

Rapid Note

Explanation of multiplet spots in low-energy electron diffraction patterns of clean GaN{0001}–1 × 1 surfaces

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Abstract. Clean, ordered, and stoichiometric GaN{0001}–1 × 1 surfaces are obtained after exposure to a Ga-flux followed by annealing in ultrahigh vacuum (UHV), after desorption of a Ga layer deposited at room-temperature or after nitrogen ion-bombardment and annealing in UHV. Samples annealed at temperatures above approximately 850 °C display 1 × 1 low-energy electron diffraction patterns. As a function of electron energy, the normal-order spots split into circular sextets. These multiplet rings periodically expand and coalesce. This observation is explained by oppositely oriented, regular step arrays in the [1000]-, [0100]- and [0010]-directions on the GaN{0001} surfaces. Quantitative analysis of the data gives terrace widths of 11.0 ± 1.0 Å and step heights of 5.25 ± 0.2 Å. The observations suggest faceting or the “development” of growth spirals with steps heights of two Ga-N bilayers by thermal etching.

PACS. 61.14.Hg Low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) – 68.35.Bs Surface structure and topography

The group-III nitrides are semiconductors with wide and direct band gaps. They became attractive for device applications after their *p*-type doping was achieved [1]. Meanwhile, electroluminescent diodes and injection lasers emitting blue light as well as solar-blind detectors for UV light are devices based on group-III nitrides that have reached the market. In spite of this, the surface and interface properties of this class of semiconductors are less well explored.

Basic research of semiconductor surfaces and interfaces always starts from clean surfaces that are then treated and investigated under ultrahigh-vacuum conditions. Recent works on the preparation of clean GaN{0001} surfaces used both *ex situ* [2–4] and *in situ* techniques [5–7]. After *in situ* cleaning, the GaN surfaces always exhibited 1 × 1 patterns in low-energy electron diffraction (LEED). We as others [7–12] observed that after treatments at temperatures above approximately 800 °C the normal beams split into a multiplet of six spots as a function of the primary electron energy. The splitting occurs along the lines connecting the normal spots. We explain this splitting where the spot sextet appears and vanishes periodically as a function of electron energy by regular step arrays in the [1000]-, [0100]- and [0010]-directions. Our interpretation that will be described in the following

uses a simple, one-dimensional approach of Henzler’s [13]. Previous studies ascribed this observation to faceting of the GaN{0001} surfaces [7–9] but our quantitative evaluation of the step parameters indicates that they might be due to screw dislocations.

In this study we used α -GaN epilayers on sapphire (Cree Research). We first treated the samples *ex situ* in a 50% aqueous HF solution for 1 min which was diluted by a buffered HF solution (HF:NH₄F:NH₄OH) with pH = 9 followed by a final rinse in de-ionized water. The samples were then blown dry with N₂ and immediately transferred into an ultrahigh-vacuum (UHV) system. It was equipped with a 4-grid LEED optics (Varian) and a cylindrical mirror analyzer having a coaxial electron gun (Varian) for Auger electron spectroscopy (AES). The electron energy distribution curves were recorded as the first derivatives and the kinetic energy and the current of the primary electrons were set to 3 keV and 2 μ A, respectively. Figure 1a shows sections of the AES spectrum obtained with an as-received sample. In addition to the Ga and N signals of the substrate, extra lines of carbon and oxygen as well as traces of sulfur and chlorine (not shown) are observed. Figure 1b demonstrates that the preparation in HF strongly reduces both the oxygen and carbon signals on GaN surfaces. No other contaminations were detected by AES while X-ray photoemission spectroscopy (XPS) additionally revealed traces of fluorine. After the HF treatment, the average ratios of the AES peak-to-peak

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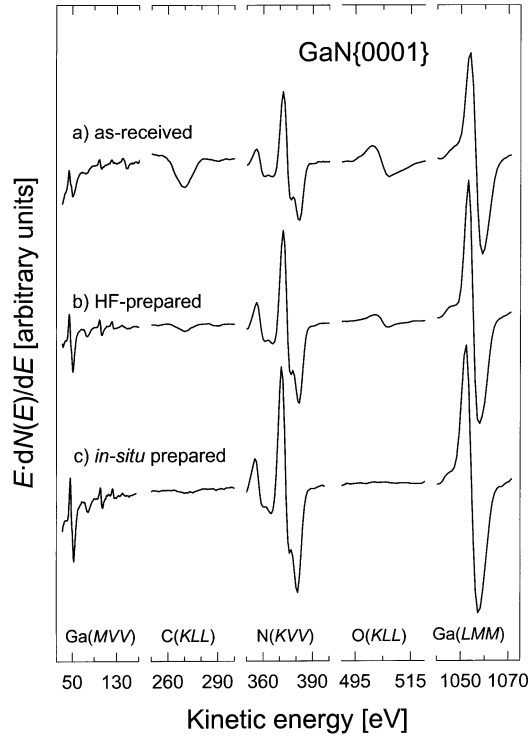


Fig. 1. Auger electron spectra of as-received (a), HF-prepared (b), and *in situ* cleaned GaN{0001} surfaces (c).

heights (PPH) are $C(KLL)/Ga(LMM) = 0.022 \pm 0.015$ and $O(KLL)/Ga(LMM) = 0.07 \pm 0.017$. These values and, because of that, the respective contaminants are well below what has been reported after other wet-chemical treatments [2,4]. HF-prepared GaN{0001} surfaces always showed sharp 1×1 LEED patterns without any extra spots.

The following *in situ* cleaning procedures were explored:

- (A) exposure to a Ga-flux followed by annealing in UHV at high temperatures [14],
- (B) desorption of a 10 nm Ga layer deposited at room temperature, and,
- (C) nitrogen-ion bombardment (1 keV, $10 \mu A/cm^2$) and annealing in UHV.

During these *in situ* treatments the sample temperatures ranged between 830 and 880 °C with a calibration error of ± 20 °C. After all three of these procedures the AES spectra looked alike and Figure 1c shows a representative example. The PPH of the carbon and oxygen lines are below 1% of the Ga(LMM) signal. The PPH-ratio $N(KVV)/Ga(LMM)$ of the substrate lines, on the other hand, remains unaffected. Furthermore, clean GaN{0001} surfaces show identical oxidation behavior irrespective of whether treatment (B) or (C) was used [15]. This observation suggests that no excess metallic Ga is present on our surfaces after these *in situ* treatments.

The LEED patterns observed with such cleaned GaN{0001} surfaces depended on the annealing

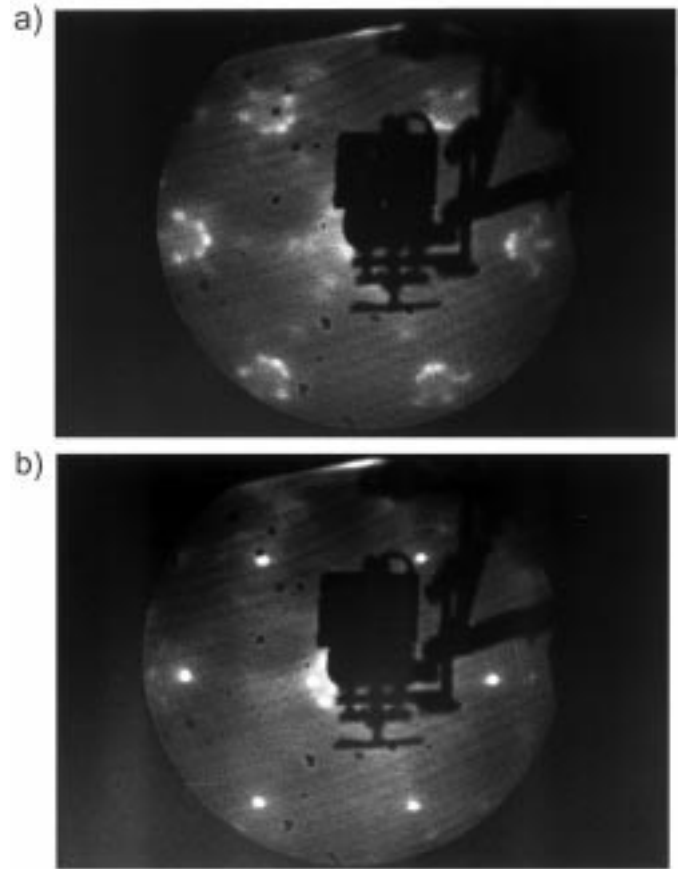


Fig. 2. LEED patterns of clean and stoichiometric GaN{0001} surfaces at electron energies of 70 eV (a) and 76 eV (b).

temperature. Ga-treated surfaces behave alike irrespective of the cleaning method used and shall be considered first. After annealing treatments in UHV at 830 °C, 1×1 LEED patterns were obtained. As a function of the electron energy, the integer-order spots periodically developed into weak diffuse rings. Annealing at temperatures above 850 °C caused the rings to decay into six separate spots that become sharper with increasing annealing temperature. Figure 2 shows two LEED patterns of a sample prepared by Ga desorption at 880 °C (treatment (B)). At an electron energy of 70 eV (Fig. 2a) multiplets of six spots hexagonally arranged around the positions of the respective integer-order spots are present. With increasing electron energy, the rings of multiplet spots gradually contract until they coalesce to sharp integer-order spots at an electron energy of 76 eV (Fig. 2b). For even larger electron energies, the integer-order beams again split in six spots and the diameters of the multiplet rings first widen and then shrink periodically. Sharp normal-order spots and no multiplets occurred at primary electron energies of 48, 64, 81, 103, 126, 152, 181, 214, and 250 eV, whereas at the second sample these values differed by 5 ± 1 eV due to a calibration difference of two different LEED electronics. Nitrogen-sputtered surfaces showed no LEED patterns

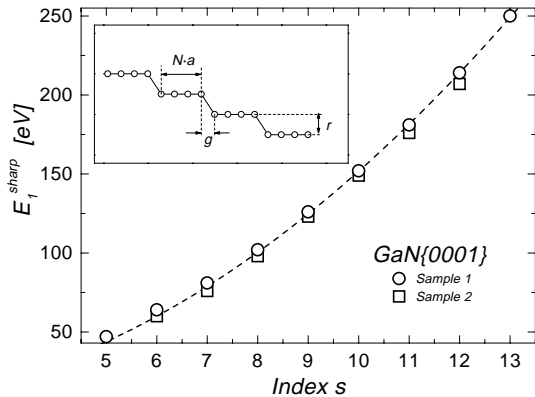


Fig. 3. Characteristic energies E_1^{sharp} at which no splitting of the first-order spots occurs as a function of serial numbers s . The dashed line represents a least-squares fit of equation (1) to the data. The inset explains the parameters of the regular step arrays.

immediately after ion-bombardment. However, after annealing at elevated temperatures also these samples alternately displayed 1×1 patterns and pronounced ring-shaped multiplets as a function of electron energy.

Splitting of integer-order LEED spots can be explained by regular step arrays [16]. The reason for that is the superposition of the diffraction at the atoms on the terraces and at the step edges. Henzler [13] considered a one-dimensional regular array of steps. He found a periodically alternating appearance of single and splitted integer-order spots or, in other words, a regular vanishing of one of the doublet spots leaving only single spots. Unlike our LEED observations, he noticed no periodic variation of the separation of the multiplet spots. However, doublets of spots will periodically open and coalesce to single beams if both ascending and descending staircases are assumed. Then, the LEED patterns observed are simply made up by the sum of the diffraction at the two types of regular step arrays. Figure 4 displays the angular dependence of the diffraction intensities calculated for two regular, one-dimensional step arrays that are oriented in opposite directions but are otherwise identical. The electron energy is stepwise increased by 3 eV. The 64, 82 and 103 eV distributions show sharp (1,0) and (-1,0) first-order spots. With increasing energy they divide up into doublets the separation of which first increases but then reduces until the two spots eventually coalesce at 82 and 103 eV, respectively. The simulation reproduces our LEED observations. It thus suggests the existence of oppositely oriented, regular step arrays in three symmetry directions on annealed GaN{0001} surfaces. Since the six multiplet spots behave the same the step parameters, *i.e.*, their treads and risers should be identical.

The simulation displayed in Figure 4 occasionally shows single spots to split into four spots. Such behavior was not observed with GaN{0001} surfaces. This may be caused either by very low intensities of two of the four peaks or by an overlap of two spots each due to their proximity.

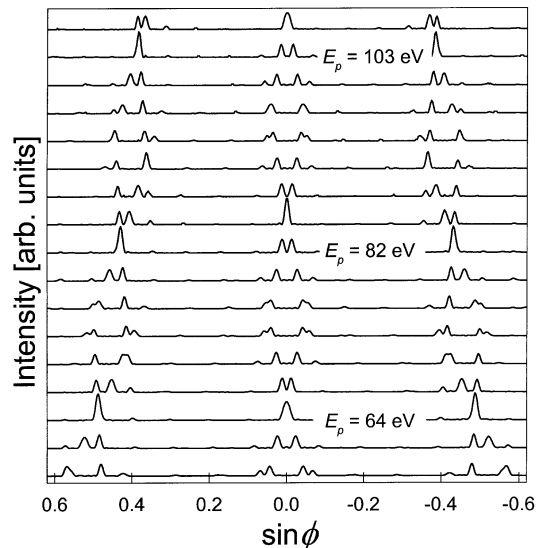


Fig. 4. Calculated angular intensity distributions for diffraction at ascending and descending one-dimensional staircases with identical step parameters $r = 5.25$ Å and $t = 11.1$ Å. The energy of the primary electrons is increased stepwise by 3 eV.

The energies E_1^{sharp} at which sharp first-order spots occur are characteristic of the staircases and they are labeled by a serial integer s . Considering kinematical scattering only Henzler [13] calculated these energies as

$$E_1^{sharp}(s) = \frac{\hbar^2}{2m_0} \left(\frac{\pi}{r}\right)^2 \left[\left(s + \frac{g}{a}\right)^2 + \frac{r^2}{a^2} \right], \quad (1)$$

where \hbar and m_0 are Planck's constant and the electron mass, respectively, and r , g , and a are the step height, a horizontal offset at the lower step edge, and the lattice constant, respectively, as explained by the inset of Figure 3.

The step height r may be directly determined from the experimental values E_1^{sharp} since from equation (1) it follows

$$E_1^{sharp}(s+1) - E_1^{sharp}(s) = (\hbar^2/m_0)(\pi/r)^2 [s + (g/a + 1/2)]. \quad (2)$$

Our data of E_1^{sharp} displayed in Figure 3 give $r = 5.2 \pm 0.2$ Å. This value equals the lattice parameter $c = 5.19$ Å along the c -axis of wurtzite GaN or, in other words, the steps that form on {0001}-oriented GaN epilayers during annealing treatments in UHV at temperatures above approximately 800 °C are two Ga-N bilayers in height. This finding agrees with the Burgers vector found by Smith *et al.* [17] at screw dislocations during MBE growth of wurtzite GaN. Therefore, screw dislocations may also be considered as a possible explanation for the step arrays besides of facets.

The determination of the offset parameter g requires a least-squares fit of the experimental data to equation (1). This procedure then also gives the absolute values

of the serial index s . Using the lattice parameter $a = 3.1892 \text{ \AA}$ of wurtzite GaN [18], we obtained the serial index $s = 5$ for $E_1^{sharp} = 48 \text{ eV}$ and the step parameters $g = 1.5 \pm 0.5 \text{ \AA}$ and, again, $r = 5.25 \pm 0.2 \text{ \AA}$. Since ideal steps of two bilayer height exhibit no offset, g represents a fitting-parameter only.

For the calculation of the intensity distributions shown in the Figure 4 we used a step height of 5.25 \AA and a terrace width of $t = 3a + g = 3a + 1.5 \text{ \AA} = 11.1 \text{ \AA}$. The simulation gives sharp first-order spots at electron energies of 47, 64, 82, 103, 127, 154, 184, 214, 250 eV, values that agree well with the ones experimentally observed. Furthermore, the model of identically ascending and descending regular step arrays also allows to estimate the terrace width from the maximum angular separation of two connected LEED beams. The maximum separation between two symmetric multiplet spots occurs when the (0,1) spots from diffraction at ascending and descending steps coincide. Therefore, the terrace width is easily calculated to $11.0 \pm 1.0 \text{ \AA}$ taking into consideration only one kind of steps. This result confirms the conclusions drawn from the comparison of the electron energies at which sharp first-order beams are found experimentally and in the simulation for identically ascending and descending step arrays.

As mentioned above, the multiplets of sharp spots evolve from weak diffuse rings when the annealing temperature of the GaN samples is increased to above $830 \text{ }^\circ\text{C}$. This may be explained by either faceting or a gradual “development” of growth spirals by thermal etching of the surface since the annealing temperature is close to where decomposition of GaN sets in [19]. This proposal agrees with the observation of steps that are two bilayers in height since screw dislocations observed by Smith *et al.* [18] during molecular beam epitaxy (MBE) growth of wurtzite GaN possess the same Burgers vector. The granulation of the diffuse rings into well-separated spots after annealing treatments at approximately $850 \text{ }^\circ\text{C}$ is then explained by the formation of straight step edges oriented perpendicular to the [1000]-, [0100]- and [0010]-directions, *i.e.*, rotated by 60° each. Such step arrangement is then equivalent to the regular arrays of ascending and descending steps of the same heights and widths as proposed by the model outlined above.

To summarize, clean, ordered and stoichiometric GaN{0001} surfaces can be prepared using different techniques that all include treatments at high temperatures. After such annealing at elevated temperatures multiplet spots are periodically observed in the 1×1 LEED patterns as a function of electron energy. They are explained by regular arrays of steps in three high-symmetry directions. Annealing above approximately $830 \text{ }^\circ\text{C}$ straightens the step edges as indicated by the observed granulation of the initially diffuse diffraction rings. The present LEED observations may be related to screw dislocations seen by scanning tunneling microscopy (STM) [17] or to faceting of the surfaces [7–9]. The step height of $5.25 \pm 0.2 \text{ \AA}$ as obtained

from the LEED data excellently agrees with the Burgers-vector component of 5.19 \AA in the [0001]-direction of the screw dislocations. The one-dimensional model of ascending and descending staircases with identical step parameters represents line-scans across such hexagon-shaped spirals. Since this arrangement of ascending and descending staircases also describes flat facets further experiments have to be carried out to clarify the microscopic nature of the step arrays. The angular distributions of the simulated LEED intensities agree well with the energy dependence of the LEED pattern experimentally observed with GaN{0001}– 1×1 surfaces annealed at high-temperatures.

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References

1. H. Amano, M. Kito, K. Hiramatsu, I. Akasaki, *Jpn J. Appl. Phys.* **28**, L2112 (1989).
2. L.L. Smith, S.W. King, R.J. Nemanich, R.F. Davis, *J. Electr. Mat.* **25**, 805 (1996).
3. H. Ishikawa, S. Kobayashi, Y. Koide, S. Yamasaki, S. Nagai, J. Umezaki, M. Koike, M. Murakami, *J. Appl. Phys.* **81**, 1315 (1997).
4. K. Prabhakaran, T.G. Andersson, K. Nozawa, *Appl. Phys. Lett.* **69**, 3212 (1996).
5. M. Asif Khan, J.N. Kuznia, D.T. Olson, R. Kaplan, *J. Appl. Phys.* **73**, 3108 (1993).
6. R.W. Hunt, L. Vanzetti, T. Castro, K.M. Chen, L. Sorba, P.I. Cohen, W. Gladfelter, J.M. Van Hove, J.N. Kuznia, M. Asif Khan, A. Franciosi, *Physica B* **185**, 415 (1993).
7. V.M. Bermudez, D.D. Koleske, A.E. Wickenden, *Appl. Surf. Sci.* **126**, 69 (1998).
8. V.M. Bermudez, T.M. Jung, K. Doverspike, A.E. Wickenden, *J. Appl. Phys.* **79**, 110 (1996).
9. V.M. Bermudez, *J. Appl. Phys.* **80**, 1190 (1996).
10. S.P. Grabowski, T.U. Kampen, H. Nienhaus, W. Mönch, *Appl. Surf. Sci.* **123/124**, 33 (1998).
11. M.M. Sung, J. Ahn, V. Bykov, J.W. Rabalais, D.D. Koleske, A.E. Wickenden, *Phys. Rev. B* **54**, 14652 (1996).
12. J. Ahn, M.M. Sung, J.W. Rabalais, D.D. Koleske, A.E. Wickenden, *J. Chem. Phys.* **107**, 9577 (1997).
13. M. Henzler, *Surf. Sci.* **19**, 159 (1970).
14. T.U. Kampen, W. Mönch, *Appl. Surf. Sci.* **117/118**, 388 (1997).
15. O. Janzen, Ch. Hahn, W. Mönch, *Eur. Phys. J.* (submitted).
16. W.P. Ellis, R.L. Schwoebel, *Surf. Sci.* **11**, 82 (1968).
17. A.R. Smith, R.M. Feenstra, D.W. Greve, J. Neugebauer, J.E. Northrup, *Phys. Rev. Lett.* **79**, 3934 (1997).
18. H.P. Maruska, J.J. Tietjen, *Appl. Phys. Lett.* **15**, 327 (1969).
19. O. Ambacher, H. Angerer, R. Dimitrov, W. Rieger, M. Stutzmann, G. Dollinger, A. Bergmaier, *Phys. Stat. Sol. (a)* **159**, 105 (1997).