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Surface Reconstruction during Molecular Beam Epitaxial Growth of GaN (0001)

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Surface reconstructions during homoepitaxial growth of GaN (0001) are studied using reflection high-energy electron diffraction and scanning tunneling microscopy. In agreement with previous workers, a distinct transition from rough to smooth morphology is seen as a function of Ga to N ratio during growth. However, in contrast to some prior reports, no evidence for a 2×2 reconstruction *during* GaN growth is observed. Observations have been made using four different nitrogen plasma sources, with similar results in each case. A 2×2 structure of the surface can be obtained, but only during nitridation of the surface in the absence of a Ga flux.

1 Introduction

Significant progress has been made in the past several years in understanding the kinetics and the equilibrium surface structures formed during growth of GaN by molecular beam epitaxy (MBE) [1] [2] [3] [4] [5] [6] [7] [8] [9] [10] [11] [12] [13] [14]. An important aspect of such studies is the *reconstruction* of the surface formed during growth. As demonstrated by MBE studies of GaAs and other III-V surfaces over the past several decades, surface reconstructions as monitored by reflection high-energy electron diffraction (RHEED) are valuable real-time indicators of temperature and surface stoichiometry during growth. In addition, since the (0001) and (000$\bar{1}$) directions of GaN are inequivalent, observation of the surface reconstructions can be used to distinguish the predominant film polarity [11] [12] [13] [14] [15]. Recent studies by scanning tunneling microscopy (STM) combined with first-principles theory have produced an understanding of most of the major reconstructions for both the GaN(0001) (or Ga-face) and GaN(000$\bar{1}$) (or N-face) surfaces [11] [12] [13] [14].

Despite the above mentioned progress in understanding the surface structures of GaN, a significant discrepancy exists concerning one particular reconstruction, namely, the 2×2 structure of Ga-face material. This is an important structure since it has been cited as an indicator of optimal growth conditions during MBE [3] [4]. Growth under Ga-rich conditions in MBE yields flat, smooth surfaces, whereas growth under N-rich conditions yields rough surfaces [8] [9], and we associate the crossover point between these morphologies with the reported transition between 1×1 and 2×2 reconstructed surfaces [4]. A number of groups observe an intense 2×2 RHEED pattern during growth [3] [4], whereas other groups, including our own, do not observe any 2×2 pattern during growth [9] [11]. It is important to resolve this discrepancy, not only to understand the usefulness of the 2×2 as a potential indicator of growth quality, but also to avoid incorrect assignments of film polarity based on the surface reconstruction. Some indication of a possible solution can be found in the previous papers, in which it is noted that the type of nitrogen source used (in particular, its energetic ion content) can affect the intensity of the observed 2×2 diffraction pattern [3]. For these reasons, we have undertaken an exhaustive search, using multiple nitrogen plasma sources, for evidence of a 2×2 structure during growth in our MBE system. Although we *do* clearly observe a distinct transition from rough to smooth morphology as a function of Ga to N ratio, no evidence for a 2×2 reconstruction during growth is found. (A 2×2 structure *can* be obtained by nitridation of the surface at

elevated temperature, but this is quite distinct from any structure which could be seen during growth with both Ga and N fluxes active). Very similar results were obtained for all four of the nitrogen sources we have used, indicating that the ion content is *not* an important parameter in the results. As discussed below, we believe that the intense 2×2 structures during growth reported previously may arise from the unintentional presence of foreign atom species on the surface.

2 Experimental

These experiments are performed in a combination growth and analysis system. Samples are prepared by MBE using an RF plasma source to activate the N_2 molecules. Four different sources have been used: the first from SVT Associates, the second being this same SVTA source combined with a home built magnetic filter which effectively removed energetic ions from this source (as evidenced by an ≈ 5× reduction in ion current emitted from the source under typical growth conditions), the third a Unibulb source from EPI Technology, and the fourth being a CARS-25 source from Oxford Applied Research. Generally, the ion content and efficiency (in terms of growth rates) varied considerably amongst the various sources. The RHEED patterns presented below were obtained with the EPI source, which yields a growth rate of about 0.4 μm/hr for a N_2 pressure of about $1×10^{-5}$ Torr and plasma power level of 500 W. However, we emphasize that all of the sources used gave identical results in terms of RHEED patterns as those shown below. The Ga-face films discussed here were grown by homoepitaxy using GaN on sapphire films grown by metal organic chemical vapor deposition (MOCVD) as an atomic-scale template. The MOCVD layers were relatively flat (RMS roughness of 0.4 nm over a 20 μm × 20 μm area) indicative of Ga-polar material [16] [17] [18], with surface morphology as seen by atomic force microscopy (AFM) very similar that reported in Refs. [19] [20]. The MOCVD films were cleaned with solvents prior to being loaded into the MBE chamber. In the growth chamber, they were exposed to a nitrogen plasma at the typical growth temperature of 750°C for about 5 minutes prior to opening the Ga shutter to begin the GaN growth. Following growth, samples were transferred through a UHV gate valve into the adjoining analysis chamber, which includes STM, low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Base pressure in the analysis chamber is $6×10^{-11}$ Torr.

3 Results and Discussion

In this section we first provide some general results of the homoepitaxial growth of GaN, all of which are in good agreement with those of previous workers [8] [9] [10], and we then focus on the controversial issues surrounding the 2×2 reconstruction. Consistent with the results of Tarsa *et al.* [9], we find that homoepitaxy of GaN by plasma-assisted MBE on the MOCVD grown layers yields films with smooth, flat morphology. In some cases we find large growth spirals on the surface [13] [14]. In other cases, depending on the precise growth conditions, the surface consists of μm-size terraces separated by trenches up to 50 nm deep, as pictured in the AFM image of Figure 1. The RHEED patterns from such surfaces are streaky, indicative of flat morphology. These films grown on MOCVD material are known to be Ga-polar, based on our prior determination of film polarity [11] [12]; the MOCVD layers themselves are believed to be Ga-polar based on their growth conditions and flat morphology [16] [17] [18], and overgrowth of the MBE film apparently preserves this polarity. This preservation of the polarity is consistent with results from cross-sectional transmission electron microscopy (TEM), in which the interface between the MOCVD and MBE layers is found to be practically invisible, as shown in Figure 2.

As described by previous workers [8] [9], an abrupt transition in the growth morphology occurs when one varies the Ga to N flux ratio from Ga-rich to N-rich conditions. In the former case, the smooth flat morphology is obtained, as described above, whereas in the latter case a spotty RHEED pattern is formed indicative of a rough morphology. We note that the labels Ga-rich and N-rich are somewhat qualitative, based primarily on the RHEED results themselves, although it is generally believed that the transition between these growth regimes does in fact occur when the effective nitrogen and the gallium fluxes are equal (this is discussed in Ref. [10] for the N-face, although, as shown below, a similar smooth-to-rough transition occurs for *both* the N-face and the Ga-face).

RHEED studies of the smooth-to-rough transition obtained in our growth system are shown in Figure 3. Those patterns were obtained in the growth environment, with the sample at 700°C and with a nitrogen pressure of $1.5×10^{-5}$ Torr and plasma power level of 550 W. Figure 3(a) shows the RHEED pattern in the Ga-rich regime, displaying streaky, somewhat faint lines with no evidence of any reconstruction along either the $(11\bar{2}0)$ or the $(1\bar{1}00)$ azimuths. When the Ga flux is reduced by a sufficient amount, this pattern shows a distinct brightening, as seen in Figure 3(b). We associate this brightening of the 1×1 pattern with the desorption of any excess Ga from the surface; recent STM results indicate the presence of a double layer of Ga on the Ga-face in the Ga-rich regime [13], and the transition from Figure 3(a) to

(b) indicates that this Ga-rich phase is no longer stable under the reduced Ga flux. We do not know the exact structure of the surface which exists under the conditions of Figure 3(b), but presumably it consists of a bulk-terminated GaN bilayer (Ga-face oriented outwards) together with some possibly mobile Ga and/or N adatoms on the surface. Most significantly for the purposes of this study, we do *not* observe any 2×2 reconstruction on this surface, despite having carefully searched for such a structure with a wide range of growth parameters and using the various nitrogen sources discussed above. It is important to note that the surface obtained in Figure 3(b) is not stable; waiting a few minutes (*i.e.* allowing for some GaN growth) produces a spotty RHEED pattern, as shown in Figure 3(c). This pattern is believed to arise from kinetic roughening of the surface due to a limited Ga diffusion in the presence of excess nitrogen on the surface [9], an interpretation which is supported by recent computations indicating substantially reduced Ga diffusion rates on N-rich GaN surfaces [21].

Figure 4 shows results for the gallium flux corresponding to the transition between rough and smooth surface morphology as a function of substrate temperature. These measurements were performed by observing the RHEED pattern while changing the gallium effusion cell temperature. The critical flux at the transition point is independent of substrate temperature below 700°C and rises above this value. This is similar to the behavior reported by Hacke *et al.* for the 1×1 to 2×2 transition [4]. Based on limited measurements of the N-face, the transition flux and its temperature dependence is similar for the nitrogen and gallium faces, as shown in Figure 4. We performed a careful search for the 2×2 reconstruction by varying the gallium flux above and below this critical transition value, for substrate temperatures between 600 and 800°C. During this search we did not at any time observe the 2×2 during growth.

As described above we find precisely the same smooth-to-rough transition as a function of decreasing Ga to N flux ratio as seen by previous workers, with the only exception being that we do *not* observe a concomitant 2×2 reconstruction as found in some of the prior reports. Several groups observe intense 2×2 patterns during growth [1] [3] [4], some groups observe relatively weak patterns [2] [6] [7] [8], and other groups including ourselves do not observe any 2×2 pattern during growth [5] [9]. We consider it important to understand the origin of this 2×2 structure, since it have been cited as a indicator of optimal growth [3] [4] and it provides a potentially important signature of the film polarity [11] [15]. Thus, we undertook the exhaustive studies described above in an effort to observe the 2×2 pattern during growth, but without success. A possible explana-

tion for this result is simply that we have failed to achieve the necessary kinetic conditions necessary to obtain this reconstruction. However, this explanation seems unlikely considering both the prominence of the 2×2 in past studies and our relatively extensive search through various growth parameters. We are thus lead to another explanation, namely, that the 2×2 arrangement observed by other groups may be of *extrinsic* origin, involving the presence of unintentional atoms, such as As or Mg, during the GaN growth.

The possible presence of arsenic in GaN MBE systems is not unlikely, since many of these systems were previously used for growing GaAs. Indeed, arsenic has been demonstrated to be a significant surface contaminant in the growth of cubic GaN(001), producing a change in surface reconstruction from 4×1 to 2×2 [22] [23]. The high vapor pressure of arsenic, of course, makes it readily available in the gas phase when parts of the chamber are heated during growth. Magnesium, a commonly used dopant in GaN, may also be present in many MBE systems. In any case, the formation of the 2×2 reconstruction from some foreign atom on the GaN surface is certainly a plausible structural arrangement, since the 2×2 adatom structure is a very common reconstruction on 3-fold symmetric semiconductor faces such as Si(111) or GaAs(111). The fact that the 2×2 pattern is seen with widely varying intensity by different groups is consistent with varying amount of foreign atoms in their vacuum systems. In our own case, the MBE chamber used in our studies has never been exposed to As or Mg. Since it was constructed, it has been used only for GaN growth, using Si as a doping source. Residual gas analysis of the background gas in the growth system reveals the usual trace ($< 10^{-10}$ Torr partial pressure) amounts of H_2, H_2O, and N_2 as well as some NH_3, but all at levels far below that which could produce significant surface contamination. Furthermore, *in situ* Auger spectroscopy is routinely performed on our samples, and no trace of any foreign species is observed within the sensitivity (few % of monolayer) of this technique.

Having argued above that the 2×2 reconstruction observed *during* growth may be due to some extrinsic adsorbates, we now must emphasize that an *intrinsic* 2×2 structure can be obtained on the GaN surface under non-growth conditions. In particular, nitridation of the surface at elevated temperature produces half-order streaks along both the ($11\bar{2}0$) and the ($1\bar{1}00$) azimuths, the former of which is shown in Figure 3(d). The RHEED pattern was obtained simply by closing the Ga shutter (*i.e.* reducing the Ga flux to zero), thereby exposing the surface at 700°C to the activated nitrogen flux. A 2×2 reconstruction is obtained; similar results have been obtained for sample temperatures in the range 550–

750°C. Other groups have also reported the occurrence of a 2×2 pattern during growth interrupts [5].

An STM image of a nitrided surface displaying a 2×2 pattern is shown in Figure 5, obtained from a surface which was nitrided at 600°C. Much of the surface is disordered, consistent with the fact that the half-order diffraction lines seen in RHEED are not very sharp. However, small domains of well-ordered 2×2 reconstruction are seen throughout the image. It is important to realize that the RHEED pattern from the surface of Figure 5 was streaky (similar to Figure 3(d)), even though the surface morphology is somewhat disordered and rough. This surface obtained by nitridation is thus distinct from that obtained growth under N-rich conditions (as in Figure 3(c)). Furthermore, the surfaces obtained by nitridation are definitely rougher than a typical Ga-rich growth surface. We thus conclude that the nitridation itself produces some surface roughening, possibly as a result of surface decomposition in the absence of the excess Ga layers which are present in the Ga-rich regime.

In Figure 5, a single corrugation maximum per 2×2 cell is observed, which is consistent with a simple adatom reconstruction (but does not exclude other types of structures such as a 2×2 ordered vacancy reconstruction). From total energy calculations for the Ga-face, two different 2×2 structures are found to be energetically favorable within a certain range of the allowed Ga chemical potential: the N-adatom (H3) 2×2 and the Ga-adatom (T4) 2×2 [12] [24]. The fact that our 2×2 surface is formed by nitridation suggests that what we observe is actually the N-adatom 2×2. It should be emphasized that the calculations which indicate that Ga adatom 2×2 structures could be stable under Ga-rich conditions have focused on structures with 2×2 unit cells. Our recent STM results reveal that larger cells, 5×5 and 6×4, are needed to describe the equilibrium structures [11] [14]. The existence of stable 5×5 and 6×4 reconstructions means that the 2×2 N adatom and 2×2 Ga adatom structures are either unstable or are stable over smaller ranges of chemical potential than indicated in Ref. [12].

We have argued above that an intrinsic 2×2 arrangement is not possible during growth of GaN, although one can be obtained during growth interrupts (*i.e.* by nitriding the surface at elevated temperature). However, for completeness, we should point out that we *have* found it possible to observe the 2×2 during growth, but only under certain unusual growth conditions and only for a short amount of time. This is achieved by first closing the Ga shutter under dim, streaky, slightly Ga-rich conditions, which then results in the brightening of the 1×1 followed by the appearance of the 2×2. Meanwhile,

the Ga flux is reduced by approximately a factor of four. Upon opening the Ga shutter at the substantially reduced Ga flux, the 2×2 remains for several minutes, but the surface begins to slowly roughen, as indicated by the RHEED pattern becoming less streaky. Thus, it seems that the 2×2 may exist under extremely N-rich growth conditions, although we find that a smooth growth front is not maintained even under these conditions.

4 Conclusions

In conclusion, we have studied the RHEED patterns formed during growth of the GaN(0001) surface. We find good agreement with previous works describing a smooth-to-rough transition of the surface morphology as a function of decreasing Ga to N flux ratio [8] [9]. In addition, we observe a distinct brightening of the 1×1 RHEED pattern at this transition point, which we associate with the desorption of excess gallium from this Ga-face surface. Nitridation of the surface in the absence of a Ga flux produces a streaky 2×2 pattern. STM imaging of the resulting surface reveals a somewhat disordered and slightly rough surface, with patches of ordered 2×2 reconstruction. In contrast, growth under N-rich conditions produces a spotty RHEED pattern, indicative of three-dimensional growth resulting from kinetic roughening of the surface [9] [21]. Despite an exhaustive search, we have been unable to observe a 2×2 reconstruction *during* growth of the GaN(0001) surface, in contradiction to the results of some previous workers [1] [2] [3] [4] [6] [7] [8]. This absence of a 2×2 *during* growth either results from the particular choice of growth parameters used in our case, or, alternatively, indicates that the 2×2 reconstruction observed by the other groups is of extrinsic origin involving the presence of unintentional atoms such as As or Mg during growth.

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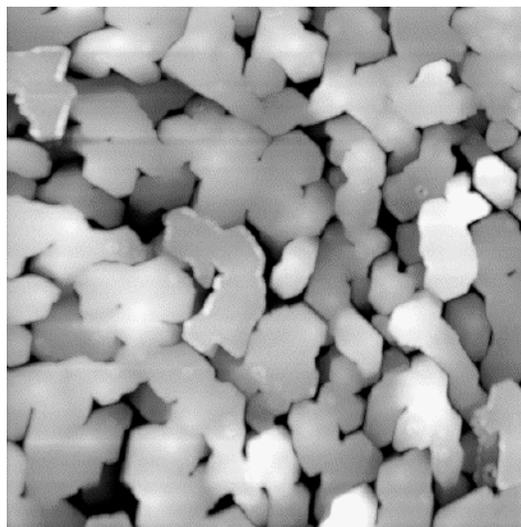[24] K Rapcewicz, MB Nardelli, J Bernholc, *Phys. Rev. B* **56** , r12725-r12728 (1997).

FIGURES

Figure 1. 5 µm × 5 µm AFM image of the surface morphology of a (0001) oriented GaN film (Ga-face). The MBE film, grown at 750°C, is about 0.7 µm thick, and was grown on top of a 1 µm thick MOCVD-grown GaN film on sapphire. The grey-scale of the image ranges from 0 (black) to 24 nm (white).

Figure 2. Cross-sectional TEM image of a GaN film, consisting of ≈160 nm of MBE-grown material (as estimated from stylus profilometry measurements) on a 1 µm thick MOCVD-grown layer. An interface between the MBE and MOCVD layers can be very faintly seen, located 190 nm below the surface; generally this interface between the layers appears to be epitaxial and continuous. The apparent large surface pit seen on the left hand side of the image is due to the specimen thinning used in TEM sample preparation.
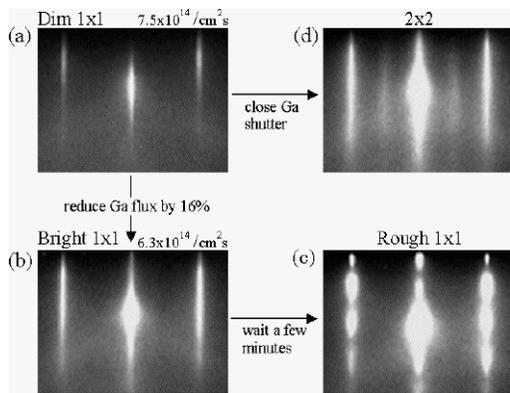
Figure 3. RHEED patterns of GaN(0001) surface with electron beam along the (11$\bar{2}$0) direction. (a) Ga flux of 7.5×10^{14} cm^{-2}s^{-1} (effusion cell temperature of 1095°C), (b) initial pattern with Ga flux of 6.3×10^{14} cm^{-2}s^{-1} (effusion cell temperature of 1085°C), (c) same flux as (b) but after waiting several minutes, and (d) same surface as (a) but after reducing Ga flux to zero.
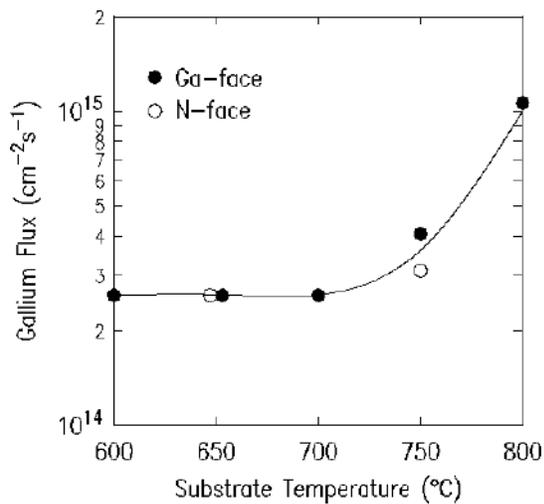

Figure 4. Critical gallium fluxes corresponding to the transition between rough and smooth surface morphology as seen by RHEED, as a function of sample temperature. The line is drawn as a guide to the eye.
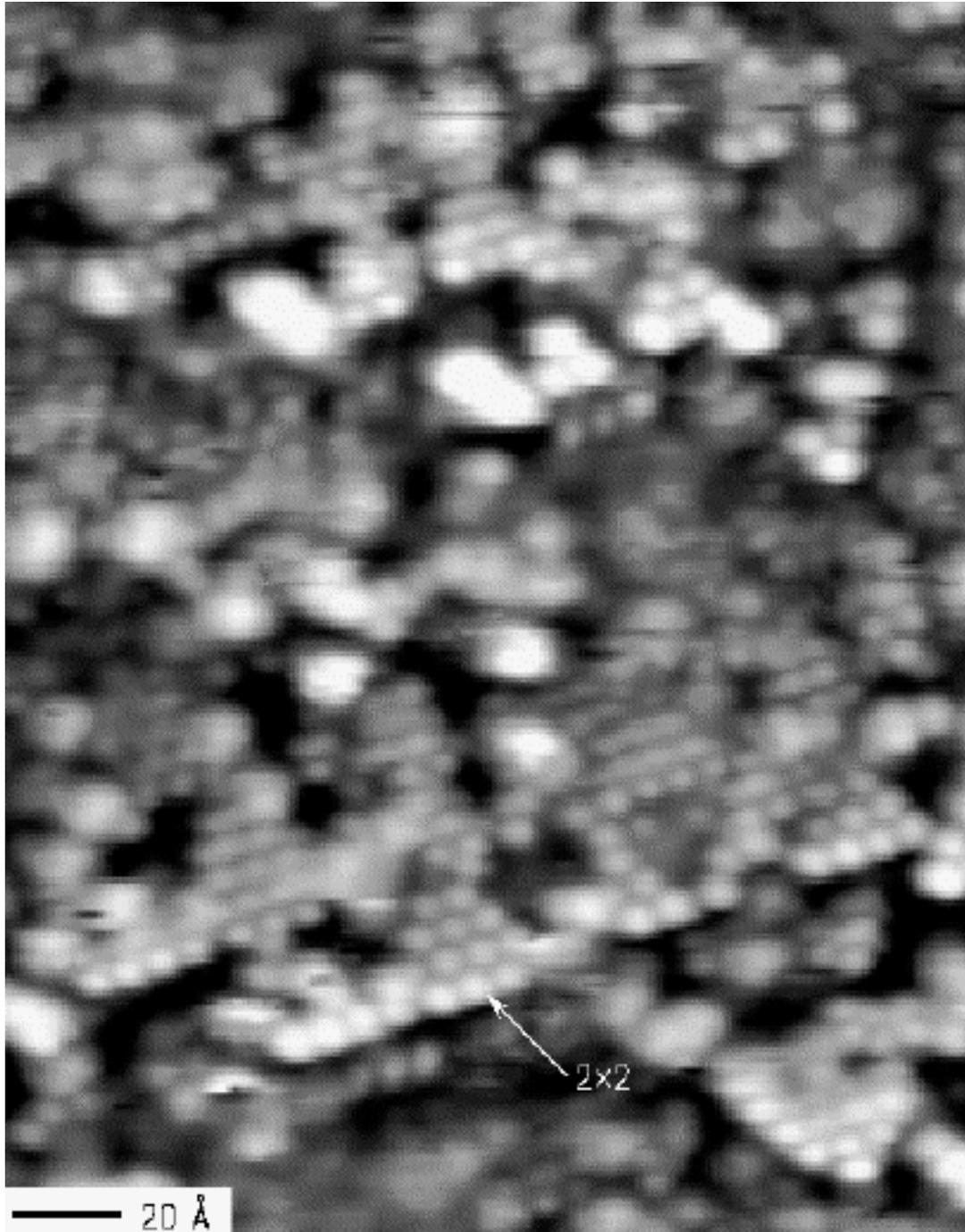
Figure 5. STM image of surface nitrided at 600°C, showing small ordered areas of 2×2 reconstruction. Sample bias = –2.0 V; tunnel current = 0.075 nA; gray scale range = 0.3 nm.