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Morphology and surface reconstructions of GaN($1\bar{1}00$) surfaces

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Abstract

GaN is grown by plasma assisted molecular beam epitaxy on ZnO($1\bar{1}00$) substrates. Well-oriented ($1\bar{1}00$) GaN surfaces are obtained, and ($1\bar{1}01$) oriented facets are also observed. On the GaN($1\bar{1}00$) surfaces under Ga-rich conditions a surface reconstruction with approximate symmetry of "4×5" is found. A model is proposed in which this reconstruction consists of ≥ 2 monolayers of Ga terminating the GaN surface.

Reconstructions of GaN have been extensively studied in the past five years, primarily for (0001) and ($000\bar{1}$) surfaces [1]. Films with these surface orientations have well known pyroelectric and piezoelectric properties [2,3]. Although such properties can have useful device applications (such as confining carriers in a two-dimensional electron gas [2]), for other applications these properties are undesirable. For this reason a few growth studies of ($10\bar{1}0$) oriented (m-plane) GaN have been performed since for this orientation the crystal symmetry precludes pyroelectric and piezoelectric effects (at least in the absence of shear stresses in the growth plane) [4]. In one recent study Waltereit et al. grew GaN on γ-$LiAlO_2$(100) [4]. Well oriented ($1\bar{1}00$) films with a slate like surface morphology were observed. No surface reconstructions were found on the films.

In this work we have used plasma assisted molecular beam epitaxy (PAMBE) to grow GaN films on ZnO($1\bar{1}00$) substrates. With lattice mismatches of 2.0% and 0.5% in the **a** and **c** directions, respectively, ZnO offers an attractive substrate for GaN heteroepitaxy. We obtain well oriented ($1\bar{1}00$) GaN films, although we also observe the formation of ($1\bar{1}01$) facets (from which we deduce that the energies of ($1\bar{1}00$) surfaces and ($1\bar{1}01$) facets are comparable). Several reconstructions on the GaN($1\bar{1}00$) surfaces are found, with the most common having approximate symmetry of "4×5". We propose a model in which this structure consists of ≥ 2 monolayers of Ga terminating the GaN surface.

ZnO($1\bar{1}00$) substrates were obtained from Cermet, Inc. The MBE growth and subsequent scanning tunneling microscopy (STM) was performed using a system previously described [1]. The ZnO substrates were cleaned prior to growth simply by heating them to about 550°C for 20 min. Growth was initiated by exposing the ZnO surface simultaneously to incident Ga and N fluxes. A ≈20 nm thick GaN layer is grown at a relatively low temperature of about 500°C, and subsequent growth was performed at about 700–750°C. (Following the growth, and with our MBE

growth cells at their standby temperature of 300°C, our chamber pressure returns within a few hours to its base level of 1×10^{-10} Torr indicating that thermal decomposition of the substrate is not a problem at least at this level). RHEED shows a streaky 1×1 pattern throughout the entire growth sequence when Ga-rich conditions are used. Consistent with our prior c-plane GaN growth on SiC [5], growth under N-rich conditions resulted in spotty RHEED patterns indicative of 3-dimensional growth.

Figure 1(a) shows a typical surface morphology for our GaN films with thicknesses of about 0.5 μm. The substrates have an unintentional miscut of several degrees oriented primarily in the [0001] direction, thus producing the steps seen extending vertically in the image. RHEED patterns of the films are streaky, as shown in Fig. 1(b), consistent with the flat terraces observed in the morphology. The RHEED patterns of Figs. 1(b) and (d) were acquired with the electron beam along $[11\bar{2}0]$; the spacing between streaks is 0.62±0.02 times that with the beam along the orthogonal [0001] direction, and the angular dependence of the pattern is identical to that of Ref. [4]. High resolution x-ray diffraction of our films, compared with our prior c-plane results for GaN on SiC [5], reveals single-phase $(1\bar{1}00)$-oriented films as shown in Fig. 2.

For thicker films the RHEED patterns display a clear evidence of facetting, as shown in Fig. 1(c) for a film with thickness of about 1.0 μm. The RHEED pattern of Fig. 1(d) displays oblique streaks indicative of $(1\bar{1}01)$ or $(1\bar{1}0\bar{1})$ facets, having an angle of 28° relative to the $(1\bar{1}00)$ surface. Our absolute sample orientation is not known for the data of Fig. 1 so we cannot distinguish between these directions, although the RHEED results do indicate that one of the facets occurs preferentially over the other. These facets are also seen in the surface morphology of Fig 1(c), as revealed in the accompanying line cut shown in Fig. 1(e). Ridges, with $(1\bar{1}01)$ and $(1\bar{1}0\bar{1})$ sidewalls, form on the surface and extend in the $[11\bar{2}0]$ direction. Assuming that the $(1\bar{1}01)$ and $(1\bar{1}0\bar{1})$ facets seen here are not kinetically induced, our observations indicate that the formation energy for the facets surface is comparable or less than that for the $(1\bar{1}00)$ surface. These facets pose a potential problem for the growth of the flat $(1\bar{1}00)$ films.

Between the ridges of Fig 1(c), as well as on the surface of the thinner film pictured in Fig. 1(a), large flat GaN$(1\bar{1}00)$ terraces are found. These terraces tend to be elongated in the $[11\bar{2}0]$ direction, forming a slate like morphology similar to that reported by Waltereit et al. [4]. We have observed several reconstructions on these terraces, with our clearest observations being for films grown under Ga-rich conditions as pictured in Fig. 3. Terraces extending in the $[11\bar{2}0]$ direction are seen there separated by narrow trenches and/or raised rows of atoms. The reconstruction most commonly found on these Ga-rich surfaces is labeled 'A' in Fig. 3(a). It consists of corrugation rows extending in directions ±7° away from the [0001] direction. A 4× RHEED pattern with the electron beam in the [0001] direction is found for this reconstruction. An expanded STM image of the structure is shown in Fig 3(b). Corrugation maxima forming rows with short segments extending in the [0001] direction are observed. Every fourth or fifth maxima, a brighter maximum occurs, and the location of this bright maximum is shifted in the $[11\bar{2}0]$ direction compared to that of one of its neighbors. The unit cell is indicated in the image. A 1×1 unit cell of the $(1\bar{1}00)$ surface has basis vectors of **a** in the $[11\bar{2}0]$ direction with length 3.19 Å and **c** in the [0001] direction with length 5.19 Å. Within our experimental uncertainty (±10%) our observed cell matches that of one with primitive translation vectors 4**a**+1**c** and –1**a**+5**c**, which contains 21 1×1 cells. This surface unit cell can be constructed from a 4**a**×5**c** cell by slightly rotating and shearing it, and so for a shorthand notation we refer to our observed structure as "4×5" (including quotation

marks to indicate an approximate symmetry). Figures 3(c) and (d) show voltage dependent imaging results for this reconstruction. Relatively little difference is found between the empty and filled states images. Also, imaging at low voltages of ±0.1 V is found to be possible, thus indicating that this surface is metallic. A second surface structure seen in Fig 3(a) is labeled 'B'. This structure is completely featureless in the STM images (indicating a small unit cell such as 1×1) and its atomic arrangement is unknown at present.

Prior theoretical calculations have been performed for the stoichiometric 1×1 surface of GaN($1\bar{1}00$) [6]. In this structure there are two surface atoms in each 1×1 cell; there is one threefold coordinated atom of each species, and the surface is stabilized by a transfer of charge from the Ga atom to the N atom. This stoichiometric dimer surface (labeled SD in Fig. 4(a)) would be expected to be present *e.g.* following cleavage on the ($1\bar{1}00$) plane. Non-stoichiometric structures that could in principle form during growth were also previously considered [6]. One such structure, formed by replacing the N atoms in the surface dimer by Ga, was found to be stable compared to the stoichiometric surface under extremely Ga-rich conditions. We will call this surface the GD surface, or gallium dimer surface. It is depicted in Fig 4(b).

Here we report first principles calculations for two additional possible structures that could form in growth under very Ga-rich conditions. The two structures are formed by the addition of two monolayers of Ga to either the SD surface or to the GD surface, and these are labeled as SD+2 and GD+2 (shown in Figs. 4(c) and (d), respectively). One monolayer is defined here to mean one atom per 1×1 unit cell. The energies of these structure were calculated, and as seen in Fig. 4(e), they are stable compared to the SD surface in very Ga-rich conditions. Now, since these structure have 1×1 symmetry they cannot correspond to the experimentally observed Ga-rich structures. Nevertheless their relative stability, albeit by a small amount, establishes the plausibility that Ga adlayer structures could wet the SD and GD surfaces. In the SD+2 surface the top Ga adlayer and the bottom Ga adlayer are separated by 0.57 Å in the [$1\bar{1}00$] direction, whereas in the GD+2 surface the top two Ga adlayers are separated by less than 0.05 Å in this direction.

Since the Ga-Ga spacing in the Ga adlayer is slightly larger than that in Ga bulk, a lowering of the energy might be achieved by increasing the density of Ga atoms in the Ga adlayer such that their density approaches something close to that of Ga bulk. To study this effect we performed additional first principles calculations on a model based on the experimentally observed "4×5" surface unit cell, in which 45 Ga atoms are deposited onto the 21 GaN dimers of the surface layer. A full description of this model is presented elsewhere [7]. The Ga coverage is 2.14 and the structure is called SD+2.14 (in analogy to the SD+2) structure. The surface energy is shown in Fig. 4(e); the SD+2.14 energy is almost degenerate with that of the SD+2 structure in very Ga-rich conditions.

In conclusion, we have grown ($1\bar{1}00$) oriented GaN films on ZnO. ($1\bar{1}01$) and ($1\bar{1}0\bar{1}$) facets are observed to coexist with the ($1\bar{1}00$) GaN face. Reconstructions of the GaN($1\bar{1}00$) surface are reported for the first time. Under Ga rich conditions a "4×5" reconstruction is observed. This structure is proposed to consist of ≥ 2 monolayers of Ga terminating the GaN crystal, and it is metallic.

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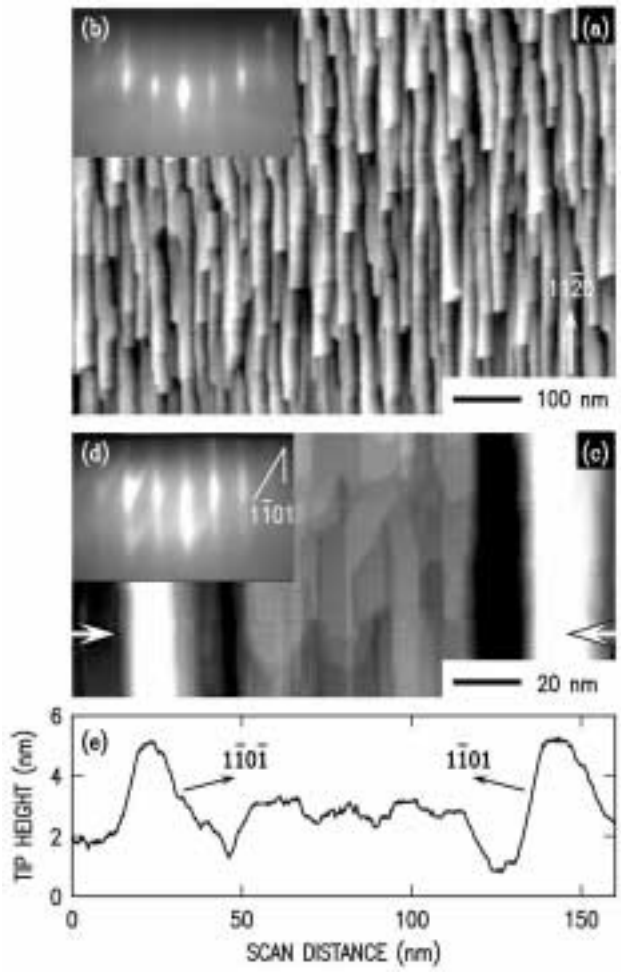

Figure 1. (a) STM image of 0.5 μm thick GaN film grown on ZnO($1\bar{1}00$) substrate (sample voltage –3.0 V, gray scale range 50 Å). (b) RHEED pattern with electron beam along [$11\bar{2}0$]. (c) STM image of a 1.0 μm thick GaN film (sample voltage –1.0 V, gray scale range 25 Å). (d) RHEED pattern with electron beam along [$11\bar{2}0$]. (e) Line cut taken at the position of the arrows in (c).

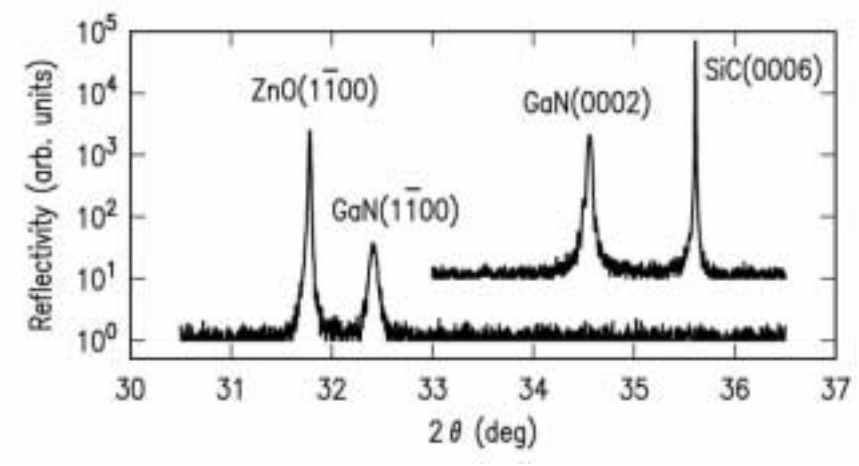

Figure 2. Symmetric triple-crystal ω-2θ x-ray diffraction scans of a GaN($1\bar{1}00$) film grown on ZnO($1\bar{1}00$) compared with a GaN(0001) film grown on 6H-SiC(0001).

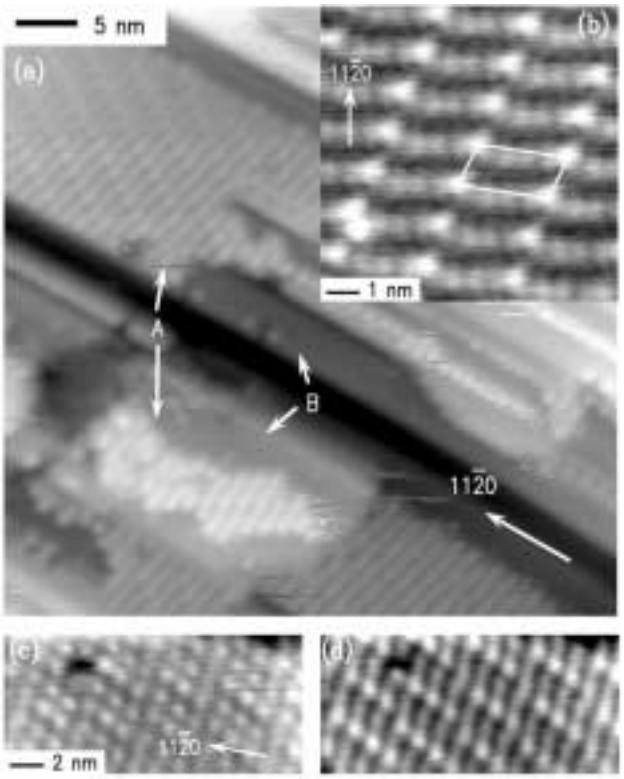

Figure 3. (a) STM image of Ga-rich GaN($1\,\bar{1}\,00$) surface (sample voltage –3.0 V, gray scale range 8 Å). (b) Expanded view of the A-type surface reconstruction (sample voltage –0.3 V, gray scale range 1.0 Å). (d) and (e) STM images acquired simultaneously at sample voltages of +1.0 and –1.0 V, respectively (gray scale range 0.7 Å).

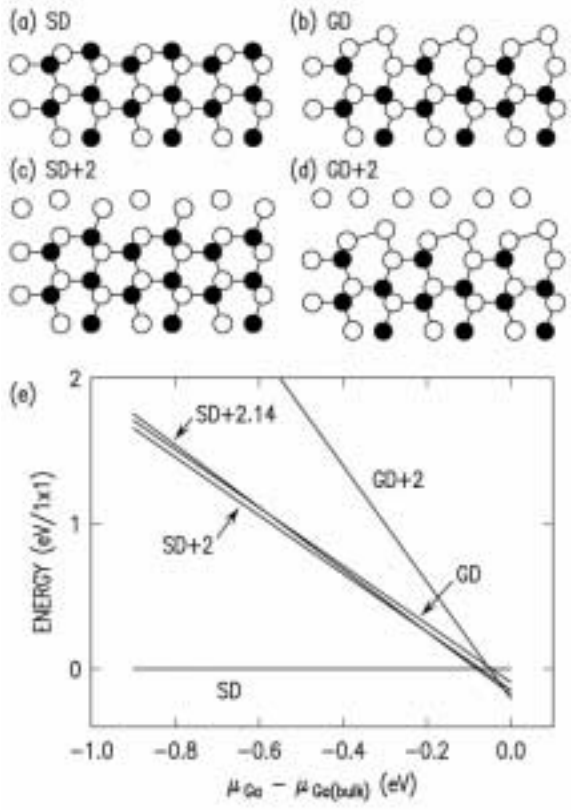

Figure 4. (a)–(d) Side views of various 1×1 structural models, shown in a $[11\,\bar{2}\,0]$ projection. Ga atoms are indicated by open circles and N by closed circles. (e) Relative energies of the structural models as a function of the Ga chemical potential.