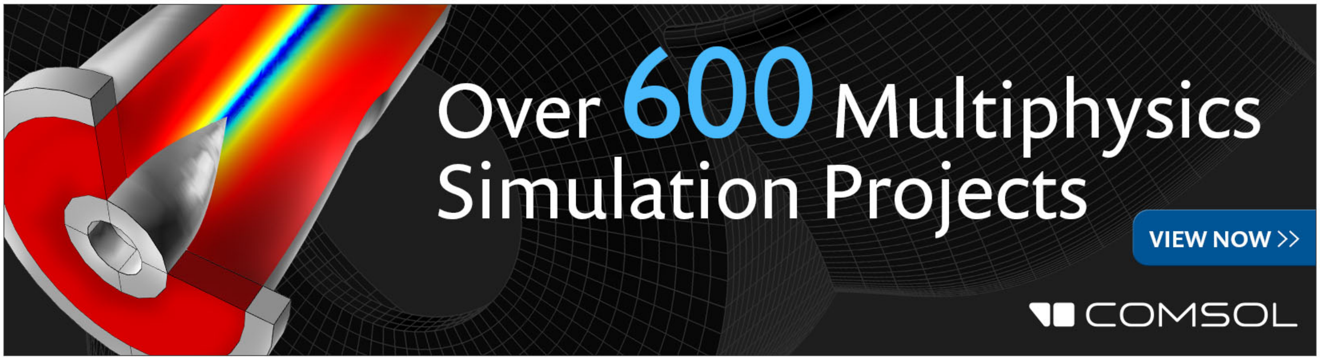
AIP Applied Physics Letters

Epitaxial growth of group III nitrides on silicon substrates via a reflective lattice-matched zirconium diboride buffer layer

J. Tolle, R. Roucka, I. S. T. Tsong, C. Ritter, P. A. Crozier, A. V. G. Chizmeshya, and J. Kouvetakis

Citation: Applied Physics Letters **82**, 2398 (2003); doi: 10.1063/1.1566099
View online: http://dx.doi.org/10.1063/1.1566099
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/82/15?ver=pdfcov
Published by the AIP Publishing



APPLIED PHYSICS LETTERS VOLUME 82, NUMBER 15 14 APRIL 2003

Epitaxial growth of group III nitrides on silicon substrates via a reflective lattice-matched zirconium diboride buffer layer

J. Tolle
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

R. Roucka and I. S. T. Tsong
Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287

C. Ritter
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

P. A. Crozier and A. V. G. Chizmeshya
Center for Solid State Science, Arizona State University, Tempe, Arizona 85287

J. Kouvetakis[a)]
Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

(Received 2 January 2003; accepted 14 February 2003)

Growth of metallic and reflecting ZrB_2 films is conducted on Si(111) substrates at 900 °C using a single-source unimolecular precursor $Zr(BH_4)_4$ in a molecular beam epitaxy chamber. Epitaxial growth of $ZrB_2(0001)$ is accomplished despite the very large lattice mismatch between ZrB_2 and Si(111). High-resolution cross-sectional transmission electron microscopy images of the sharp $ZrB_2/Si(111)$ interface show a heteroepitaxial relationship involving a ‘‘magic mismatch’’ of coincidence lattices. The GaN films grown on the $ZrB_2/Si(111)$ template is virtually homoepitaxy because of the very small lattice mismatch, 0.6%, between the in-plane lattice parameters of $ZrB_2(0001)$ and GaN(0001). © *2003 American Institute of Physics.* [DOI: 10.1063/1.1566099]

The growth of group III nitrides including GaN is most commonly accomplished by heteroepitaxy using methods of metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). The substrates employed are generally sapphire and α-SiC(0001), with lattice mismatch of 16% and 3.6% respectively with GaN. Coupled with mismatches in thermal expansion coefficients, the misfit dislocations produced in GaN during heteroepitaxial growth pose a limitation to the ultimate performance of nitride-based electronics. Various growth schemes involving patterned substrates such as epitaxy by lateral overgrowth[1] and pendeoepitaxy[2] have been developed to improve the dislocation density. Nevertheless, the quest for lattice-matched substrates continues. Bulk GaN crystals grown under high pressures[3] have been used as substrates, but they are hampered by their small size. Another approach to homoepitaxy is the growth of thick GaN layers by hydride vapor phase epitaxy,[4] but such substrates suffer from poor crystallinity and the highly strained layers often develop cracks and other undesirable morphologies.

Most recently, single crystals of zirconium diboride, $ZrB_2(0001)$, have been grown to provide an electrically conductive lattice-matched substrate for GaN growth.[5] ZrB_2 has a hexagonal structure with lattice constants $a=3.169$ Å and $c=3.530$ Å. The in-plane lattice constant has only 0.6% mismatch with that of GaN ($a=3.189$ Å). The thermal expansion coefficients along $[10\bar{1}0]$ on the basal plane are also well matched between ZrB_2 and GaN, being 5.9×10^{-6} K^{-1} and 5.6×10^{-6} K^{-1}, respectively. The similarities in structural and thermal properties between ZrB_2 and GaN suggest that the use of $ZrB_2(0001)$ as a substrate would lead to a reduction of both dislocation density and biaxial strain in GaN films. Preparation of single crystals of ZrB_2 requires very high temperatures since the melting point of ZrB_2 is 3220 °C. A float-zone method has been developed by Otani and Ishizawa,[6] in which a 1 cm diameter rod was isostatically pressed at 1700 °C from ZrB_2 powder and melted in a floating zone by rf heating. The molten zone was ~0.5 cm long and a growth rate of 2–3 cm per hour was obtained.[5,6] The ZrB_2 single crystals thus grown have a typical size of 1 cm in diameter and 6 cm long. Successful epitaxial and strain-free GaN and AlN growth on such ZrB_2 substrates using MBE[7] and MOCVD[8] have been reported. However, the size limitation of the ZrB_2 substrate remains an unresolved issue.

In this letter, we describe a method to produce epitaxial ZrB_2 buffer layers on Si(111) using a single-source unimolecular precursor zirconium borohydride, $Zr(BH_4)_4$. We will show that the $ZrB_2/Si(111)$ serves as an ideal template for growth of GaN epitaxial films. The area of the GaN films is limited only by the available size of the Si(111) substrates.

The unimolecular precursor $Zr(BH_4)_4$ has a vapor pressure of ~8 Torr at room temperature and is therefore highly useful as a single gas source for MBE applications. The growth of ZrB_2 films on Si(111) substrates at 900 °C proceeds via the following reaction:

$$Zr(BH_4)_4(gas)\rightarrow ZrB_2(film)+B_2H_6(gas)+5H_2(gas).$$

The base pressure in the MBE chamber was $\sim2\times10^{-10}$ Torr. The Si(111) substrate surface was cleaned by flashing briefly to 1100 °C prior to deposition. For ZrB_2 film growth, the gaseous $Zr(BH_4)_4$ precursor was admitted via a leak valve and delivered through a gas inlet tube positioned

---

[a)] Electronic mail: jkouvetakis@asu.edu

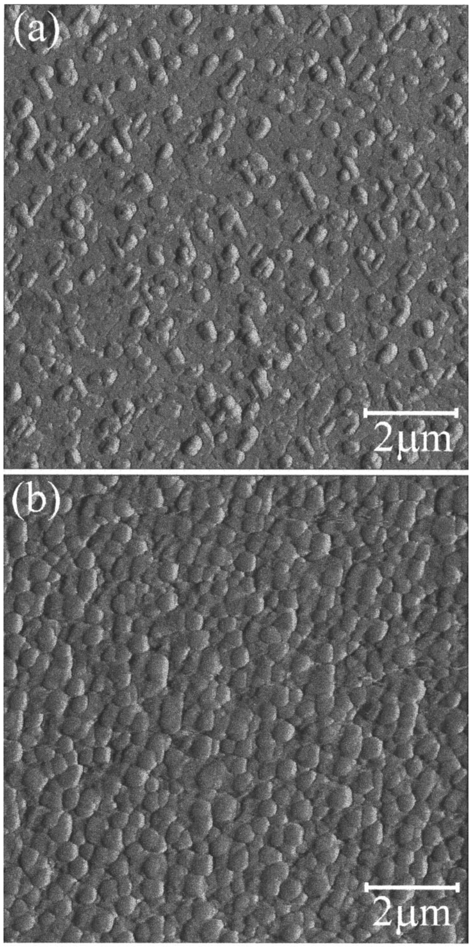


FIG. 1. AFM images of the surface morphology of (a) $ZrB_2(0001)$ and (b) GaN(0001) grown by plasma-assisted MBE on $ZrB_2(0001)$. The rms roughness is 1.4 nm in (a) and 4.4.nm in (b).

~2 cm from the substrate surface, whereupon the pressure in the chamber increased to $\sim 5\times 10^{-9}$ Torr. The growth rate of the ZrB_2 film was ~1.2 nm/min and was deliberately limited to such a slow rate. We found that higher fluxes of $Zr(BH_4)_4$ would lead to very high growth rates and the resulting ZrB_x films were invariably amorphous, similar to those reported previously.[9,10] The fact that crystalline ZrB_2 films were obtained only under slow growth conditions at 900 °C suggests that while the formation of ZrB_2 from $Zr(BH_4)_4$ is thermodynamically driven, the epitaxial growth of ZrB_2 films is controlled by kinetics.

A typical ZrB_2 buffer layer with a thickness of 25 nm has a metallic appearance and is 100% reflecting in the visible to UV wavelength range. The surface morphology of such a film is shown in an atomic force microscopy (AFM) image in Fig. 1(a), with a rms roughness of 1.4 nm. A GaN film of 500 nm thickness grown by plasma-assisted MBE on the ZrB_2 buffer layer at 650 °C has a surface morphology shown in Fig. 1(b), with a rms roughness of 4.4 nm The x-ray rocking curve of the (001) reflection taken on the ZrB_2 buffer layer yields a full width at half maximum (FWHM) of 3.5 arc min as shown in Fig. 2, very close to the FWHM reported for ZrB_2 bulk single crystals,[5] indicative of good crystalline quality. The photoluminescence (PL) spectra of the MBE-grown GaN film at 300 and 10 K are shown in Fig. 3. The PL peak at 10 K is located at 359 nm (3.45 eV) with a FWHM of 20 nm (190 meV), close to the neutral donor bound exciton D^0X line at 3.47 eV usually associated with low-temperature PL of GaN. No yellow luminescence around 560 nm was observed. The intensities of the PL peaks are comparable to those of undoped GaN films grown on sapphire by MOCVD.

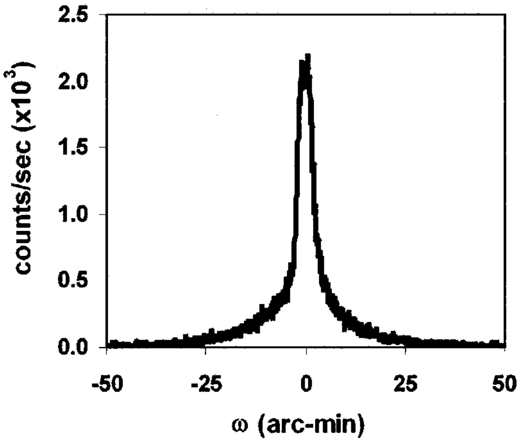


FIG. 2. The x-ray rocking curve of the (001) reflection of a ZrB_2 film grown on Si(111). The FWHM is 3.5 arc min.

The microstructure of the system $GaN/ZrB_2/Si(111)$ is shown in the cross-sectional transmission electron microscopy (XTEM) image in Fig. 4 taken in the $[\underline{1}10]$ projection referenced to the diamond cubic Si crystallographic habit. Remarkably, near-perfect epitaxial growth of $ZrB_2(0001)$ is observed in spite of the large mismatch between $d_{Si-Si} = 3.84$ Å, the in-plane distance between atoms on Si(111), and $a = 3.17$ Å, the in-plane lattice parameter for ZrB_2. The growth axis is along the [0001] or [111] direction with $[11\underline{2}0]_{ZrB2}//[\underline{1}10]_{Si}$. A close examination of the interface reveals that the misfit is taken up by a pure edge-type dislocation from the insertion of extra $\{1\underline{1}00\}$ lattice planes along the $[11\underline{2}0]$ direction. No threading dislocations propagating in a direction normal to the substrate are observed. The ratio of the parameters $d_{Si-Si}/a(ZrB_2)$ gives 1.21, which translates into an approximate coincidence of 6 ZrB_2 lattice planes with 5 Si lattice planes. The high resolution XTEM

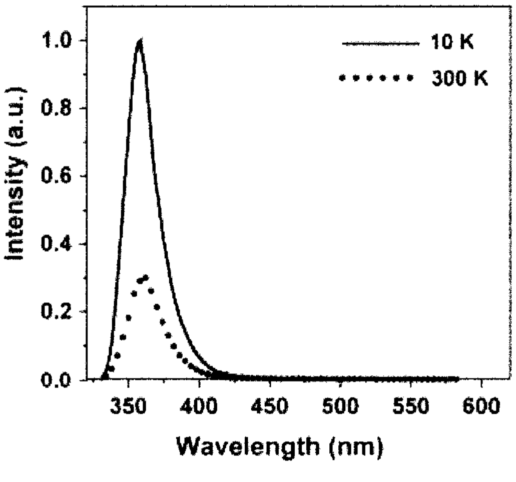


FIG. 3. The PL spectra of the GaN(0001) film grown by plasma-assisted MBE on a $ZrB_2/Si(111)$ substrate. The PL peak taken at 300 K is located at 362 nm (3.43 eV) and the peak at 10 K is located at 359 nm (3.45 eV) with a FWHM of 20 nm (190 meV).

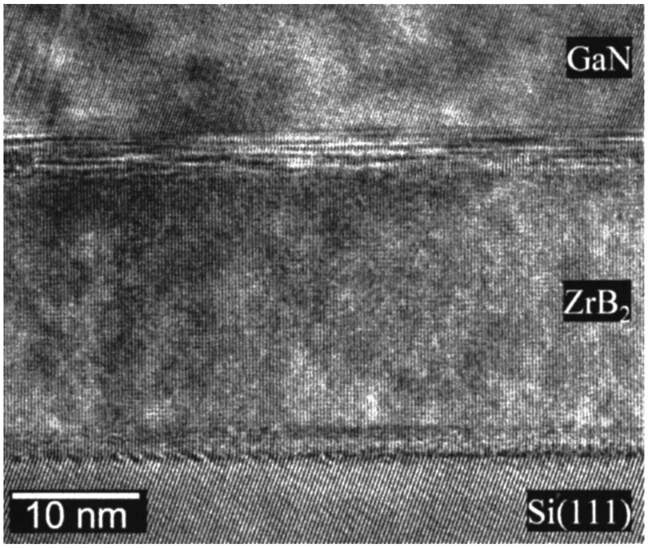


FIG. 4. An XTEM image of a 25-nm-thick ZrB_2 grown on Si(111) and a 500-nm-thick GaN film grown on ZrB_2. The epitaxial quality of both ZrB_2 and GaN films is clearly demonstrated. The image was taken in the $[\bar{1}10]$ projection of Si.

image of the interface shown in Fig. 5(a) shows exactly such a 6:5 coincidence. The occurrence of such a ''magic mismatch'' between hexagonal ZrB_2 and Si(111) accounts for the epitaxial growth of ZrB_2 even when the lattice mismatch between the two materials is very large. A magic mismatch of 4:5 between cubic GaN and GaAs(001) has been reported previously for the epitaxial growth of GaN on GaAs(001) in spite of the large lattice mismatch.[11]

The very sharp transition between Si(111) and $ZrB_2(0001)$ at the interface is confirmed by the *Z*-contrast XTEM image shown in Fig. 5(b). In this image, the contrast is a function of the atomic number *Z* of the element under observation. Thus, the Zr atoms, with $Z=40$, appears considerably brighter than the Si atoms where $Z=14$. One can observe that the epitaxy of the ZrB_2 layer is uninterrupted even across an atomic step on the Si(111) substrate.

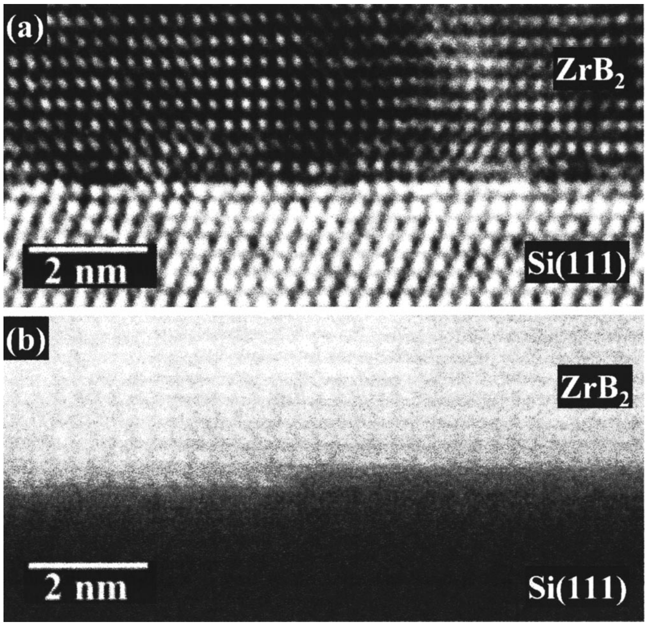


FIG. 5. (a) High-resolution XTEM image of the ZrB_2/Si(111) interface showing the magic mismatch of 6:5 coincidence of the ZrB_2 and Si(111) lattice planes at the interface. (b) *Z*-contrast XTEM image of the ZrB_2 layer grown on Si(111) showing the sharp transition at the interface. The Zr atoms show a much brighter contrast than the Si atoms due to the large difference in atomic number *Z*.

The transition between GaN and ZrB_2 is also reasonably sharp, as shown in Fig. 4. The GaN layer initially grows in a 2H–wurtzite structure, but switches over to a cubic structure, and then finally back to the 2H–wurtzite structure as the layer grows thicker (not shown in Fig. 4). The switching between wurtzite and cubic structures in the initial growth stages of GaN is well known. We do not observe the formation of an intermediate cubic phase of $Zr_xB_yN_z$ at the GaN/ZrB_2 interface as reported recently by Liu *et al.*[8] for the growth of GaN/AlN on ZrB_2 single-crystal substrates. The nonoccurrence of nitridation of ZrB_2 is probably due to the fact that our GaN films were grown by MBE at relatively low temperatures, i.e., around 650 °C.

The ZrB_2 buffer layer on Si(111) provides a near lattice-matched template for the growth of epitaxial GaN. Integration of III-nitrides with silicon electronic circuits is readily achieved. The reflective nature of the ZrB_2 surface presents an added bonus to optoelectronic applications of the III-nitrides. Silicon is ~45% absorbing for UV or near-UV light.[12] However, with the use of ZrB_2 buffer layer as a template, the Si(111) substrate becomes 100% reflecting, thus avoiding any loss of emission intensity from the III nitrides.

In summary, we have shown that under appropriate kinetic conditions, $ZrB_2(0001)$ can be grown epitaxially on Si(111) despite large lattice mismatch. The ZrB_2 layer serves as a reflective and conductive template for the growth GaN which is nearly lattice matched with ZrB_2. The ZrB_2/Si(111) substrate offers many distinct advantages in both microelectronic and optoelectronic applications of group III nitrides, the most important of which is the integration with silicon electronics. The size of the substrate is limited only by the availability of the size of silicon wafers.

This work was supported by the US Army Research Office Grant No. DAAD19-00-1-0471 and the National Science Foundation Grants Nos. DMR-0221993 and DMR-0303237.

[1] Y. Kato, S. Kitamura, K. Hiramatsu, and N. Sawaki, J. Cryst. Growth **144**, 133 (1994).
[2] K. Linthicum, T. Gehrke, D. Thomson, E. Carlson, P. Rajagopal, T. Smith, D. Batchelor, and R. F. Davis, Appl. Phys. Lett. **75**, 196 (1999).
[3] S. Porowski, J. Cryst. Growth **189/190**, 153 (1998).
[4] R. J. Molnar, W. Götz, L. T. Romano, and N. M. Johnson, J. Cryst. Growth **178**, 147 (1997).
[5] H. Kinoshita, S. Otani, S. Kamiyama, H. Amano, I. Akasaki, J. Suda, and H. Matsunami, Jpn. J. Appl. Phys., Part 2 **40**, L1280 (2001).
[6] S. Otani and Y. Ishizawa, J. Cryst. Growth **165**, 319 (1996).
[7] J. Suda and H. Matsunami, J. Cryst. Growth **237–239**, 1114 (2002).
[8] R. Liu, A. Bell, F. A. Ponce, S. Kamiyama, H. Amano, and I. Akasaki, Appl. Phys. Lett. **81**, 3182 (2002).
[9] J. Sung, D. M. Goedde, G. S. Girolami, and J. R. Abelson, J. Appl. Phys. **91**, 3904 (2002).
[10] M. Chirita, H. Xia, R. Soorykumar, J. B. Tolle, V. M. Torres, B. J. Wilkens, D. J. Smith, J. Kouvetakis, and I. S. T. Tsong, J. Appl. Phys. **89**, 4349 (2001).
[11] A. Trampert, O. Brandt, H. Yang, and K. H. Ploog, Appl. Phys. Lett. **70**, 583 (1997).
[12] E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983).