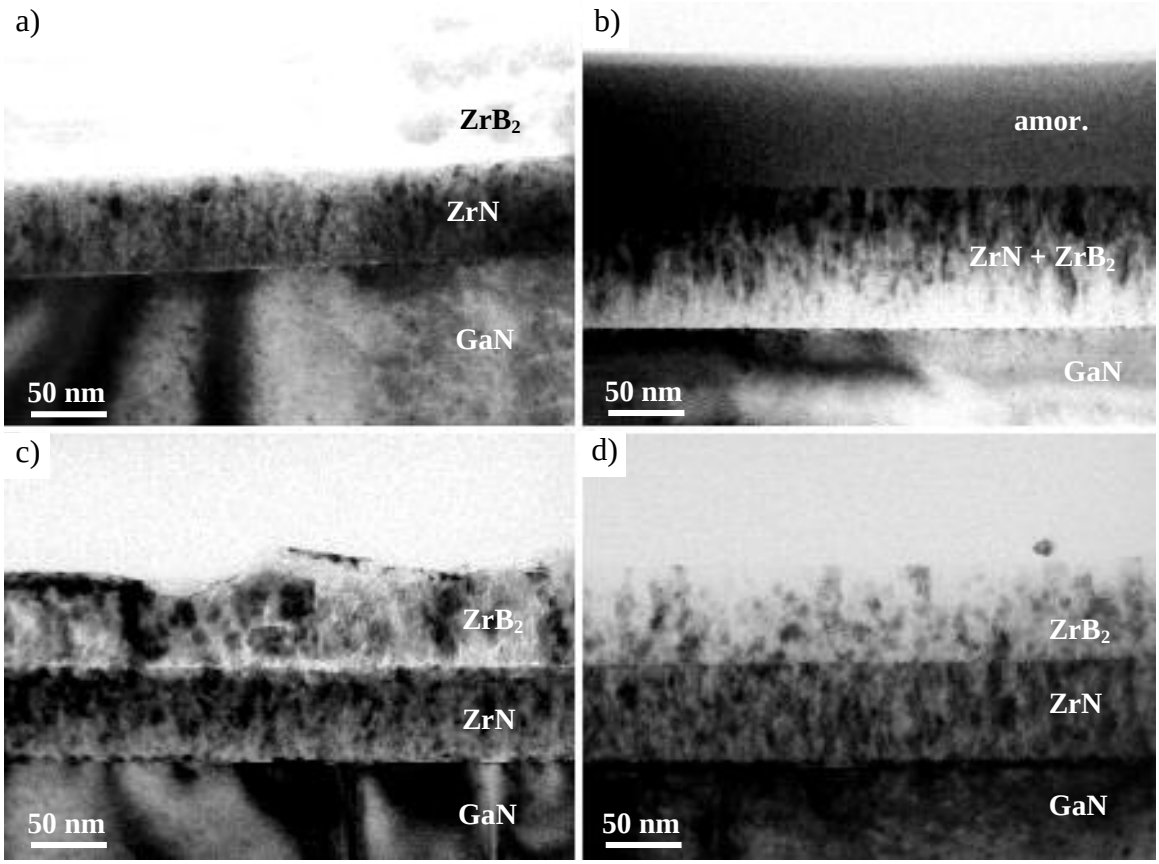

Fig.1. XTEM micrographs of ZrN/ZrB_2 bilayers deposited on GaN MOCVD layers: (a) as-deposited structure, (b) structure annealed under O_2 flow for 5min at 800^oC and (c), (d) structures annealed under N_2 flow for 5min at 800^oC and 30s at 1000^oC, respectively.

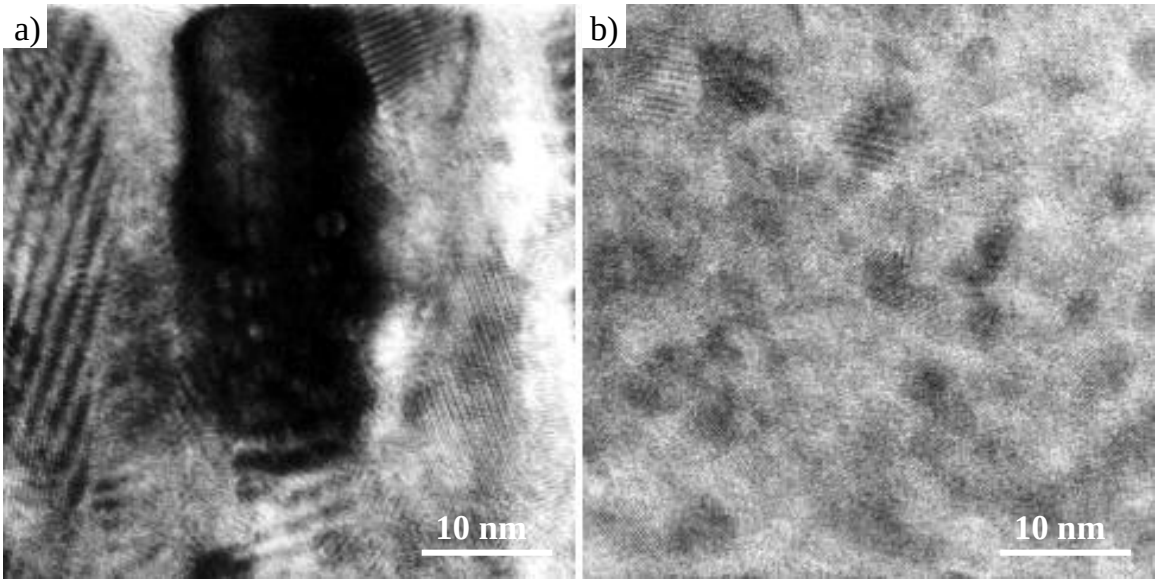

Fig.2. High resolution TEM micrographs of: (a) ZrN and (b) ZrB_2 layers present in ZrN/ZrB_2 bilayer structure deposited on MOCVD GaN layer and annealed for 30s at 1100^{o}C under N_2 flow.

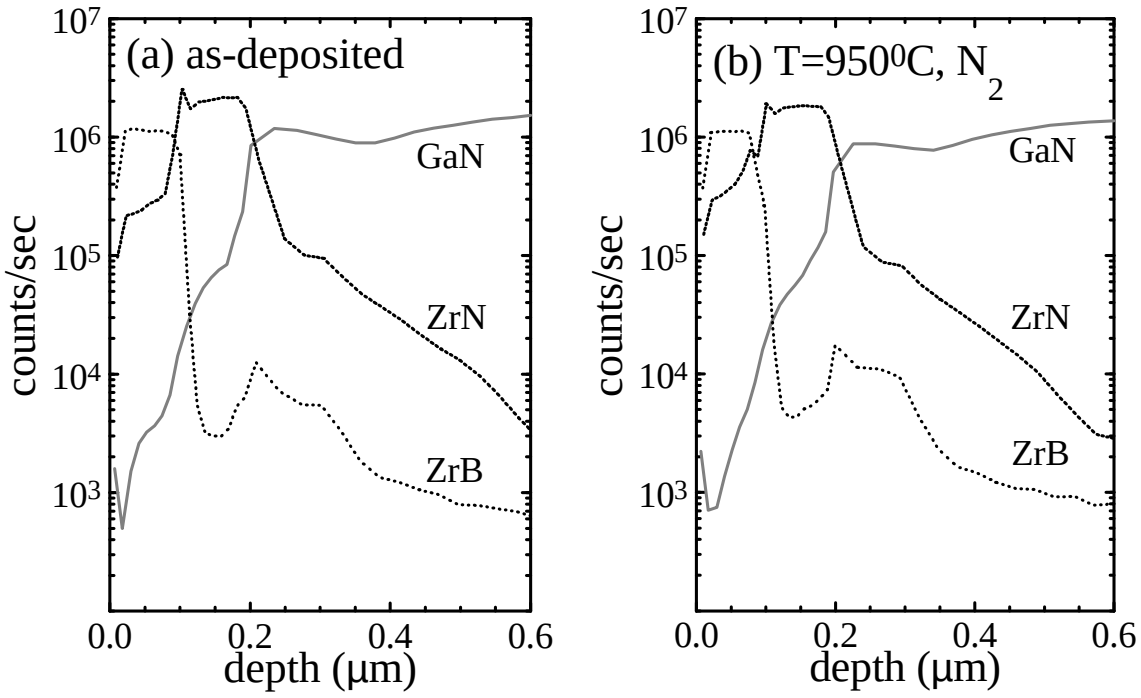

Fig.3. SIMS in-depth profiles for ZrN/ZrB2 bilayers deposited on MOCVD GaN layers: (a) as-deposited structure, (b), (c), (d) and (e) structures annealed under N_2 flow for 30s at 950^{o}C, 1000^{o}C, 1050^{o}C and 1100^{o}C, respectively, and (e) structure annealed under O_2 flow for 5min at 800^{o}C.

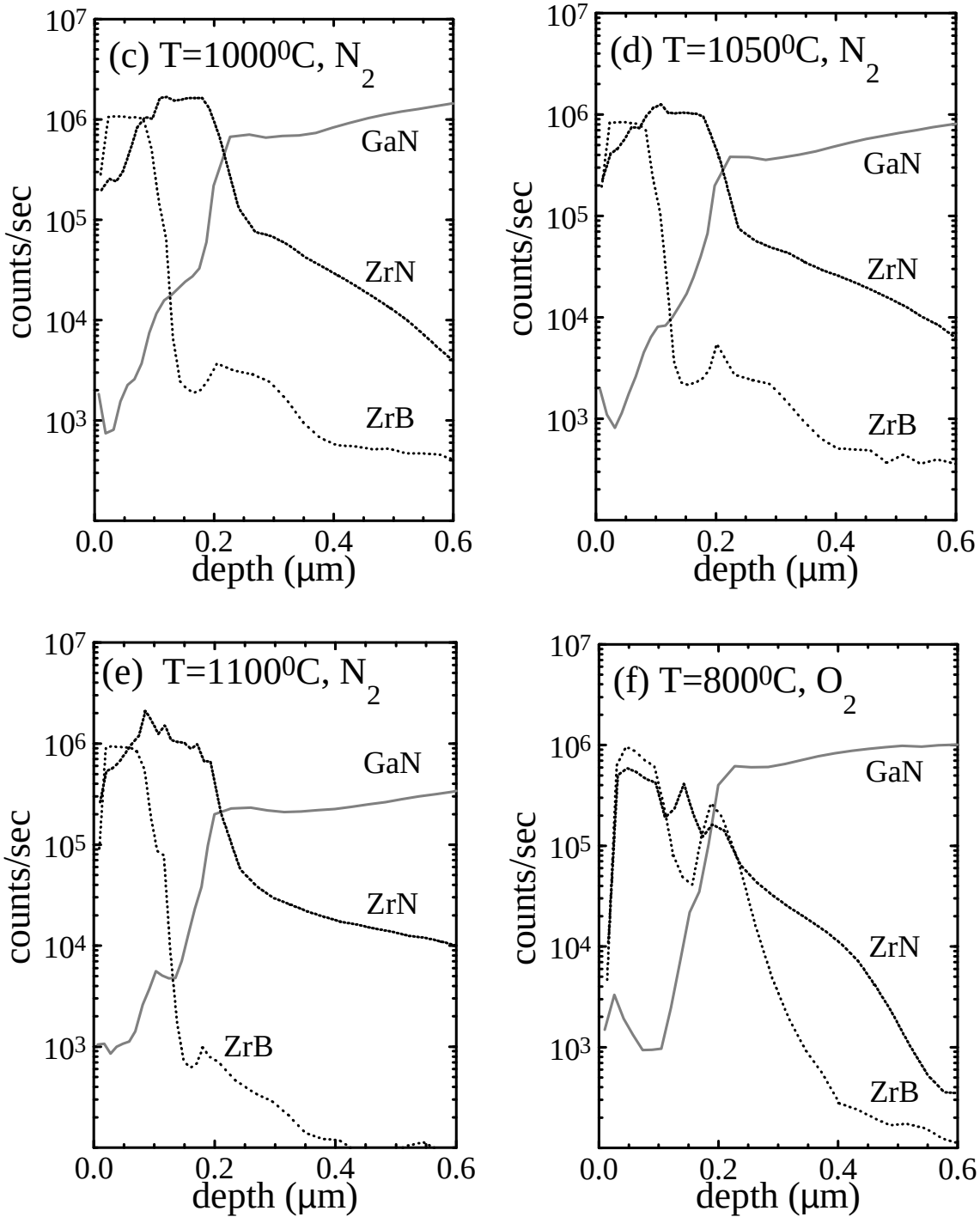

Fig.3. (continued).

DISCUSSION AND CONCLUSIONS

In this work we have studied the microstructure and the thermal stability of ZrN/ZrB_2 bilayer on GaN with emphasis on the determination of the influence of gas ambient during heat treatment. Of particular importance is the fact, that annealing of the contact structure at 1100^0C in N_2 atmosphere does not lead to any observable metal/semiconductor interaction, thus we can conclude that the applied metallization scheme demonstrates an outstanding thermal stability. This is the most probably the result of the advantageous local structure arrangement at ZrN/ZrB_2 interface due to differences in the microstructure of these materials. The recrystallization mode of ZrN film results in a columnar structure, while the heat treated ZrB_2 layer consists of fine, regularly-shaped grains.

Another important finding is the failure of the integrity of ZrN/ZrB_2 metallization at 800^0C, when the heat treatment is performed in oxygen ambient. Here, the annealing in O_2 causes the amorphization of the upper part of the metallization and the intermixing of both Zr-based compounds. As the importance of annealing in O_2 flow or in air has been demonstrated beneficial for the fabrication of low-resistivity ohmic contacts to p-type GaN [7,8], further work is needed to understand the above effect.

ACKNOWLEDGEMENTS

This work was partially supported by the Polish Committee for Scientific Research (grant No.PBZ 28.11/P9) and by Dr. K. Wu from BMDO (order N W31RPD-8-A8015).

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