

Structural and compositional characterization of MOVPE GaN thin films transferred from sapphire to glass substrates using chemical lift-off and room temperature direct wafer bonding and GaN wafer scale MOVPE growth on ZnO-buffered sapphire



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ABSTRACT

GaN thin films were grown on ZnO/c-Al₂O₃ with excellent uniformity over 2 in. diameter wafers using a low temperature/pressure MOVPE process with N₂ as a carrier and dimethylhydrazine as an N source. 5 mm × 5 mm sections of similar GaN layers were direct-fusion-bonded onto soda lime glass substrates after chemical lift-off from the sapphire substrates. X-Ray Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy confirmed the bonding of crack-free wurtzite GaN films onto a glass substrate with a very good quality of interface, i.e. continuous/uniform adherence and absence of voids or particle inclusions. Using this approach, (In) GaN based devices can be lifted-off expensive single crystal substrates and bonded onto supports with a better cost-performance profile. Moreover, the approach offers the possibility of reclaiming the expensive sapphire substrate so it can be utilized again for growth.

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1. Introduction

Recently, InGaN/GaN based devices have been proposed for use as the active layers in future high efficiency photovoltaics [1]. In a field where cost and total device area are critical, the question of the substrate used to fabricate the solar cell is the key. Soda lime glass is an interesting alternative substrate for solar cells, and III-N devices in general as well in that it is cheap, readily available in large formats and easy to integrate in buildings.

Nevertheless, direct growth of III-nitride photovoltaics onto glass is not possible, mainly due to, the high temperatures required for III-nitride epitaxy by MOVPE (in excess of 1000 °C, as compared with a glassy temperature for soda lime glass of around 600 °C).

In order to overcome this incompatibility, the use of lift-off and direct wafer bonding is proposed in order to transfer the

nitride-based structure from the expensive single crystal substrate required for epitaxy to a substrate of choice (i.e. glass).

In this work, transfer consisted of (i) growing GaN at an optimal temperature by MOVPE on a ZnO-buffered single crystal c-sapphire (c-Al₂O₃) substrate [2], (ii) chemically lifting off the GaN from the substrate by selectively etching away the ZnO layer [3] and (iii) direct-bonding the GaN onto a soda lime glass substrate.

After presenting the growth of GaN on 2 in. ZnO/c-Al₂O₃ wafers the paper discusses the microstructural, compositional and cross-sectional characterizations of the GaN after such a transfer in order to seek improved understanding of the bonding process.

2. Experimental details

2.1. Template preparation and GaN thin film MOVPE growth

ZnO thin films were grown on c-Al₂O₃ substrates using pulsed laser deposition (PLD) from a 5 N, sintered, ZnO target in molecular

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oxygen with a Coherent LPX KrF ($\lambda=248$ nm) excimer laser. Homogeneous 2-in. diameter wafer coverage was obtained using optical rastering of the laser beam, as described elsewhere [4]. These wafers were then used as templates for GaN regrowth. GaN layers were grown by MOVPE in a T-shaped reactor that has demonstrated high growth uniformity [5] and the capacity to grow low temperature GaN films [2]. The MOVPE growth conditions were adapted in order to avoid the dissociation of ZnO commonly observed during the conventional MOVPE process. Back-etching issues, described in references [6–10], were overcome through the use of pure N₂ carrier gas, trimethylgallium as a group III (Ga) source, plus a combination of ammonia and dimethylhydrazine (DMHY) as group-V (N) atomic sources, respectively, as described in Ref. [11]. DMHY was chosen because of its low decomposition temperature, which reduced the required GaN growth temperature to 600 °C for the initial regrowth [2]. For the samples considered in this paper (with typical thicknesses ranging from 150 to 500 nm) subsequent growth temperature and pressure were fixed at 730 °C and 450 Torr, respectively.

2.2. Chemical lift-off & room temperature direct fusion wafer bonding

GaN films were transferred onto optically-flat Corning microscope slides (soda-lime glass) via a process of chemical lift-off and direct fusion-bonding modeled on that developed for the chemical lift-off of ZnSe from GaAs substrates and bonding onto glass/silica using MgS release layers [12–17] and for InGaN films by Liu et al. [18]. The process flow is shown in Fig. 1.

In this approach, the ZnO interlayer plays two roles. It acts first as a crystallographic template for GaN epitaxial growth (step 1) and second as a sacrificial release layer, which is selectively etched away in 0.1 M HCl in order to separate the GaN from the sapphire substrate (step 3). A temporary “host” substrate of Apiezon “W” wax is used to maintain the integrity of the GaN film during the transfer process (steps 2 to 4). After etching away the sacrificial ZnO layer, the GaN layer is transferred onto a glass substrate (step 5). This process, is conducted at room temperature, and consists of applying a small compressive force so as to promote capillary action between the GaN and the glass. After drying, the wax is removed by dissolution in xylene. In this case, the wafer bonding process was applied to $\sim 5 \times 5$ mm² samples.

2.3. Characterization

The film surface was observed using backscattered-electron imaging conducted in a Zeiss Supra 55 Scanning Electron Microscope (SEM). The overall crystalline nature of the materials was investigated using X-Ray Diffraction (XRD) measurements performed in a Panalytical X’pert Pro MRD system with Cu K_{α1} radiation and a 2-bounce Ge (220) monochromator in the incident beam path. ω scans were performed with an open detector and $2\theta/\omega$ scans were performed with a 0.5 receiving slit in front of the detector.

Local structural and compositional data was acquired using High Resolution Transmission Electron Microscopy (HR-TEM) of Focused Ion Beam (FIB) milled cross-sections in an aberration-corrected Scanning TEM (STEM) equipped with High Angle Annular Dark Field (HAADF) capability for atomic number contrast enhancement plus Energy Dispersive X-Ray (EDX) fluorescence spectroscopy for compositional microanalysis. The EDX had a probe diameter of 1 nm, a penetration pattern in the sample with a truncated cone of 1.5 nm length and an apex diameter of 0.1 nm.

3. Results and discussions

3.1. Growth of GaN on 2-in. ZnO/c-Al₂O₃ wafers:

An X-Ray Diffraction $2\theta/\omega$ scan for this sample is shown in Fig. 2a. The scan reveals 2 distinct peaks characteristic of wurtzite GaN and ZnO layers, respectively. The ZnO peak position corresponds to a “c” lattice parameter of 5.200 Å (comparable to the value of 5.206 Å expected for equilibrium wurtzite ZnO). The GaN peak position corresponds to a c lattice parameter of 5.186 Å. In contrast to the compressively strained growth of GaN on ZnO observed for smaller samples [3], both materials have near-equilibrium lattice parameters for this 2” wafer growth. A more detailed study is in progress and will be published in a forthcoming paper. In-wafer variation of thickness and structural quality was probed by measuring GaN (0002) peak intensity as a function of position along a diametric scan (Fig. 2b). The scan shows a 50 mm-wide plateau with $\pm 5\%$ of variation in peak intensity, which implies excellent in-wafer uniformity of the thickness and structural properties over 2 the wafer.

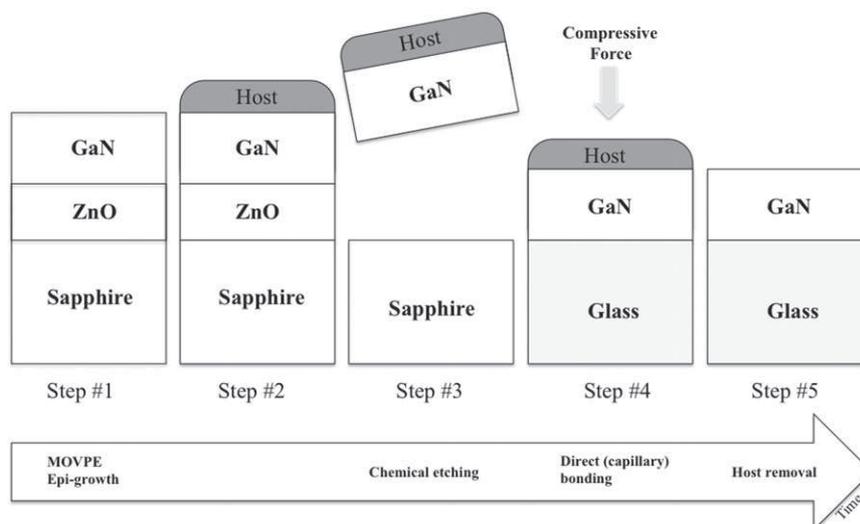


Fig. 1. Process flow for chemical lift-off and direct fusion-bonding of GaN onto glass.

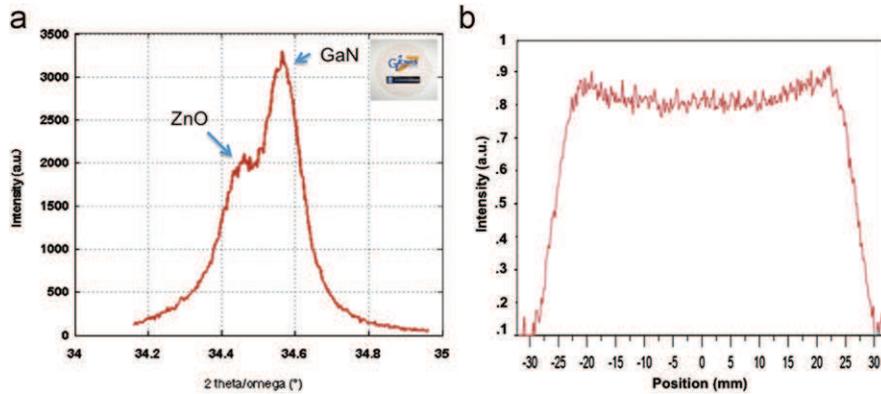


Fig. 2. (a) XRD $2\theta/\omega$ scans for the GaN/ZnO/c-sapphir 2-inch wafer, plus an image showing the excellent optical transparency. Fig. 6b, In-wafer variation for the (0002) XRD peak intensity as a function of position for a diametric scan across the wafer.

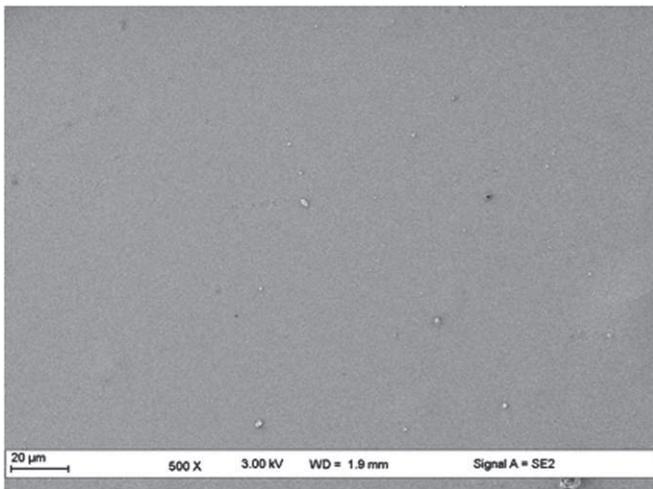


Fig. 3. SEM micrograph of a GaN film direct-wafer-bonded onto a glass substrate.

3.2. GaN/glass wafer-bonded structure properties:

Fig. 3 shows a relatively low magnification SEM micrograph of the GaN surface after bonding to glass.

The surface is flat and free of cracks or pinholes. This attests to the bonded film integrity having been preserved by the wax host during the transfer process. In addition, even in larger field micrographs, there is no evidence of the characteristic tent-like structures, which would have been expected had there been particles trapped between the GaN layer and the glass substrate [12]. This indicates a uniform adherence of the film to the glass substrate over an area significantly greater than the size of standard devices.

Fig. 4 shows, low-resolution mode, XRD $2\theta/\omega$ scan for the GaN wurtzite (0002) reflection after bonding to glass.

The peak position after the transfer process corresponds to lattice spacing of 5.23 Å which confirms that wurtzite GaN grown by MOVPE was successfully transferred to glass with intact wurtzite structure after the removal of the ZnO. The (0002) GaN ω rocking curve linewidths before and after transfer were 0.23° and 9.9° , respectively. The significant broadening after bonding may be due to the relatively large ($\sim 5 \text{ mm} \times 5 \text{ mm}$) XRD spot integrating a contribution from an unbonded section of GaN at the periphery of the sample ($\sim 30\%$ of the overall sample area), which was curling up from the glass.

STEM measurements were then performed on both the as-grown GaN/ZnO/sapphire and the GaN/glass bonded sections (stages 1 and 5 of the process in Fig. 1). The HAADF-STEM image

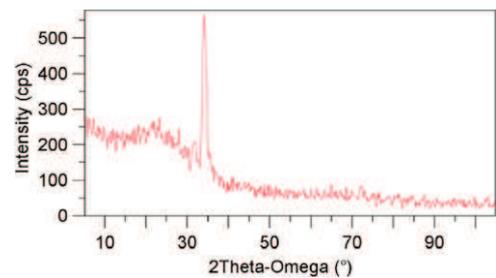


Fig. 4. XRD $2\theta/\omega$ scan around the GaN (0002) peak after bonding to glass.

of Fig. 5a shows the as-grown GaN/ZnO/sapphire structure. The different shades demarking the GaN, ZnO and sapphire layers are enhanced by the strong chemical contrast between the three materials. Continuous, well-defined and sharp interfaces are observed between them with no obvious intermixing zones that would hinder the chemical etching of the ZnO layer and, consequently, the GaN lift-off process. The layer thicknesses for the GaN and ZnO are about 500 and 200 nm, respectively, which is similar to the estimates made from SEM images of fracture sections [19].

The cross section in Fig. 5b shows the GaN film bonded onto the glass slide (step 5 in Fig. 1).

The HAADF-STEM micrograph obtained from the FIB slice shows the chemical contrast that exists between the GaN and the glass. It reveals an abrupt and even interface over a length scale greater than several microns. This result is consistent with the sharp interface observed between the GaN and ZnO prior to lift-off. Neither cracks, nor voids, nor particle inclusions are observed at the interface between the structure layers over the several microns of the FIB section, for which there is continuous and uniform adherence of the GaN to the glass.

In order to investigate the interface more closely, a higher magnification HAADF STEM picture was taken (Fig. 6). The image confirms an abrupt and smooth interface, as observed at larger scale (Fig. 6b). In addition, the presence of a darker, homogeneous and amorphous, interfacial layer (about 10-nm-thick) is revealed at this magnification. Its chemical composition was estimated through EDX spectrometry to be (within detection uncertainty) 60–75% of carbon (C), 25% of oxygen (O), 5% of sodium (Na) and 5% of silicon (Si) along with traces of potassium (K). Similar interfacial layers have been widely reported for various materials bonded in this way and they are observed to exhibit thicknesses ranging from a few nm up to about 20 nm, depending on the nature of the bonded materials. The origin of such interlayers is still not fully understood, but it has been reported that it could be

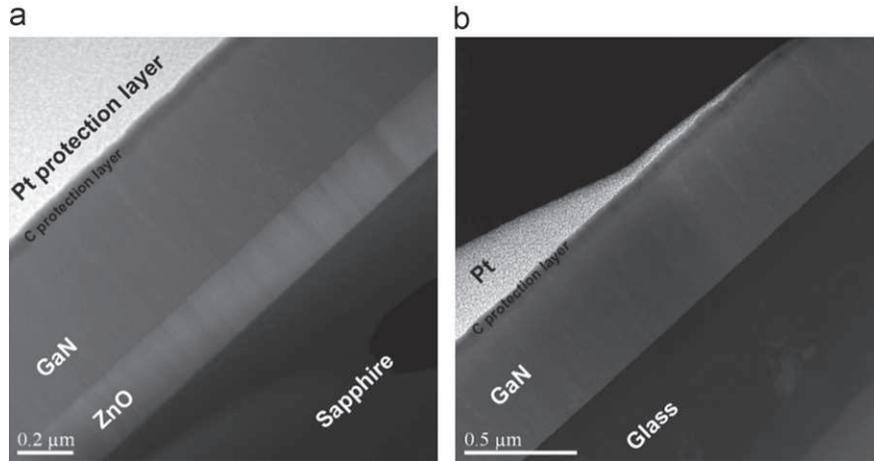


Fig. 5. HAADF-STEM picture of FIB cross-sections for (a) the as-grown GaN/ZnO/sapphire, i.e. before lift-off and (b) the GaN film wafer-bonded onto the glass slide.

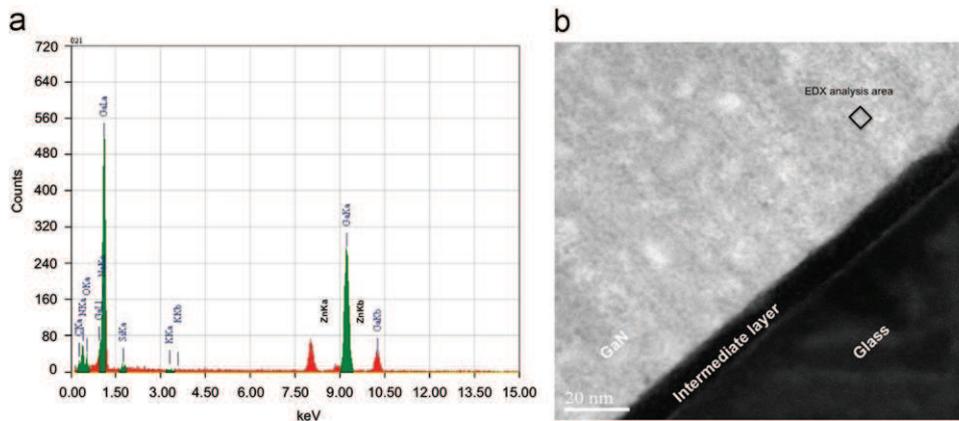


Fig. 6. (a) EDX spectrum for the GaN layer after wafer bonding, and (b) high magnification HAADF-STEM picture of the GaN/Glass interface showing the position where EDX spectrum was acquired.

a “semiconductor oxide” layer [12] and/or a contamination with organic material during the wafer bonding process and/or attributable to glass corrosion by air due to the sodium and potassium lixiviation associated with reaction with carbon dioxide [20,21].

Interestingly, EDX spectra for the GaN layer (Fig. 6a) did not show any measurable trace of Zn signal, which is coherent with the lack of ZnO back-etching during the GaN growth, as reported previously [3,4,19,22] and is consistent with prior Secondary Ion Mass Spectroscopy compositional depth profiling [22], which showed no sign of Zn contamination in the GaN layer and negligible interdiffusion at the GaN/ZnO interface. This further implies that the ZnO was completely removed in the chemical lift-off process.

Also of note, is that the STEM samples were realized by means of a FIB tool. The fact that the structure GaN/Glass remained intact in spite of the aggressive FIB milling testifies to the existence of relatively strong bonding forces established in this fusion-bonding process. Yablonovich et al. investigated the nature of the chemical bonding in such a process and concluded that it is probably via the Van der Waals interaction [12]. This may be enhanced due to the polar character of the GaN film along with the flatness of the GaN bottom (epitaxial [3]) surface obtained after etching the ZnO away. This reduces the spacing between the two materials, and thus maximizes the Van der Waals forces (which decay as $1/r^6$). On the other hand, it is also possible that such bonding could be molecular in nature, as a result of chemical activation [12]

There are many potential approaches for the transfer of GaN from one substrate to another. Compared with laser lift-off, this process has the advantages of not requiring sophisticated laser processing and of not damaging the GaN layer. Compared with mechanical lift-off [23], this process has the advantage of not straining the samples and of reclaiming the substrates. Compared with “smart-cut” [24], this process has the advantage of not requiring expensive/complicated equipment and it avoids proprietary issues. This approach also offers the general advantages of being a low temperature process with no bonding agent at the interface (which could create problems for thermal processing or optical/electrical coupling).

4. Conclusion

GaN thin films were grown on ZnO-buffered $c\text{-Al}_2\text{O}_3$ substrates by MOVPE, with excellent thickness and structural uniformity over a 2-in. wafer. Transfer of $\sim 5\text{ mm} \times 5\text{ mm}$ sections of such GaN layers onto glass was achieved by chemically etching away the ZnO underlayer and direct wafer bonding. Morphological and structural observations demonstrated that a crystalline GaN film was successfully transferred with no trace of residual Zn, to within the accuracy of EDX analysis. Cross sectional STEM observations demonstrated continuous and uniform bonding of the GaN film onto the soda lime glass, which was probably facilitated by the smooth GaN surface provided by the epitaxial

GaN/ZnO interface after removal of the ZnO. This work thus introduces the perspective for nitride-based optoelectronic structures to be wafer-bonded to glass with high interface/surface quality that is crucial for device processing plus excellent thermal/optical coupling between the nitride-based device and the substrate.

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References

- [1] E. Matioli, et al., *Applied Physics Letters* 98 (2011) 021102.
- [2] S. Sartel, et al., *Journal of Superlattices and Microstructure* 40 (4–6) (2006) 476–482.
- [3] D.J. Rogers, et al., *Applied Physics Letters* 91 (2007) 071120.
- [4] D.J. Rogers, et al., *Proceedings of SPIE* 5732 (2005) 412.
- [5] A. Mircea, et al., *Journal of Crystal Growth* 93 (1–4) (1988) 235–241.
- [6] N. Li, et al., *Proceedings of SPIE* 6337 (2006) 63370Z.
- [7] J. Nause, et al., in: *Proceedings of the 3rd International Workshop on ZnO and Related Materials*, Sendai, Japan, 2004.
- [8] L.T. Romano, et al., *Applied Physics Letters* 71 (16) (1997) 2283.
- [9] A. Strittmatter, et al., *Materials Science and Engineering B* 59 (1999) 29.
- [10] S. Gu, et al., *Applied Physics Letters* 76 (23) (2000) 3454.
- [11] S. Gautier, et al., *Journal of Crystal Growth* 298 (2007) 428.
- [12] E. Yablonovich, et al., *Applied Physics Letters* 56 (1990) 2419.
- [13] M. Konagai, et al., *Journal of Crystal Growth* 45 (1978) 277.
- [14] E. Yablonovich, et al., *Applied Physics Letters* 51 (26) (1987) 2222.
- [15] A. Balocchi, et al., *Applied Physics Letters* 86 (2005) 011915.
- [16] C. Bradford, et al., *Journal of Crystal Growth* 278 (2005) 325–328.
- [17] A. Curran, et al., *Semiconductor Science and Technology* 22 (2007) 1189–1192.
- [18] H.F. Liu, *Journal of Vacuum Science and Technology* 28 (2010) 590–594.
- [19] D.J. Rogers, et al., *Proceedings of SPIE* 8263 (2012) 82630.
- [20] L. Robinet, et al., *Journal of Non-Crystalline Solids* 355 (2009) 1479–1488.
- [21] G. Kojima, et al., *Journal of Non-Crystalline Solids* 292 (2001) 50–58.
- [22] D.J. Rogers, et al., *Journal of Vacuum Science & Technology B* 27 (3) (2009) 1655–1657.
- [23] Y. Kobayashi, et al., *Nature* 484 (2012) 223.
- [24] M. Bruel, *Electronics Letters* 31 (14) (1995) 1201–1202.