EPITAXIAL GROWTH AND STRUCTURAL CHARACTERIZATION OF SINGLE CRYSTALLINE $ZnGeN_2$

L.D. Zhu*, P.H. Maruska*, P.E. Norris*, P.W. Yip**, L.O. Bouthillette**

*NZ Applied Technologies, 8A Gill Street, Woburn, MA 01801, zhu@nzat2.tiac.net
**Air Force Research Laboratory, 80 Scott Dr., Hanscom AFB, MA 01731

Cite this article as: MRS Internet J. Nitride Semicond. Res. 4S1, G3.8(1999)

Abstract

A new nitride semiconductor, single crystalline $ZnGeN_2$ has been successfully grown by MOCVD for the first time. The epitaxial $ZnGeN_2$ is found to be of hexagonal wurtzite lattice without ordering of the zinc and germanium atoms in the pseudomorphic Group III sublattice. Lattice constants of the $ZnGeN_2$ are $a = 3.186 \pm 0.007$ A, $c = 5.174 \pm 0.012$ A, which gives $c/a = 1.624$.

Introduction

After three decades of fundamental research, Group III-nitrides research and development activity is in a renaissance. Bright and efficient blue and green LEDs are in the marketplace, InGaN/GaN/AlGaN heterostructure laser diode research is progressing at a rapid pace. Many other optoelectronic and high temperature electronic devices are being contemplated[1]. These achievements are attributed mainly to the breakthroughs in the course of GaN research, such as first synthesis of GaN[2], HVPE growth of single crystalline GaN[3], first demonstration of GaN LED, invention of buffer layer technology, success in p-type conversion, as well as epitaxial lateral over growth.

Compared to the conventional III-V semiconductors, Group III-nitrides system has some inherent limitations. In Group III-arsenides and phosphides, there are choices to construct lattice matched dissimilar band gap heterostructures to design various optoelectronic and electronic devices with excellent crystal quality. However, lattice mismatch between GaN and AlN, GaN and InN is as large as 2.4% and 11.3%, respectively. The large mismatch forces the use of low Al composition AlGaN, which causes carrier overflow in GaN/AlGaN heterojunctions. Increasing Al composition results in cracking of the AlGaN layer beside the increased resistivity. The situation in InGaN seems even more serious. The huge atomic size differences are the cause of instability in the alloy and results in phase separation. This fact limits utility of InGaN for use in photonic devices with longer wavelengths beyond green as well as other devices requiring high In composition or thick InGaN layers. Another limiting factor in GaN/AlGaN system is the low p-type conductivity. Resistivity of p-GaN is around 0.2 Ω-cm, and it is higher for p-AlGaN. This is a heating source as well as origin of parasitic RC time constant in high power laser diodes and HBTs.

To explore the potential of wide band gap semiconductors with a broad horizon, we noticed a set of nitride semiconductors which can be expressed as II-IV-N_2 compound system. Early in1957 Goodman pointed out that by ordered substitution of Group II and Group IV atoms for the Group III atoms in the III-V compounds a new ordered semiconducting II-IV-V_2 compounds could be prepared[4]. Crystallographically, this set of compounds evolves from the tetrahedral diamond structure with the Group V atom surrounded by two Group II and two Group IV atoms and the Group II or IV atom surrounded by four Group V atoms tetrahedrally.

https://doi.org/10.1557/S1092578300002374 Published online by Cambridge University Press

This coordination obeys the four electrons per site rule, and the atomic bonding in the crystal is of covalent nature. The transfer from III-V to II-IV-V_2 compounds brings about new properties of the materials such as band gap, electronic band structure, and non-linear optical properties caused by the drop in symmetry due to superlattice formation. Chalcopyrite II-IV-As_2 and II-IV-P_2 compounds are relatively extensively investigated in search of superior thermoelectric and non-linear optic materials[5]. An outstanding achievement in chalcopyrite research is the nonlinear optical applications of $ZnGeP_2$ and $CdGeAs_2$[5]. There is little work on II-IV-N_2, even including powder synthesis, perhaps due to the need for high temperature and pressure[6,7]. The goal of our research is an exploration of single crystalline II-IV-N_2 materials in conjunction with Group III-nitrides and SiC research.

Experiment

The initial growth experimentation was carried out by microwave plasma enhanced activated nitrogen MOCVD. However, most of the materials reported here have been grown by ammonia source MOCVD. The growth reactor is a water cooled stainless steel vertical chamber, in which the wafer can be rotated to ensure film thickness uniformity. The precursors used as zinc and germanium sources are diethylzinc and germane. Activated nitrogen was supplied from ammonia. Ammonia flow rate was kept at 180 mmole/minute, and total flow rate of diethylzinc and germane was varied around 30 mmole/minute. Corresponding $[NH_3]/([DEZ] + [GeH_4])$ ratio is 5000. Crystalline deposition could be obtained with the growth temperature from 550°C to 700°C. During the growth the chamber was kept at a pressure in a range of 40-500 Torr. The substrate used to grow $ZnGeN_2$ was c- and r-plane sapphire, and $ZnGeN_2$ was grown via an intermediate GaN seed layer.

Surface morphology of the epitaxial films were examined by photomicroscopy, scanning electron microscopy and atomic force microscopy. Crystallinity of the $ZnGeN_2$ layers was investigated by x-ray diffraction $\theta-2\theta$ scans, double crystal x-ray rocking curve analysis and reflection high energy electron diffraction images.

Results

The epitaxial $ZnGeN_2$ layer is smooth, shiny, and the color looks yellowish by visual examination. A scanning electron microscope picture of the surface shows, sometimes, shiny particulates, the size and amount of which is dependent on the DEZ to GeH_4 molar ratio, suggesting that it is accumulation of extra zinc. Atomic force microscopy was utilized to examine the surface microscopic structure and roughness. Inclined height images of $ZnGeN_2$ layers grown on c- and r-plane sapphire substrates are shown in Figs. 1a and 1b, respectively. A common feature in the two microscopic pictures is a spike shaped morphology, which demonstrates that the growth is columnar from discontinuous seed islands, similar to the grain or domain structure of GaN on Sapphire. However, there is a distinct difference in the two surfaces. The crystal domains of $ZnGeN_2$ layer on r-plane sapphire is more fine and uniform in size and height with RMS value of 10.4 nm, while $ZnGeN_2$ film on c-plane sapphire is composed of larger and flatter domains with RMS value of 17.1 nm, even though there are some tall and rounded columns. These features can also be confirmed from phase images of the two surfaces shown in Figs.2a and 2b. An interesting feature in Fig. 2b compared to Fig.2a is domain orientation in plane. This feature is consistent with the conclusion about epitaxial crystallographic relationship derived from x-ray diffraction analysis given below.

https://doi.org/10.1557/S1092578300002374 Published online by Cambridge University Press

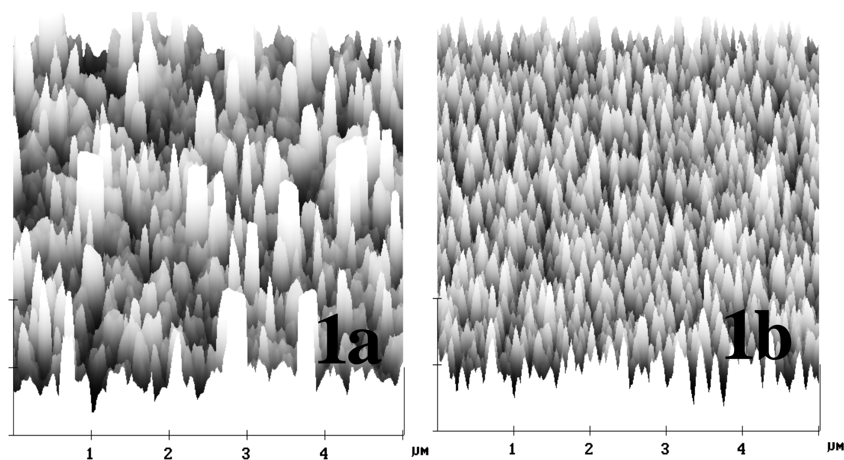

Fig.1. AFM height images of $ZnGeN_2$ surfaces grown on c-sapphire(1a) and r-sapphire(1b).

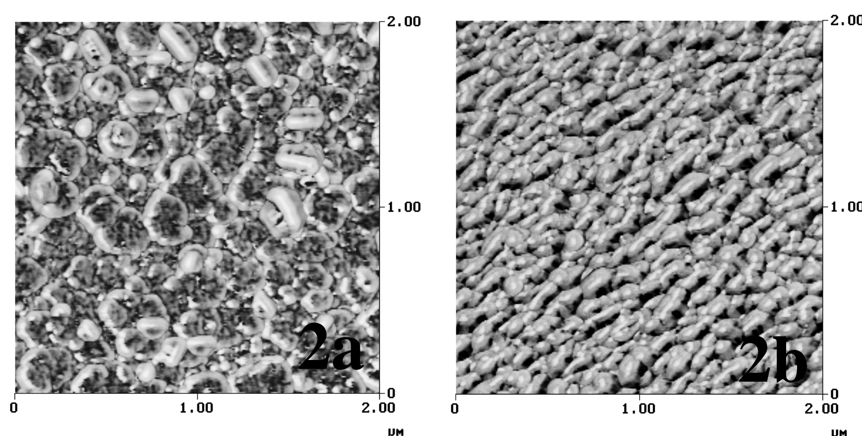

Fig.2. AFM phase images of $ZnGeN_2$ surfaces grown on c-sapphire(2a) and r-sapphire(2b).

Chemical composition ratios were determined by energy dispersive spectroscopy (EDS) measurement. Nitrogen K-line, zinc L-line and germanium L-line were used for the measurement. GaN and bulk $ZnGeP_2$ were used for calibration of the equipment. Zinc to germanium ratio in the solid can be controlled in 0.97-1.00 range by monitoring [DEZ] to [GeH_4] ratio in the gas phase at a given growth temperature. It is found that there is a self stoichiometric mechanism in a limited range of growth parameters. Detailed results in this aspect will be published elsewhere.

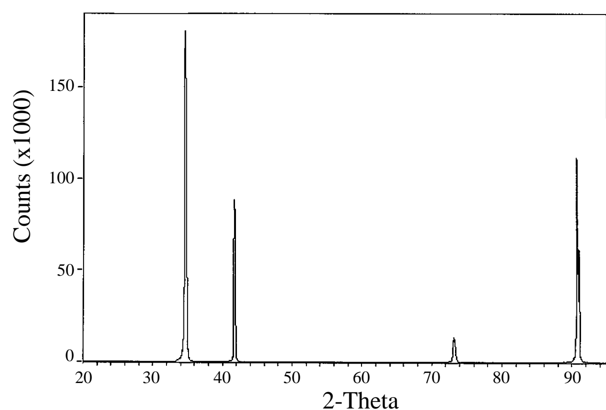

Fig. 3. X-ray diffraction θ–2θ spectrum of $ZnGeN_2$ grown on c-sapphire substrate.

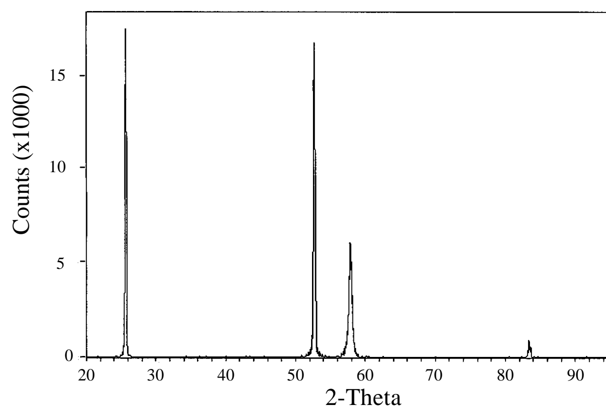

Fig. 4. X-ray diffraction θ–2θ spectrum of $ZnGeN_2$ grown on r-sapphire substrate.

https://doi.org/10.1557/S1092578300002374 Published online by Cambridge University Press

Crystallinity of the $ZnGeN_2$ epitaxial layers were characterized using x-ray $\theta-2\theta$ scan measurement. A typical x-ray diffraction spectrum of a $ZnGeN_2$ layer grown on c-plane sapphire substrate is shown in Fig. 3. The strong peak at $2\theta=34.65^o$ and second peak at $2\theta=73.10^o$ are from the epitaxial layer. Another typical $\theta-2\theta$ scan on a $ZnGeN_2$ layer grown on r-plane sapphire is shown in Fig. 4. The only prominent diffraction peak coming from the epitaxial layer is at $2\theta=57.80^o$. Because these diffraction spectra are almost indistinguishable from that of corresponding GaN on c- or r-plane sapphire, a further scrutinizing is needed to identify the crystallinity of the $ZnGeN_2$ layers. In this regard, two kinds of experiment have been carried out: one is growth of the same GaN intermediate layers as the actual ones and comparing the x-ray diffraction intensities; the other is reflection high energy electron diffraction study with very low incident angle to characterize the surface epitaxial layer. With a fixed diffractometer settings, the x-ray diffraction intensity counts of the intermediate GaN layers on c- and r-plane sapphires are 10000 for the (0002) diffraction and 300 for the (11-20) diffraction, respectively, while the corresponding counts from the $ZnGeN_2$ layers, chemical compositions of which have been confirmed by EDS in the range of measurement error, are 180,000 for the $2\theta=34.65^o$ diffraction (Fig.4) and 16,000 for the $2\theta=57.80^o$ diffraction (Fig.5), respectively. These experiments prove that the $ZnGeN_2$ layers are single crystals and the crystal structure is the same as GaN, wurtzite structure, and lattice constants of the two materials are almost indistinguishable. The other experiment to verify single crystalline nature of the $ZnGeN_2$ layers is reflection high energy electron diffraction (RHEED) study using JEOL 100-CX. The electron beam impingement angle was 1°, and the beam energies used were 20 and 100 keV. A RHEED pattern, taken with 100 keV, of a $ZnGeN_2$ sample grown on c-plane sapphire is shown in Fig. 5. The bight spot pattern is due to $ZnGeN_2$, while the dim fine points come from the sapphire substrate. The beam angle was essentially orthogonal to the c-axis of the film, leading to a (10-10) RHEED pattern, which is rectangular. This pattern assures that the $ZnGeN_2$ layer is an excellent single crystal with wurtzite lattice.

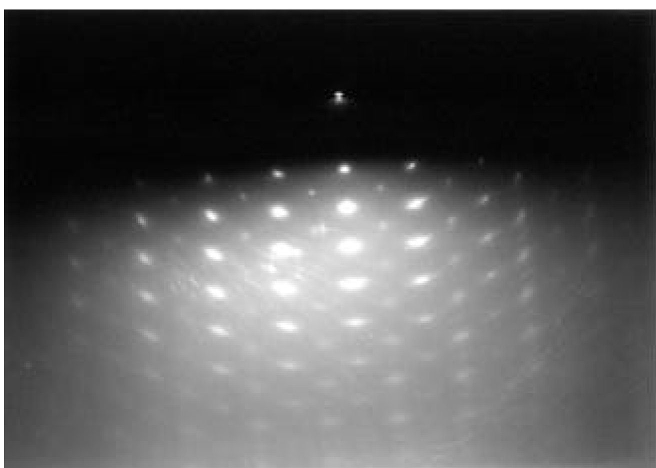

Fig. 5. RHEED pattern of $ZnGeN_2$ grown on c-sapphire substrate.

Improper seed layer preparation results in a polycrystalline $ZnGeN_2$ layer, which results in extra diffraction peaks. Our x-ray diffraction data obtained from single and polycrystalline epitaxial layers are compared in table I with that of Maunaye and Lang [6], who synthesized polycrystalline $ZnGeN_2$ powder in1970. From x-ray diffraction studies of the powder material they claimed that zinc and germanium atoms are ordered in the otherwise hexagonal sublattice, resulting in a monoclinic lattice structure with the deformed angle 118.88^o. The data in table I clearly indicate that the split diffraction peaks due to the ordering in the powder crystal are degenerated in our epitaxial crystals. The diffraction line angles of the epitaxial $ZnGeN_2$ are

https://doi.org/10.1557/S1092578300002374 Published online by Cambridge University Press

between the corresponding split lines of the powder. These data lead to a conclusion that in the epitaxial $ZnGeN_2$ single crystal, zinc and germanium atoms are disordered, resulting in a hexagonal wurtzite lattice.

Table I Comparison of x-ray diffraction data of synthesized powder and epitaxial $ZnGeN_2$ crystals

Synthesized powder $ZnGeN_2$		Epitaxial film $ZnGeN_2$	
monoclinic index	2θ	2θ	hexagonal index
0 0 1	32.28		
-1 0 1	32.84	32.40	1 0 -1 0
0 2 0	34.54	34.65	0 0 0 2
0 1 1	36.74		
-1 1 1	37.23	36.77	1 0 -1 1
1 0 1	57.22		
-1 0 2	58.24	59.91	1 1 -2 0

This phenomenon can be understood from the crystallographic relationship in the epitaxy. In the growth of $ZnGeN_2$ on c-plane sapphire substrate, the relationship is $ZnGeN_2${0001}// sapphire{0001}, $ZnGeN_2${11-20}//sapphire{10-10}. This is a configuration putting Zn-N or Ge-N molecular unit on lattice points and centers of the triangles in the close packed sapphire c-plane. There is a rotation symmetry around the perpendicular c-axis in this configuration and the freedom for zinc and germanium atomic ordering has been lost. For $ZnGeN_2$ layer grown on r-plane sapphire, the epitaxial relationship is $ZnGeN_2${11-20}//sapphire{1-102}. The c-axis of the $ZnGeN_2$ is located in the plane of the rectangular sapphire surface lattice which brings about a mirror symmetry for the Zn and Ge atomic arrangement. This results in a loss of freedom for the ordering, which exists in the freely nucleating high temperature powder synthesis.

Lattice constants of the epitaxial $ZnGeN_2$ crystal, determined from the x-ray diffraction data, are $a = 3.186 \pm 0.007$ A, $c = 5.174 \pm 0.012$ A, which gives $c/a = 1.624$. The error mainly comes from the strain and defects existing in the $ZnGeN_2$ layers with different thickness and composition deviation.

This crystal structurally matches to GaN nearly perfectly. Lattice mismatch for c-plane growth is 0.09% on GaN, 15.98% on sapphire. For r-plane sapphire, three rectangular $ZnGeN_2$ two dimensional lattices can be accommodated on the rectangular surface lattice of the sapphire. If the c-axes are in the same direction as with epitaxial relationship $ZnGeN_2${1-100}//sapp.{11-20}, lattice mismatches are 0.89% in $ZnGeN_2$ c-direction and 15.98% in other direction. If $ZnGeN_2$ c-axis is rotated 90° as with the relationship $ZnGeN_2${11-20}//sapp.{11-20}, corresponding mismatches are 7.6% and 8.7%, respectively. Both arrangements are favorable compared to the growth on c-sapphire, and the 90° rotation arrangement has about half strain energy compared to the other one.

Crystal quality of the $ZnGeN_2$ was manifested by x-ray rocking curve FWHM of 24 arc minutes for 1 mm thick $ZnGeN_2$, as shown in Fig. 6.

https://doi.org/10.1557/S1092578300002374 Published online by Cambridge University Press

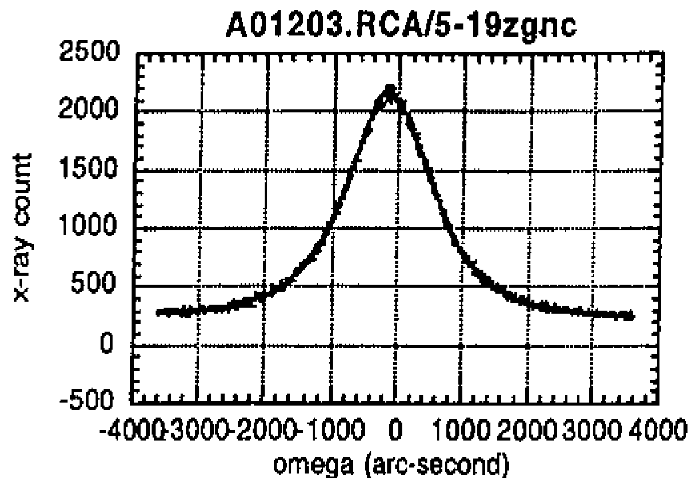

Fig. 6. X-ray double crystal diffraction rocking curve of a $ZnGeN_2$ epi-layer.

Conclusions

Single crystalline $ZnGeN_2$ has been successfully grown on sapphire and GaN/sapphire substrates by low pressure MOCVD for the first time. Precursors are DEZ, GeH_4 and ammonia. Appropriate growth temperature was in the range of 550-700°C. Chemical composition of the compound was monitored by EDS and adjusted to stoichiometric by varying [DEZ]/[GeH_4], [NH_3]/{[DEZ]+[GeH_4]} ratios in the gas phase. It is found that there is a self stoichiometric growth mechanism in a limited range of conditions. Single crystalline nature of the epitaxial $ZnGeN_2$ was verified by x-ray diffraction and RHEED. X-ray double crystal rocking curve FWHM was 24 arc minutes for a 1 mm thick $ZnGeN_2$ layer. Zn and Ge atoms are disordered in the epitaxial crystal, resulting in hexagonal wurtzite structure. Lattice constants of the $ZnGeN_2$ are $a = 3.186 \pm 0.007$ A, $c = 5.174 \pm 0.012$ A, with $c/a = 1.624$.

Acknowledgment

NZ Applied Technologies gratefully acknowledges the support of the Air Force Office of Scientific Research under Contract F49620-96-C-0048 and contract monitor Major Michael Prairie. Brian Demczyk and John Larkin at Hanscom AFB are acknowledged for the RHEED study.

References

1. J.I. Pankove, The satellite Workshop of the 2nd Int. Conf. on Nitride Semicond. (Nov.1, 1997 Tokushima, Japan) p.1.
2. W.C. Johnson, J.B. Parsons, and M.C. Crew, J. Phys. Chem., **36**, 2561 (1932).
3. H.P. Maruska and J.J. Tietjen, Appl. Phys. Lett., **15**, 367 (1969).
4. C.H.L. Goodman, Nature, **179**, 828 (1975).
5. J.L. Shay and J.H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications, Pergamon Press, 1975.
6. M. Maunaye et J. Lang, Mater. Res. Bull., **5**, 793 (1970).
7. T. Endo, Y. Sato, H. Takizawa, M. Shimada, J. Mater. Sci. Lett., **11**, 424 (1992).

https://doi.org/10.1557/S1092578300002374 Published online by Cambridge University Press