Growth of *c*-axis oriented gallium nitride thin films on an amorphous substrate by the liquid-target pulsed laser deposition technique

R. F. Xiao,[a] H. B. Liao, and N. Cue
Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

X. W. Sun and H. S. Kwok
Department of Electrical and Electronic Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

(Received 5 April 1996; accepted for publication 2 July 1996)

Gallium nitride (GaN) thin films with a wurtzite structure were grown on fused silica (FS) substrates by pulsed laser ablation of a liquid gallium target in the presence of ammonia gas. X-ray diffraction measurement shows a single *c*-axis orientation for the GaN film grown with a thin (<1000 Å) zinc oxide (ZnO) film as an alignment layer. There is a great improvement in the surface morphology as well as optical transmission for the GaN film grown on the ZnO buffered FS substrate. The energy band gap obtained from the absorption spectrum is about 3.45 eV. © *1996 American Institute of Physics.* [S0021-8979(96)06619-4]

During the last few years, gallium nitride (GaN) has emerged as the most promising compound semiconducting material. Great progress has been made in GaN thin film growth and light emitting device (LED) (light emitting diode and quantum well laser) fabrication.[1,2] The current record of external emission efficiency of blue light from GaN LEDs has reached 9.1% at 20 mW output power with an extended lifetime.[3] This is far more superior than that made from II–VI semiconductors. The commercial applications of such LEDs are vast, ranging from large screen full color displays, to optical storage, to lighting for traffic signals and automobiles. The current deposition techniques for GaN related thin films are mainly metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE).[1] The substrates largely used are sapphire and silicon carbide. One of the current directions in GaN research is to find other alternative substrates that not only have good lattice match but are also inexpensive.[3]

This communication reports on our first effort to grow GaN thin films using liquid-target pulsed laser deposition (LTPLD).[4] Deposition was performed as well on low cost amorphous substrates such as fused silica (FS). The LTPLD system has been successfully used to grow diamond films.[5] Since gallium is naturally a liquid above 29.8 °C, it is an ideal material system for LTPLD. The advantages of LTPLD are its efficient utilization of low-cost source materials and safe experimental operation (no metalorganic chemicals are involved). Also, as will be shown later, the deposition temperature needed in PLD is, in general, much lower than that used in MOCVD to achieve the same film crystallization. This property is important for simplifying the experimental design and for fabricating GaN-based optoelectronic devices with sharp interfaces. In comparison to solid-target PLD.[6] LTPLD has overcome the problem of target deterioration and large particulate splashing over the growing film.

The reasons for using FS as a substrate for GaN film are its excellent optical transparency, low refractive index, and good mechanical strength. If optical-grade GaN film can be grown on such a substrate, GaN-based wave guide devices can be fabricated. Although epitaxial growth of GaN film on FS is impossible due to its amorphous nature, it is possible to grow a highly aligned GaN film with columnlike domains on it if one can identify a buffer layer that can induce the GaN film to grow in a preferred direction. Fortunately, such a buffer material exists. Recently, during the preparation of ZnO films for optical application, we found that *c*-axis oriented ZnO columnar film can be easily formed on many different kinds of substrates including FS and regular glass. Since ZnO is an isomorphic material with wurtzite GaN and the lattice mismatch in their basal plane is only 2.2% for pure GaN and perfectly matched for $In_{0.22}Ga_{0.78}N$,[7] it will be a good buffer material for GaN. Actually, several research groups have recommended use of the ZnO crystalline substrate or ZnO-buffered sapphire substrate for GaN growth.[8] Another advantage of using ZnO as a buffer layer to grow GaN film is that ZnO can be made either semiconducting or conducting by controlling the amount of oxygen in the film. Therefore, the ZnO buffer layer can also be used as a transparent conducting electrode for GaN in the fabrication of a photonic device in addition to being an alignment layer.

Our experiment is a two step process. First, a thin ZnO film was deposited on FS by using either magnetron dc sputtering[9] of pure Zn targets or pulsed laser ablation of a solid ZnO target. With optimized O_2 ambient pressure during the deposition, a stoichiometric ZnO film can be easily obtained. We found that ZnO films grown by both methods are always aligned with their *c* axis perpendicular to the substrate even at a deposition temperature as low as 100 °C. After the ZnO film was grown, it was quickly transferred to a LTPLD system for GaN growth. The details of our LTPLD system are described elsewhere.[4] Basically, the system consists of an ArF excimer laser and a small, upright vacuum-tight deposition chamber. The ArF excimer laser beam is focused by a quartz lens and guided through a quartz window onto the liquid gallium target that is held by a stainless

[a]Electronic mail: phrfxiao@usthk.ust.hk

 0021-8979/96/80(7)/4226/3/$10.00

steel cup with the temperature regulated at 30 °C (just above the melting point of Ga). Before the deposition, a high vacuum ($\sim 10^{-6}$ Torr) is achieved by turbopumping. Then, a mechanical pump is used during the deposition to maintain the necessary vacuum condition. Ammonia (NH_3) gas is used to supply atomic nitrogen to form GaN. We have also tried to use N_2 gas as a nitrogen source, but have failed to obtain GaN. The experimental conditions for the results reported here are as follows. A pulsed laser (wavelength—193 nm) with a 250 mJ pulse energy and a 10 Hz repetition rate was focused onto an area of 1×2.5 mm^2 on the surface of the liquid gallium target which was located about 5 cm below the substrate. The substrate temperature was kept at 600 °C. The NH_3 gas, at a flow rate of 20 sccm, was guided into the deposition chamber and spread over the surface of the growing GaN film. The total NH_3 pressure in the deposition chamber was maintained at 1 mbar during the deposition. With these conditions, a deposition rate of about 0.05 Å/laser pulse was obtained. The total number of laser pulses used in this experiment was 40 000, yielding a film with a thickness of about 2000 Å. After the deposition, the substrate temperature was immediately ramped down at a rate of 6 °C/min in N_2 atmosphere. No postannealing was used for the results reported here. The substrate temperature of 600 °C was important for film crystallization and alignment. It was found that, when the deposition temperature was below 550 °C, the GaN films obtained were either amorphous or polycrystalline with random oriented domains.

Figure 1 shows the x-ray diffraction (XRD) measurement for, respectively, GaN films grown on a plain FS substrate (upper curve), ZnO on FS (middle curve), and GaN on ZnO-coated FS (lower curve). As one can see, the film grown directly on FS is polycrystalline with all three orientations, (1010), (0002), and (1011), present. Also, the diffraction intensity is very low (note that the scale for the diffraction intensity for each film is different). However, once a ZnO buffer layer is used, the GaN film grows only along [0002] direction (lower curve), in alignment with the orientation of the underlying ZnO buffer layer. This is because ZnO has the same crystal structure as wurtzite GaN, and the lattice mismatch is very small in their basal plane. Therefore, growth of GaN on ZnO in the (0002) orientation can be considered as an epitaxial growth. At this point we would like to point out that, although (0002) oriented ZnO film can be easily formed on FS substrates even at a very low substrate temperature, we have found that the formation of (0002) oriented GaN film on ZnO can be obtained only when the deposition temperature for the ZnO film is sufficiently high. Otherwise all three crystalline orientations, (1010), (0002) and (1011), would be present in the GaN film even if the deposition temperature is the same. We think this is due to the size effect of the columnlike ZnO domains. At a low deposition temperature, the cross section of ZnO columns is small. If a GaN film is grown on such small crystalline ZnO columns, it would be more difficult to meet the epitaxial condition because of the presence of defects and strains along the grain boundaries of these ZnO columns. On the other hand, when the deposition temperature is high, the cross section of the columnlike ZnO single-crystalline domains will become big, and hence a better epitaxy will be achieved between GaN and ZnO. We have found that the optimal deposition temperature for the ZnO buffer layer

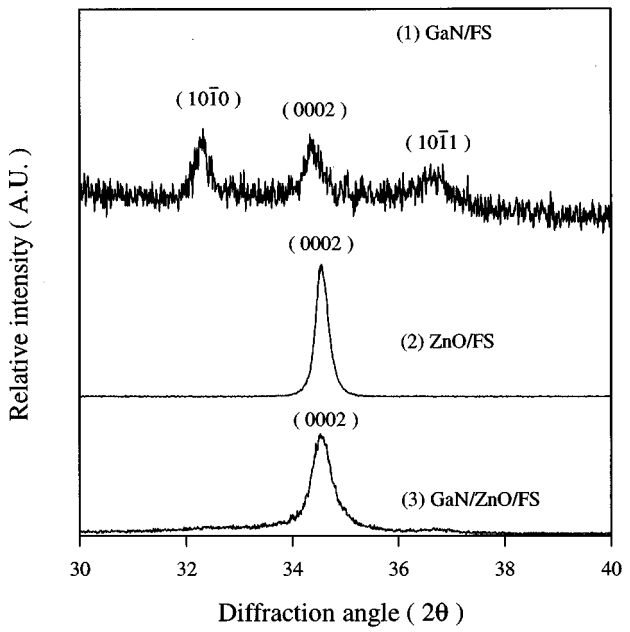

FIG. 1. X-ray diffraction of GaN and ZnO films deposited at 600 °C. Upper curve: GaN on fused silica (FS), vertical scale (×60); middle curve: ZnO on FS, vertical scale (/3); lower curve: GaN on ZnO/FS, vertical scale (×1).

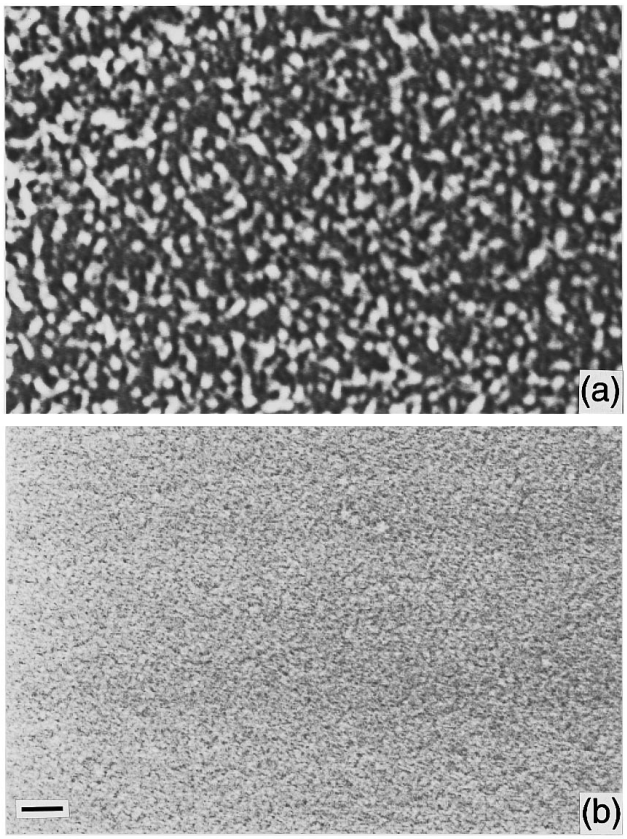

FIG. 2. SEM pictures of the surface growth morphologies of GaN films deposited at the same growth conditions: (a) without ZnO buffer layer; (b) with a ZnO buffer layer. The scale shown is 1 μm.

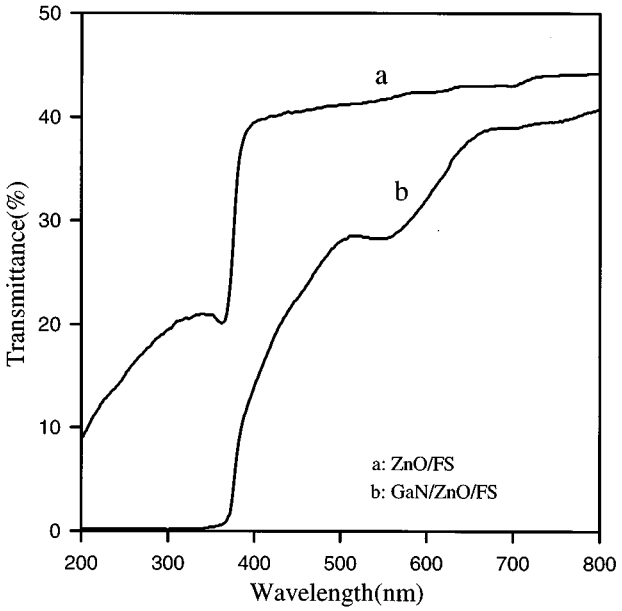

FIG. 3. Optical transmittance of ZnO/SF (upper curve) and GaN/ZnO/SF (lower curve) at room temperature. The absorption by the FS substrate has not been subtracted from the data.

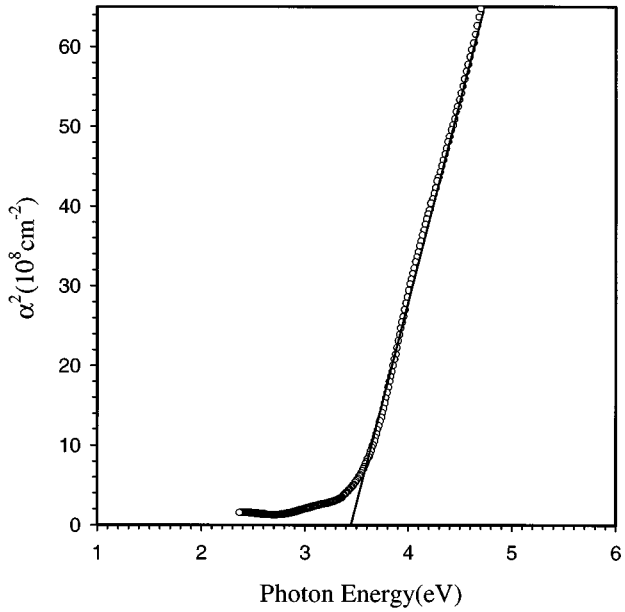

FIG. 4. The squared absorption coefficient as a function of photon energy measured at room temperature for the GaN film grown on a ZnO/FS substrate.

should be the same as that for the growth of the GaN film. The films (both GaN and ZnO) shown in curve 3 of Fig. 1 were all grown at a deposition temperature of 600 °C.

Figure 2 gives scanning electron microscopy (SEM) pictures showing the growth morphologies of GaN films without [Fig. 2(a)] and with [Fig. 2(b)] the ZnO buffer layer. As one can see from Fig. 2, the surface morphology of GaN film grown on a plain FS substrate is very rough, and the average domain size is in the range of sub-μm. However, once a ZnO buffer layer is used, the growth morphology of the GaN film improves dramatically, and the surface of the film becomes much smoother than without a ZnO buffer layer. This is also reflected in the optical transparency of the films. Without a ZnO buffer layer, the GaN film looks like ground glass and incident light is largely scattered. With a ZnO buffer layer, the GaN film becomes highly transparent.

The optical transmission spectra of GaN/ZnO/FS and ZnO/FS are shown in Fig. 3. Because of the small thickness of the ZnO buffer, finite transmission exists below 360 nm even though it is below the band gap of ZnO (388 nm). As one can see from Fig. 3 the decrease of light transmission in GaN at short wavelength is not due to the presence of the ZnO layer. The absorption peak near 550 nm in GaN film is the result of an etalon interference effect within the film (the peak positions change with film thickness). Using the relationship between absorption coefficient α and photon energy $(h\nu)$ of the incident light,[10] $\alpha^2 \sim (h\nu - E_g)$, we have obtained an energy band gap E_g for the GaN film that is about 3.45 eV (Fig. 4), a little bit bigger than the earlier experiment results.[11]

In conclusion, we have grown wurtzite-structured gallium nitride (GaN) thin films on FS substrates by pulsed laser ablation of a liquid gallium target in the presence of NH_3 gas at a deposition temperature of 600 °C. X-ray diffraction measurement shows a single c-axis (0002) orientation for the GaN films grown with a thin (<1000 Å) ZnO layer as a guiding (buffer) layer for c-axis alignment. There is a great improvement in surface morphology and optical transmission for the GaN film grown on the ZnO-buffered FS substrate. The energy band gap obtained is about 3.45 eV.

[1] See, for example, *Gallium Nitride and Related Materials: The First International Symposium on Gallium Nitride and Related Materials*, Proceedings of Materials Research Society Meeting, Vol. 395, Boston, 1995 (Materials Research Society, Pittsburgh, PA, 1995).
[2] *Compound Semiconductor* (Franklin, St. Paul, MN, 1995, 1996), Vols. 1, 2, and 3.
[3] S. Naskamura, M. Senoh, N. Iwasa, S. I. Nagahama, T. Yamasa, and T. Mukai, Jpn. J. Appl. Phys. Lett. **34**, 1332 (1995).
[4] R. F. Xiao, Appl. Phys. Lett. **67**, 1022 (1995).
[5] R. F. Xiao, Appl. Phys. Lett. **67**, 3117 (1995).
[6] *Pulsed Laser Deposition of Thin Films*, edited by D. B. Chrisey and G. K. Hubler (Wiley, New York, 1994).
[7] T. Matsuoka, N. Yoshimoto, T. Sasaki, and A. Katsui, J. Electron. Mater. **21**, 157 (1992); S. Strite, and H. Morkoç, J. Vac. Sci. Technol. B **10**, 1237 (1992).
[8] T. Detchprohm, K. Hiramatsu, H. Amano, and I. Akasaki, Appl. Phys. Lett. **61**, 2688 (1992); T. Matsuoka, J. Cryst. Growth **124**, 433 (1992).
[9] H. B. Liao, R. F. Xiao, P. Yu, and G. K. L. Wong, J. Vac. Sci. Technol. A **14**, 2651 (1996).
[10] L. H. Hall, J. Bardeen, and F. J. Blatt, Phys. Rev. **95**, 559 (1954); T. L. Tansley and C. P. Foley, J. Appl. Phys. **59**, 3241 (1986).
[11] H. P. Maruska and J. J. Tietjen, Appl. Phys. Lett. **15**, 327 (1969); L. H. Qin, Y. D. Zheng, D. Feng, Z. C. Huang, and J. C. Chen, J. Appl. Phys. **78**, 7424 (1995), and references therein.