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MOCVD Growth of High Quality GaN-AlGaN Based Structures on Al_2O_3 Substrates with Dislocation Density less than $10^7\,cm^{-2}$

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Abstract

We report the MOCVD growth of high quality GaN/AlGaN heterostructures on (00•1) sapphire substrates with a density of screw and mixed dislocations less than ~$10^7\,cm^{-2}$. 50Å-GaN/100Å-AlGaN superlattices have been grown with atomically sharp interfaces, as determined through high resolution TEM. Published by Elsevier Science Limited.

1 Introduction

Wide-bandgap III-Nitrides (AlN, GaN, InN and alloys thereof) are superior to other semiconductor materials for photonic devices operating in the visible-ultraviolet (UV) spectral range. These materials cover a large spectral bandwidth (650 to 200 nm), and large heterojunction band offsets can be achieved. They are physically hard, strong against radiations, thermally stable, they have high thermal conductivities, high charge carrier velocities and low dielectric constants. These properties are expected to extend the reliability and lifetime of devices made from III-Nitride materials.

Photonic devices such as blue/UV light-emitting and laser diodes, solar-blind UV photodetectors find their applications in high brightness flat panel displays, high density optical storage, underwater communications, space-to-space communications secure from earth and missile detection above the ozone layer where there is a strong visible and infrared background.[1,2]

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For the past decade, most of the research effort has focused on the synthesis of device quality materials. It is only recently that high quality photonic devices, such as blue/UV light emitting diodes (LEDs),[3] laser diodes[4] and UV photodetectors[5–7] have been demonstrated. However, the material used in these devices is still defective. For instance, the density of threading dislocations in the GaN-based blue/UV LEDs is typically ~$10^{10}\,cm^{-2}$.[8] This number is very large, considering that dislocation densities of ~$10^4\,cm^{-2}$ can limit the efficiencies of GaAs based LEDs. To improve the reliability and lifetime of GaN-based devices, in particular blue/UV laser diodes and solar-blind UV photodetectors, the dislocation densities need to be reduced below $10^5\,cm^{-2}$ in GaN-based materials.

The present work reports a methodology to reduce the density of screw and mixed dislocations, below $10^7\,cm^{-2}$, in GaN/AlGaN heterostructures grown the metalorganic chemical vapor deposition (MOCVD).

2 Experimental

2.1 Material growth

The AlN, GaN and $Al_xGa_{1-x}N$ thin films were deposited on basal plane sapphire substrates, (00•1) α-Al_2O_3. The substrates were placed on an SiC-coated graphite susceptor, into a horizontal low-pressure MOCVD reactor (AIXTRON Semiconductor GmbH). The susceptor was RF-heated and spun at a speed of ~60 rpm to increase the epilayer uniformity across the wafers. The growth pressure ranged from 10–100 mbar. The source materials include trimethyl-aluminum, trimethyl-gallium, triethyl-gallium and ammonia. The carrier gases were hydrogen and purified nitrogen. The Al and Ga molar flow rates ranged from 10–40 μmol min^{-1}, while the V/III ratio was between 1000 and 3000.

The AlN films were deposited directly on (00•1) α-Al_2O_3 substrates at a growth temperature ~1000°C, with a growth rate of ~0·15 μm hr^{-1}. For the growth of GaN films, we first deposited a thin (~350 Å) AlN buffer layer[9] using the same growth conditions as described previously. The growth temperature for GaN was also ~1000°C and the growth rate was ~0·7 μm hr^{-1}. The growth conditions tor the $Al_xGa_{1-x}N$ films were similar to those of GaN and the composition was controlled by varying the Al to Ga molar ratio.

2.2 Characterization

High resolution X-ray diffraction measurements and transmission electron microscopy (TEM) were conducted to assess the structural and microstructural properties of the films. The TEM specimens were realized by first M-bonding two pieces face-to-face. They were then mechanically polished down to a thickness of ~10μm, followed by Ar^+ ion milling (5 Kv, 0·5 mA) to reach electron transparency. TEM observations were carried out on a Hitachi HF 2000 field-emission microscope operated at 200 keV. The absorption edge of the $Al_xGa_{1-x}N$ compounds for $0 \leq x \leq 1$ was determined through optical absorption.

3 Results

3.1 AlN, GaN and $Al_xGa_{1-x}N$ thin films

The optimized growth conditions described previously yielded AlN and GaN thin films on Al_2O_3 substrates with high crystalline perfection. The epilayers were transparent and had smooth, mirrorlike surface morphologies. Figure 1(a) shows a typical X-ray rocking curve of the 00•2 diffraction peak for a ~0·3 μm AlN grown on Al_2O_3, with a linewidth of ~100 arcsecs. Pendellösung oscillations can be seen on the spectrum and confirm the excellent quality of the films and the interfaces. The separations between the oscillation peaks allowed to confirm the film thicknesses. Figure 1(b) shows a typical X-ray rocking curve of the 00•2 diffraction peak for a 0·7 μm GaN grown on Al_2O_3, with a linewidth of ~30 arcsecs. This value is close to the theoretical minimum for an ideal GaN bulk crystal.[10] The optical transmission spectra of AlN, GaN and $Al_xGa_{1-x}N$ films are shown in Fig. 2. The observed Fabry-Perot oscillations confirm the smoothness of the films.

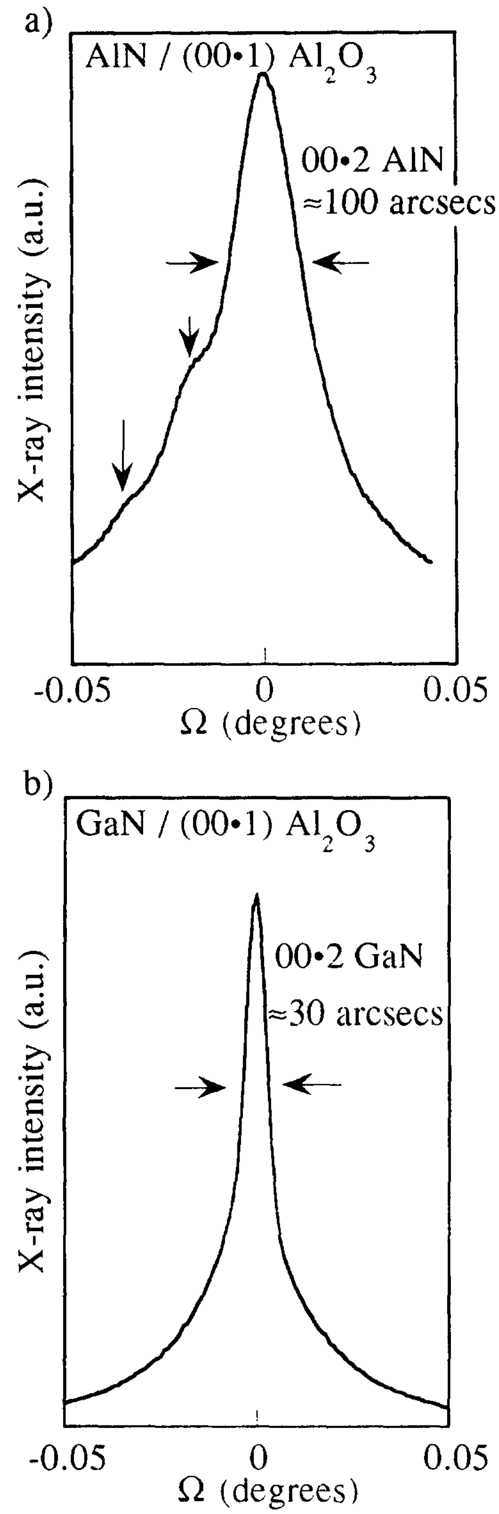

Fig. 1. Typical rocking curve of the 00•2 diffraction peak of: (a) AlN grown on (00•1) Al_2O_3; (b) GaN grown on (00•1) Al_2O_3.

By varying the Al to Ga molar ratio, we grew ~0·5 to ~1·5 μm thick $Al_xGa1_{-x}N$ compounds on Al_2O_3 substrates for $0 \leq x \leq 1$. The films were also transparent and had smooth, mirrorlike surface morphologies. Figure 2 shows the room temperature optical transmission spectra of these films for selected compositions and thicknesses. The cut-offs at the absorption edge are sharp and there is very little absorption tail in the lower energy side near the bandedge, confirming the high optical quality

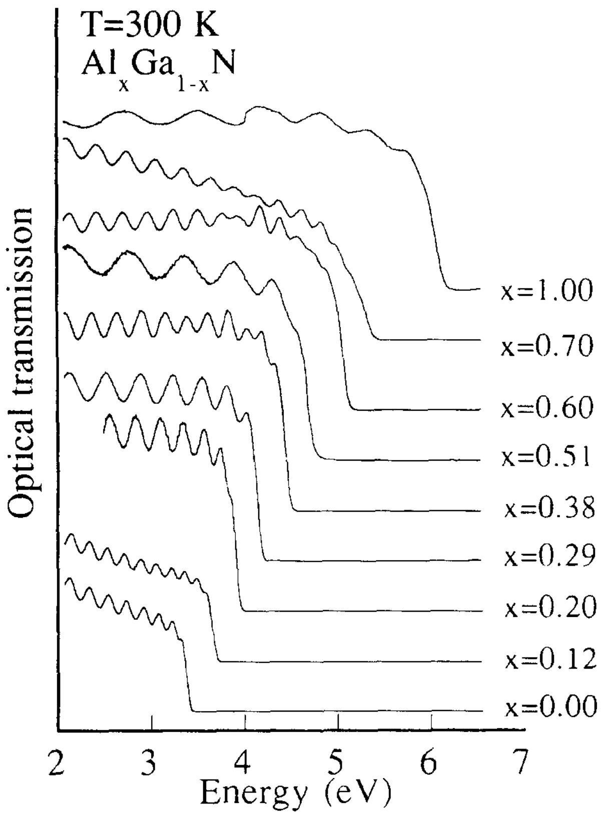

Fig. 2. Optical transmission spectra of $Al_xGa_{1-x}N$ thin films grown on (00•1) Al_2O_3 for selected compositions x.

of the films.[11] The compositions of the epilayers were determined by applying Vegard's law to the optical absorption and X-ray diffraction measurements.

3.2 TEM of a GaN/AlGaN/GaN heterostructure

Upon optimizing $Al_xGa_{1-x}N$ thin films $0 \leq x \leq 1$, we grew a GaN/AlGaN double heterostructure which consisted of a 0·7 μm $Al_{0.33}Ga_{0.67}N$ layer sandwiched between two 0·6 μm GaN layers. The structure was grown on (00•1) Al_2O_3 using a thin (~350 Å) AlN buffer layer. The sequence of layers in this structure was selected in order to help the relaxation of stress due to lattice mismatch, as will be discussed later.

Figure 3 shows the cross-sectional bright field TEM micrograph of this heterostructure with **g** = 00•2. The threading dislocations that can be seen are screw dislocations or have a mixed character, which have Burgers vectors non-perpendicular to **g**. The bottom GaN layer, closer to the sapphire substrate, is highly defective. The high density of dislocations does not seem to be reduced with the thickness of the GaN film up to 0·6 μm. By contrast, in the $Al_{0.33}Ga_{0.67}$ layer, it is significantly reduced. A stacking fault in the ternary layer can be visualized as the line separating the brighter area from the darker one. More interestingly, Fig. 3 shows that most of the screw and mixed dislocations visible in this configuration are stopped at the second GaN/AlGaN interface. An estimate of the dislocations which thread through this GaN/AlGaN interface yields $< \sim 10^7\,cm^{-2}$.

A simple interpretation for the annihilation of dislocations at each interface is the way the stress due to the lattice mismatch is relaxed through the heterostructure. GaN has a large (~16%) lattice mismatch with (00•1) Al_2O_3, which results in a significant amount of compressive stress at the interface between GaN and the sapphire substrates, as well as a large amount of misfit dialocations in the interface plane.[12] By using an AlN buffer layer, the stress in GaN is somewhat reduced because there is only a ~2·5% lattice mismatch between GaN and AlN, but the GaN film will still be under compressive stress because its lattice constant in the *c*-plane (3·189 Å) is larger than that of AlN (3·112 Å) in the same plane. By using layers with graded lattice parameters (e.g. $Al_xGa_{1-x}N$) from AlN to GaN, the lattice mismatch can be gradually reduced, but the stresses due to the lattice mismatch would remain compressive at all the interfaces.

In the case of our structure, by sandwiching an $Al_{0.33}Ga_{0.67}N$ layer between two GaN layers, the stress has been reversed several times: from compressive (for GaN on the AlN buffer) to tensile (for $Al_{0.33}Ga_{0.67}N$ on GaN) and to compressive again (for GaN on $Al_{0.33}Ga_{0.67}N$). By inverting the stress at successive interfaces, the screw and mixed dislocations bend and are stopped by annihilating themselves with the misfit dislocations formed at each interface, as shown in Fig. 3.

3.3 TEM of a GaN/AlGaN superlattice

It is well known that multilayers are effective in reducing the density of threading dislocations in conventional III-V compounds.[13] In order to further reduce the dislocation density in GaN, we grew a structure which consisted of a 15 period

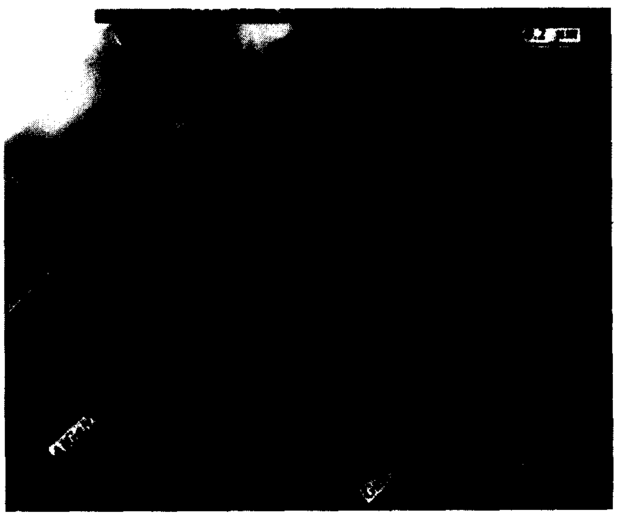

Fig. 3. Cross-section bright field TEM micrograph of a GaN/$Al_{0.33}Ga_{0.67}N$/GaN heterostructure grown on (00•1) Al_2O_3.

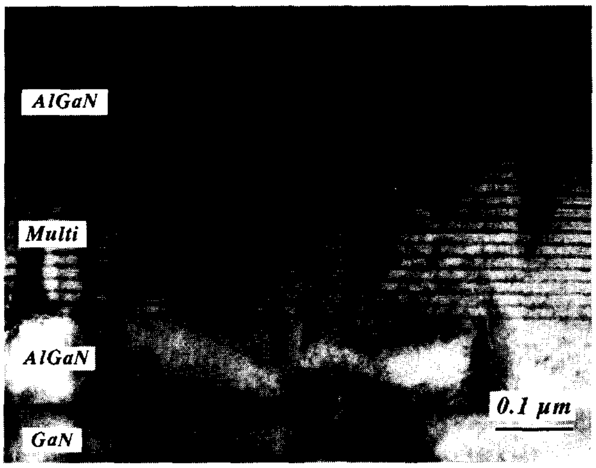

Fig. 4. Cross-sectional bright field TEM micrograph of a 15 period {50 Å-GaN/100 Å-$Al_{0.33}Ga_{0.67}N$} superlattice structure grown on (00•1) Al_2O_3.

{50 Å-GaN/100 Å-$Al_{0.33}Ga_{0.67}N$} superlattice (SL), sandwiched between two 0·1 μm thick $Al_{0.33}Ga_{0.67}N$ layers, on a 0·8 μm thick GaN. This structure is similar to the one previously discussed by replacing the top GaN layer with the superlattice.

Figure 4 shows the cross-sectional bright field TEM micrograph of this superlattice structure with **g** = 00•2. The same types of screw and mixed threading dislocations can be seen. The propagation of these dislocations does not seem to be stopped at the GaN/AlGaN interfaces in the superlattice but rather goes through the entire SL structure. One reason may be that the thicknesses of each layer in the SL are too small to modify the stress profile across the structure.

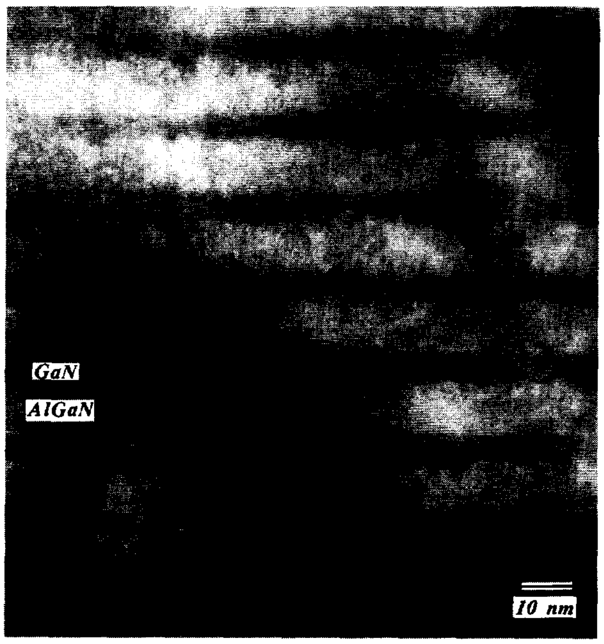

Fig. 5. High resolution cross-sectional bright field micrograph of superlattice structure showing the atomic scale interface sharpness.

Figure 4 also shows the excellent sharpness control of the GaN/AlGaN interfaces, we were able to confirm the expected period layer thicknesses in the superlattice. A high resolution bright field TEM micrograph of the SL structure is shown in Fig. 5, demonstrating that the interfaces are atomically smooth.

4 Conclusions

We have reported the MOCVD growth and characterization of high quality AlN, GaN and Al_x-$Ga_{1-x}N$ thin films on Al_2O_3 substrate. By sandwiching a AlGaN layer between two GaN layers, we have reduced the density of screw and mixed dislocations in GaN to less than $\sim 10^7\,cm^{-2}$. Atomically sharp interfaces in 50 Å-GaN/100 Å-AlGaN superlattice structures have been demonstrated by high resolution electron microscopy.

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References

1. Davis, R. F., Thin films and devices of diamond, silicon carbide and gallium nitride. *Physica B*, 1993, **185**, 1–15.
2. Razeghi, M., Choi, Y. H., He, X. and Sun, C. J., Exploration of entire range of III-V semiconductors and their device applications. *Materials Science and Technology*, 1995, **11**, 3–30.
3. Nakamura, S., Senoh, M., Iwasa, N. and Nagahama, S. I., High-power ImGaN single-quantum-well-structure blue and violet light-emitting diodes. *Appl. Phys. Lett.*, 1995, **67**, 1868–1870.
4. Nakamura, S., Senoh, M., Nagahama, S. I., Iwasa, N., Yamada, T., Matsushita, T., Kiyoku, H. and Sugimoto, Y., InGaN-Based Multi-Quantum-Well-Structure Laser Diodes. *Jpn. Journal of Appl. Phys.*, 1996, **35**, L74–L76.
5. Zhang, X., Kung, P., Walker, D., Piotrowski, J., Rogalski, A., Saxler, A. and Razeghi, M., Photovoltaic effects in GaN structures with p-n junctions. *Appl. Phys. Lett.*, 1995, **67**, 2028–2030.
6. Kung, P., Zhang, X., Walker, D., Saxler, A., Piotrowski, J., Rogalski, A. and Razeghi, M., Kinetics of photoconductivity in m-type GaN photodetector. *Appl. Phys. Lett.*, 1995, **67**, 3792–3794.

7. Walker, D., Zhang, X., Kung, P., Saxler, A., Javadpour, S., Xu, J. and Razeghi, M., AlGaN ultraviolet photoconductors grown on sapphire. *Appl. Phys. Lett.*, 1996, **68**, 2100–2101.
8. Lester, S. D., Ponce, F. A., Craford, M. G. and Steigerwald, D. A., High dislocation densities in high efficiency GaN-based light-emitting diodes. *Appl. Phys. Lett.*, 1995, **66**, 1249–1251.
9. Hiramatsu, K., Itoh, S., Amano, H., Akasaki, I., Kuwano, N., Shiraishi, T. and Oki, K., Growth mechanism of GaN grown on sapphire with AlN buffer layer by MOVPE. *Journal of Cryst. Growth*, 1991, **115**, 628–633.
10. Kung, P., Saxler, A., Zhang, X., Walker, D., Wang, T. C., Ferguson, I. and Razeghi, M., High quality AlN and GaN epilayers grown on (00•1) sapphire, (100), and (111) silicon substrates. *Appl. Phy. Lett.*, 1995, **66**, 2958–2960.
11. Zhang, X., Kung, P., Saxler, A., Walker, D., Wang, T. C. and Razeghi, M., Growth of $Al_xGa_{1-x}N$:Ge on sapphire and silicon substrates. *App. Phys. Lett.*, 1995, **67**, 1745–1747.
12. Saxler, A., Kung, P., Sun, C. J., Bigan, E. and Razeghi, M., High quality aluminum nitride epitaxial layers grown on sapphire substrates. *Appl. Phys. Lett.*, 1994, **64**, 339–341.
13. Matthews, J. W. and Blakeslee, A. E., Defects in epitaxial multilayers. *Journal of Cryst. Growth*, 1974, **27**, 118–125.