Epitaxial growth of zinc blende and wurtzitic gallium nitride thin films on (001) silicon

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Zinc blende and wurtzitic GaN films have been epitaxially grown onto (001)Si by electron cyclotron resonance microwave plasma-assisted molecular beam epitaxy, using a two-step growth process. In this process a thin buffer layer is grown at relatively low temperatures followed by a higher temperature growth of the rest of the film. GaN films grown on a single crystalline GaN buffer have the zinc blende structure, while those grown on a polycrystalline or amorphous buffer have the wurtzitic structure.

Gallium nitride is a wide band-gap III-V compound semiconductor. It usually has a wurtzitic structure (α-GaN) with a direct band gap 3.4 eV at room temperature,[1] which offers the potential for fabricating a variety of near ultraviolet (UV) optoelectronic devices, such as blue light-emitting diodes.[2,3]

GaN films have been grown with a wide range of growth techniques,[2,3] such as chemical vapor deposition, metal-organic chemical vapor deposition, and molecular beam epitaxy. A variety of substrates such as silicon, spinel, silicon carbide, and various crystallographic orientations of sapphire have been used in these studies. Most of the films grown are wurtzitic, and have n-type conductivity with high carrier concentration,[4] which is believed to result from nitrogen vacancies[4,5] or oxygen impurity incorporation.[6] Intentional p-type doping of GaN, which is desired in order to make efficient light-emitting devices, has met little success. In a recent study, p-type conductivity was reported in wurtzitic GaN thin films exposed to low-energy electron beam irradiation after their growth.[7]

Zinc blende GaN(β-GaN), which is the thermodynamically metastable phase of GaN, is hoped to be more amenable to doping than the wurtzitic GaN, since all of the III-V compounds that can be efficiently doped n type or p typed are cubic.[2] β-GaN has been reported to be grown on β-SiC and MgO(100) substrates,[8,9] which are closely lattice matched to β-GaN, and on GaAs substrate,[10,11] which has a significant mismatch to β-GaN.

Growth of GaN onto silicon substrate offers very attractive potential to incorporate future GaN devices onto silicon-based very large scale integrated circuits. However, due to the large difference in lattice constant, crystal structure, and thermal expansion coefficient, it is rather difficult to epitaxially grow GaN on Si substrate. Early attempts have led to amorphous or polycrystalline GaN,[12,13] except one report which claims to have grown wurtzitic single-crystalline GaN on Si(111) substrates.[14]

In the present letter, we report for the first time the growth of GaN thin films in the zinc-blende structure on Si(001) substrate, by electron cyclotron resonance microwave plasma-assisted molecular beam epitaxy (ECR-MBE).

The deposition system consists of a Varian Gen-II MBE unit with an AsTeX model-1000 ECR source attached to one of the ports of the source flange. The base pressure in the overall system is 10^{-11} Torr. A reflection high-energy electron diffraction (RHEED) setup is an integral part of the apparatus. A conventional Knudsen effusion cell was used to evaporate gallium. Atomic and ionic nitrogen were produced by passing molecular nitro-

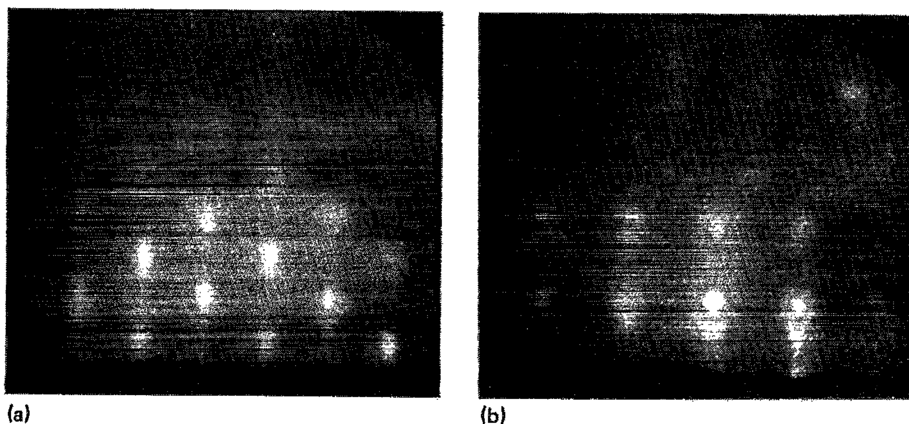

FIG. 1. RHEED Patterns of a (001) GaN film grown on a single-crystalline GaN buffer. (a) for [110] azimuthal incidences of the electron beam; (b) for [100] azimuthal incidence of the electron beam.

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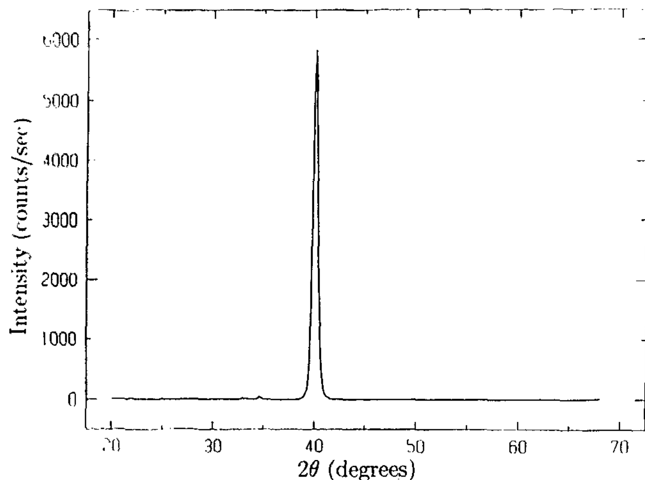

FIG. 2. X-ray diffraction of the (001) GaN film described in Fig. 1.

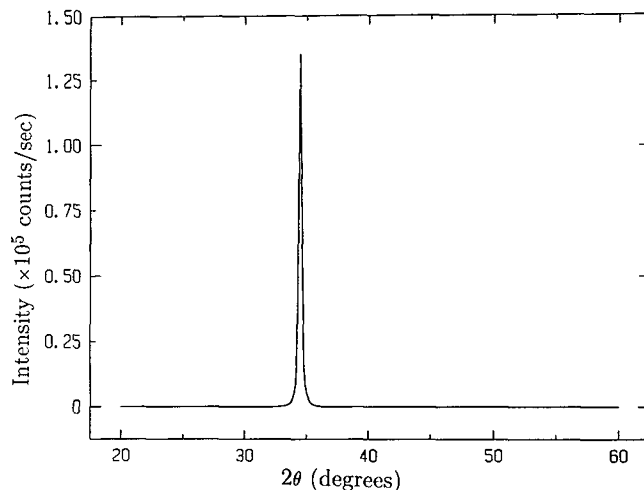

FIG. 4. X-ray diffraction of the polycrystalline GaN films described in Fig. 3.

gen through the ECR source. Details of the deposition system are to be described elsewhere.

The substrates used in this study were slightly *p*-type doped silicon of (001) orientation. The substrates were ultrasonically degreased in solvents and etched in buffered HF, prior to their introduction in the MBE unit. In the preparation chamber, the substrates were outgassed for 15 min at 850 °C. The silicon substrates after this type of preparation were examined by RHEED and were found to have unreconstructed (001) surfaces. The structure and microstructure of the films were investigated by *in situ* RHEED, *ex situ* x-ray diffraction using a Cu K_α radiation and scanning electron microscopy.

The GaN films were grown using a two-step growth process. The first step is a short low-temperature deposition, which produces a thin buffer layer. Typically, this step was carried out at temperature from 175 to 400 °C for 10–30 min, which resulted in a GaN buffer layer of about 300–900 Å thick. The substrate temperature was then raised to higher temperature, typically 600 °C, and a GaN film of about 1 μm thick was grown at this temperature. RHEED studies indicate that the buffer layer grown at 400 °C is single crystalline, while that grown at lower temperatures was found to be either amorphous or polycrystalline.

GaN films grown during the second stage were strongly influenced by the structure of the buffer layer. GaN films grown on a crystalline buffer layer were found to be single crystalline with its (001) planes parallel to the substrate. Shown in Fig. 1 are the RHEED patterns of the film for [110] and [100] azimuthal incidence of the electron beam. This clearly indicates that the GaN film has a zincblende structure. X-ray diffraction, shown in Fig. 2, shows a strong peak at $2\theta = 40.1°$, whose *d* spacing is 2.245 Å,

FIG. 3. RHEED Pattern of a polycrystalline GaN film grown on a polycrystalline GaN buffer.

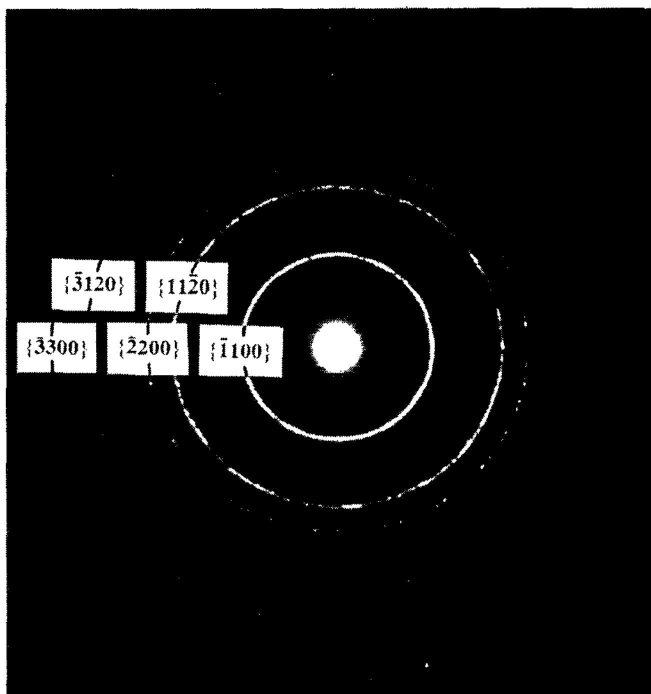

FIG. 5. Electron diffraction pattern of the polycrystalline GaN film described in Fig. 3.

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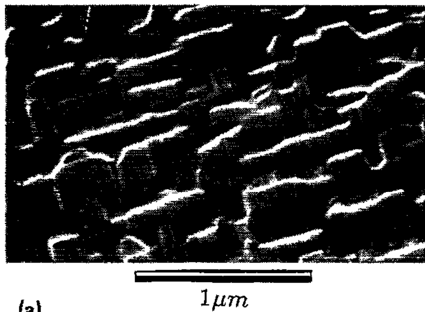

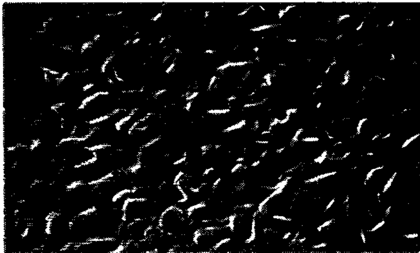

FIG. 6. Surface Morphology of (a) the (001) zinc blende GaN film; (b) the (0002) wurtzitic GaN film.

which is due to (002) reflection from β-GaN. So we found the lattice constant for β-GaN to be 4.49 Å. A small peak was also observed at $2\theta = 34.6°$, which could be due to the scattering from (111) planes of β-GaN or (0002) planes of α-GaN. This suggests that the GaN film has some misoriented domains. These domains may have been developed in the early stage of the buffer layer deposition. Similar structural faults have also been reported in transmission electron microscopy (TEM) studies of the interface of GaN on GaAs(001).[11]

GaN thin films grown on amorphous or polycrystalline buffer were found to be highly oriented polycrystalline. Shown in Fig. 3 are RHEED patterns of the polycrystalline GaN films. The RHEED pattern was observed to be independent of the azimuthal incidence of the electron beam. The Bragg peaks, although quite broad, reflects the long-range order in the direction normal to the substrate. However, the invariance of the RHEED pattern under the azimuthal rotation suggests random orientation of the crystal grains in azimuthal planes. X-ray diffraction shown in Fig. 4 shows only one Bragg peak, confirming that the GaN film is well oriented. From the peak position in the x-ray diffraction, the interspacing between the planes parallel to the substrate is found to be 2.59 Å, which can be the spacing of the (111) planes of the zinc-blende structure or the (0002) planes of the wurtzitic structure. Electron diffraction studies shown in Fig. 5 indicated that the material has the wurtzitic structure with lattice constant $\alpha = 3.2$ Å.

The surface morphology of two types of the GaN films grown on (001) Si are shown in Fig. 6. The (001) oriented films have relatively flat surfaces, roughened with many well oriented rectangular shaped "tiles," which reflects the symmetry of the β-GaN (001) surface. Contrary to the order of the surface morphology of the (001) GaN films, the surface of the polycrystalline GaN film was found to be characteristic of columnar morphology.

In conclusion, GaN films have been grown onto Si(001) substrates by ECR-assisted MBE, using a two-step growth process, which involves the deposition of a GaN buffer layer at relatively low temperature, followed by the growth of a thicker GaN film at higher temperatures. Depending on the structure of the buffer layer, the GaN films were found to have either the zinc-blende or the wurtzitic structure.

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[1]H. P. Maruska and J. J. Tietjen, Appl. Phys. Lett. **15**, 327 (1969).
[2]J. I. Pankove, MRS Symp. Proc. **162**, 515 (1990).
[3]R. F. Davis, Z. Sitar, B. E. Williams, H. S. Kong, H. J. Kim, J. W. Palmour, J. A. Edmond, J. Ryu, J. T. Glass, and C. H. Carter, Jr., Mater. Sci. Eng. B **1**, 77 (1988).
[4]J. I. Pankove, S. Bloom, and G. Harbeke, RCA Rev. **36**, 163 (1975).
[5]O. Lagerstedt and B. Monemar, J. Appl. Phys. **45**, 2266 (1974).
[6]W. Seifert, R. Franzheld, E. Butter, H. Sobotta, and V. Riede, Crystal Res. Technol. **18**, 383 (1983).
[7]H. Amano, M. Kito, K. Hiramatsu, and I. Aksaki, Jpn. Appl. Phys. **28**, L2112 (1989).
[8]M. J. Paisley, Z. Sitar, J. B. Posthil, and R. F. Davis, J. Vac. Sci. Technol. B **7**, 701 (1989).
[9]R. C. Powell, G. A. Tomasch, Y. W. Kim, J. A. Thornton, and J. E. Greene, MRS Symp. Proc. **162**, 525 (1990).
[10]M. Mizuta, S. Fujieda, Y. Matsumoto, and T. Kawamura, Jpn. J. Appl. Phys. **25**, L945 (1986).
[11]S. Strite, J. Ruan, Z. Li, N. Manning, A. Salvador, H. Chen, D. J. Smith, W. J. Choyke, and H. Morkoc (unpublished).
[12]E. Butter, G. Fitzi, D. Hirsch, G. Leonhardt, W. Seifert, and G. Preschel, Thin Solid Films **59**, 25 (1979).
[13]Z. Sitar, M. J. Paisley, B. Yan, and R. F. Davis, MRS Symp. Proc. **162**, 537 (1990).
[14]Y. Morimoto, K. Uchiho, and S. Ushio, J. Electrochem. Soc. **120**, 1783 (1973).

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