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Molecular beam epitaxy-scanning tunneling microscopy study of wurtzite GaN thin film growth

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Using scanning tunneling microscopy (STM), reflection high-energy electron diffraction (RHEED) and first-principles total-energy calculations, we have investigated the surface reconstructions occurred on the wurtzite GaN(0001). We will show that the structures of the surfaces are consistent with a simple Ga-adatom-based scheme. We will further show that the structural motifs for the conventional III-V semiconductor surfaces are insufficient and additional electron collective effects have to be considered to explain stability of the GaN surfaces.

Keywords: GaN, STM, MBE, wide-bandgap semiconductors

1. INTRODUCTION

Primary GaN surfaces have drawn much attention following the recent technological breakthrough in GaN-based short wavelength optoelectronic devices by Nakamura et al. [1]. At present, GaN-based device applications depend predominantly on heteroepitaxy of GaN thin films on dissimilar substrates. As epitaxy of any thin film is essentially a surface process, complete knowledge of the surface atomic structure of this technologically important material is critical for understanding epitaxial growth and improving device processing. From the viewpoint of surface science, a study of its surface reconstructions is also of particular interest since GaN represents an interesting case of the III-V compound semiconductors. It is made up of the atom species possessing large differences in atom-radius, electronegativity and cohesive energy, and contains both covalent and ionic bonds. It is also the only III-V which crystallizes in both hexagonal and cubic forms. The hexagonal GaN has further a freedom in thin film polarity[2], and the surface under different polarity has been shown to exhibit different properties, such as work function and reconstruction [2, 3, 4], and to influence growth processes [5-7]. A number of reconstructions, such as 1x1, 2x2, 2x3, 3x2, 3x4, 4x4, 5x5 etc., have been reported [8-13]. STM has been used to investigate some of the reconstructions and its correlation with film polarity [3, 12, 14-16]. However, the information on the atomic structures of these surfaces is still rather limited.

In this paper we report a systematic STM study of the superstructures occurred on the Ga-polar (0001) surface, which include1x1, 2x2, 4x4, 5x5, $5\sqrt{3}$x$2\sqrt{13}$ in order of increasing Ga coverage [17]. Based on the STM images and preparation conditions, we will discuss possible atomic structures of these phases. In terms of the unique properties of GaN and other wide bandgap materials, the implications of the results on surface energy minimization will be also discussed [18].

2. EXPERIMENTAL

The experiments are performed in an UHV dual-chamber MBE-STM system that has advantage for the *in-situ* study of the epitaxial films [19]. The GaN film is grown by solid source MBE, and an EPI radio-frequency N plasma source is employed to activate the N_2 molecules, and the details of preparation of the 6H-SiC substrate and Ga-rich phases of GaN(0001) surface have been reported elsewhere [17, 20, 21]. The typical surface morphology of the 6H-SiC(0001) prepared by this method is shown in Fig. 1(a). The surface consists of uniformly distributed and atomically flat terraces with an average width of ~0.4μm, separated by straight steps that extends for at least 10μm along the $[10\bar{1}0]$ direction. High resolution STM image (Fig. 1(b)) taken from the terrace reveals that the surface is very ordered and displays well-defined 3x3 superstructure.

3. RESULTS AND DISCUSSION

There is no reversed symmetry center in the hexagonal GaN, its surfaces with different species termination are not equivalent. The $(000\bar{1})$ polarity ends with a Ga-N bilayer with the N-termination while the (0001) ends with an N-Ga bilayer with the Ga-termination. Under optimized growth conditions, we find that the Ga-polarized (0001) film forms on the Si-terminated 6H-SiC(0001) substrate. The assignment is consistent with a simple consideration

of electronegativity which favor a Si-N and C-Ga interface bonding and maintain a natural epitaxial relationship between the substrate and epilayer, and is further justified by chemical wet etching test and observation of a different set of reconstructions [22]. Except for some transition phases whose domain size is rather small, there are eight defined superstructures appeared on the Ga-polar (0001) surface. With increasing Ga coverage, they are 1x1, 2x2, 4x4, 5x5, $5\sqrt{3}x2\sqrt{13}$, 10x10 and 1x1-fluid.

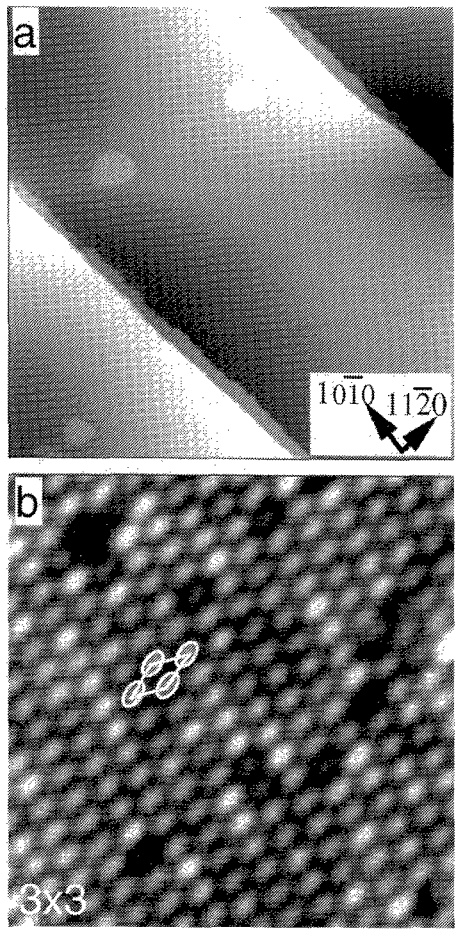

Fig.1. Filled-states STM images of the Si-terminated 6H-SiC(0001) surface prepared by the combined H_2 etching and UHV annealing under Si molecular beam. (a) Large-scale scan (0.5μmx0.5 μm). (b) Zoom-in image (350Åx350Å) from (a) displaying 3x3 reconstruction.

3.1. As-grown 1x1 surface

A (1x1) RHEED pattern usually results when the as-grown GaN sample is cooled down to room temperature. Figure 2(a) shows the morphology of the as-quenched 1x1 surface without further post-growth treatment. The surface exhibits a well-defined terrace-plus-step structure with a measured step height of 2.55Å (corresponding to the bilayer height of the hexagonal GaN along the c-axis). This kind surface often extends to approximately 0.5μm, and is achieved under a Ga-rich growth condition. Under less Ga-rich condition, the surface is usually rough and is covered by many irregular big islands and deep pitches of more than several hundreds angstroms in the lateral directions.

According to the preparation conditions and observed 1x1 RHEED pattern, this as-quenched surface should correspond to the bulk-terminated 1x1-Ga structure [17]. Despite of the smooth morphology, no long-range ordering has been observed (see Fig. 2(b)). If the surface is indeed the ideal 1x1-Ga, the highly-lying dangling bond of each Ga atom will be filled with 3/4 electron. The surface may optimize its energy by an order-disordered transition. Many dark holes (indicated by the arrows) with diameter of approximately 10Å distribute randomly on the surface, indicating an incomplete full monolayer of Ga.

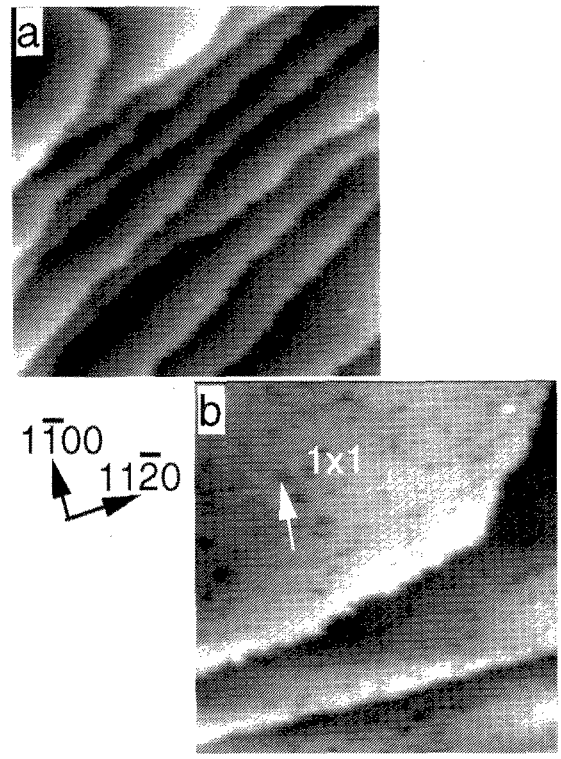

Fig.2. Filled-states STM images of the as-grown 1x1 surface of GaN(0001): (a). 1500Åx1500Å. (b) 250Åx250Å. The arrow indicates the defect on the surface.

3.2. 2x2 and 4x4 phases

The 2x2 reconstruction corresponds to a stable growth front which yields good quality thin films [9, 10, 13, 14, 23-25], and has been regarded as a basis of the (0001) polarity. A detailed discussion of the 2x2 and 4x4 based on our STM and first-principles theoretical calculation study has appeared elsewhere, and it is found that their structure is consistent with the T_4 adatom model [18]. The high resolution STM images of the 2x2 and 4x4 are shown in Fig. 3(a) and (b) respectively. The bright spots are interpreted to tunneling from the states derived from the outmost Ga adatoms of the model in Fig. 3(c) and (d). The 4x4 atomic model does not agree with the electron counting, and our theory reveals that the coulomb repulsive interaction between the charged Ga adatoms plays a key role in stabilizing the structure.

Thus, the stability of the surface cannot be understood merely by the single-particle band theory, and the 4x4 might be a Mott-Harbbard insulator.

We did observe a N-rich 2x2 phase by RHEED when the as-grown surface was bombarded by N-plasma for 20min and annealed at 500°C~600°C for 10min. When the sample is cooled down to room temperature, the 2x streak in the RHEED pattern becomes very weak. This 2x2 phase was also observed by Smith et al. [16]. In their STM image, only small 2x2 ordered domains were present. Despite a resolved 2x2 RHEED pattern, the surface is extremely rough, and we failed to image this structure. The results suggest that the N-rich 2x2 phase is difficult to access kinetically. According to the theory, the 2x2 structure with the N adatom on the H_3 site is energetically favorable under the N-rich condition[14, 18]. We, therefore, conclude that the observed N-rich 2x2 phase corresponds to such an adatom structure.

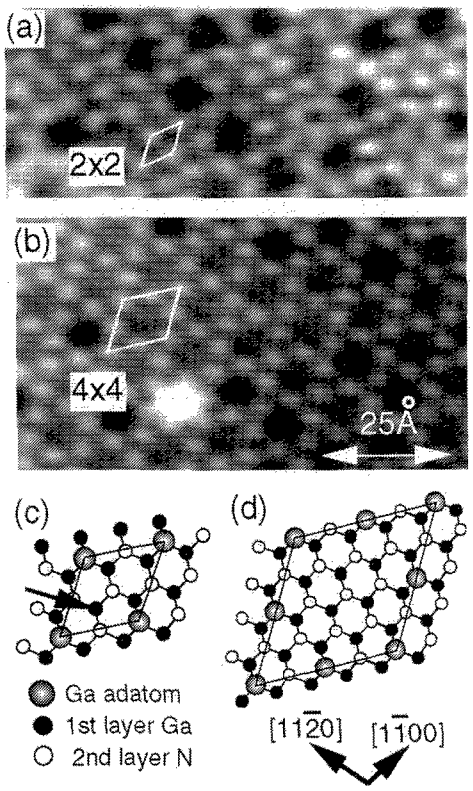

Fig.3. Filled-states STM images of GaN(0001) surface showing the (a) 2x2 and (b) 4x4 reconstructions. Their atomic model is displayed in (c) and (d) respectively. A Ga adatom (big shadowed circle) sits at the T4 site right above the second-layer N atom (open circle).

3.3. 5x5 and 5√3x2√13 phases

5x5 and 5√3x2√13 are two unique phases, and their structures exhibit a quasi-one-dimensional characteristic. Our preliminary study reveals that both surfaces are not auto-compensated, and atom relaxation due to Peierls distortion might be involved [17]. In this section, we will present some evidences to justify the case. A comprehensive theoretical and low-temperature STM study will appear elsewhere.

The 5x5 surface exhibits a very sharp streaky "5x" RHEED pattern along the [11$\bar{2}$0] azimuth while there is a strong background along the [1$\bar{1}$00] azimuth. A typical STM image is shown in Fig. 4(a), where a characteristic structure made of regular linear chains oriented along the [11$\bar{2}$0] direction is visible. The distance among the chains along the [1$\bar{1}$00] direction is 15.8Å, corresponding to $5\mathbf{a_0}$ ($\mathbf{a_0}$=3.19Å, the in-plane lattice constant of the GaN(0001) surface). A high-resolution image (Fig. 4(b)) further reveals that each chain is actually a doublet, composed of two lines with a distance of 6.38Å (2x) along the [1$\bar{1}$00] direction. The lines consist of individual bright spots. It is interesting to note that these bright spots are not evenly separated, by either 2x or 3x or 2.5x of the lattice constant with an average separation of 2.5x (~7Å). Therefore, there exists a one-dimensional disorder along the [11$\bar{2}$0] direction, and thus the 5x5 can be best described as a "5x2.5" structure [18]. If the observed spots correspond to tunneling from the Ga adatoms, some of these adatoms must occupy non-lattice site. All these observations consistently suggest that atomic relaxation has occurred.

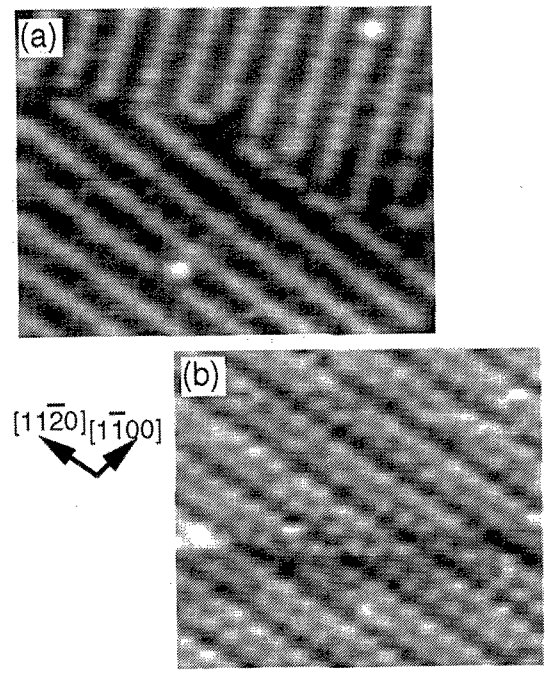

Fig.4. Filled-states STM images of 5x5 phase. (a) low-resolution image displaying the clear 5x periodicity along the [1$\bar{1}$00] direction. (b). High resolution image showing the one-dimensional disorder along [11$\bar{2}$0] direction.

It is further found that the STM images are strongly bias and tunneling current dependent. Similar result was also observed by Smith et al. [12]. In their model, the irregular distribution of the bright features is attributed to the different occupation of the Ga-adatom (at T4) and N-adatom (at H3). Experimental condition does not seem to support such a Ga-N mixing. On the other hand, under Ga-

adatom scheme, we cannot find any structure that satisfies the electron counting with fully empty Ga dangling bonds. Realizing the characteristic one-dimensional structure, we speculate that what we observed is more like a charge density wave (CDW) surface associating with a Peierls distortion due to the electron-phonon interactions. It is well-known that, in all quasi-one-dimensional configuration, metallic states are unstable to the formation of collective electronic ground states, which will open a small energy gap at the metallic Fermi level and convert to a semiconducting band structure [26]. This metal-insulator phase transition is usually accompanied with lattice relaxation (Peierls distortion). In this sense, the irregular arrangement of the bright spots might be a result of the T4 Ga-adatom relaxation, rather than different occupations of both Ga and N adatoms. If we assume that the average 2.5x separation is the periodicity of this incommensurate lattice along the $[11\bar{2}0]$ direction, the 5x (two times 2.5x) separation by RHEED will correspond to the wavelength (λCDW) of this one-dimensional CDW, i.e., $\lambda CDW = 5\,\mathbf{a_0}$. In this case, it is not necessary for the surface to satisfy the electron counting model. The surface Ga coverage is 1.16ML, compared to 1.18ML for the 4x4 phase [17].

Now we move to the $5\sqrt{3}x2\sqrt{13}$ phase. The $5\sqrt{3}x2\sqrt{13}$ is prepared by deposition of about 2ML Ga on the as-grown 1x1-Ga surface followed by annealing at 400°C for 10min, suggesting that the surface is slightly more Ga-rich than 4x4. The filled state STM image is shown in Fig. 5 and the $5\sqrt{3}x2\sqrt{13}$ superstructure is formed by the minima (dark holes) or the maxima (brightest spots). Careful study reveals that many behaviors of this surface are similar to what we observed on the 5x5 surface. First, the surface consists of chains made from regularly arranged spots and paired-spots along the $[11\bar{2}0]$ direction. Second, there exists an irregular distribution of the bright spots forming the linear chain. Finally, there is a strong dependence of the STM image on the bias voltage and tunneling current. Under the Ga-adatom scheme, these observations suggest that the $5\sqrt{3}x2\sqrt{13}$ phase also exhibits a strong CDW at room temperature. Different from the 5x5, the $5\sqrt{3}x2\sqrt{13}$ CDW is commensurate with the atomic lattice.

Despite the rotated unit cell, along the $[11\bar{2}0]$ close-packing direction the surface has a well-defined one dimensional unit cell of $25\mathbf{a_0}$. So the CDW wavelength along this direction is $25\mathbf{a_0}$. The measured contrast modulation among the spots is less than 0.3Å, indicating a weak coupling. The whole STM image is thus a superimposition of the atomic lattice and an one-dimension CDW. Due to lattice relaxation, it is not necessary for all the adatoms to take the equivalent lattice sites. So, the spot assigned to the H3 Ga adatom in our previous work [17], might correspond to the relaxed T4 adatom or CDW. Although a good understanding of the structure and CDW is still lacking, we believe that the formation of CDW on the GaN and other wide bandgap semiconductors should be a common phenomenon.

3.4. Implications

The above mentioned surface structures are

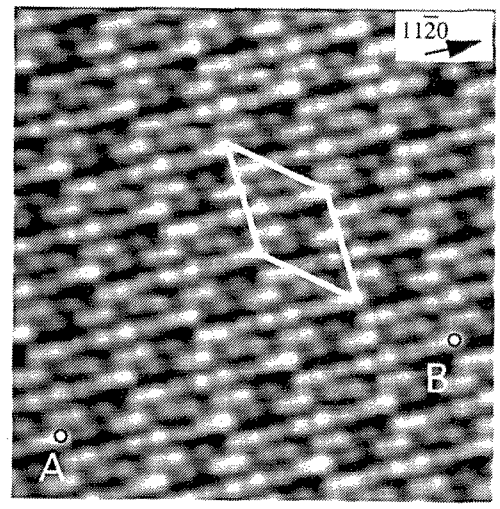

Fig.5. Filled-states STM image of $5\sqrt{3}x2\sqrt{13}$ phase with high-lighted unit cell. The A and B sites indicate the $25a_0$ periodicity along $[11\bar{2}0]$ direction.

obtained by deposition of some amount of Ga on the as-grown surface, and thus all the surfaces should be terminated with Ga atoms. Attempt to prepare an ordered N-induced structure has not been successful. The STM images showed a rough surface where it was difficult even to find a terrace. This may be attributed to a lower mobility of N atom on the Ga face of GaN [27]. Meanwhile, under N-rich growth condition, in order to reduce the surface dangling bond number the N adatoms on the growing surface may try to dimerize. However, the very strong N-N bond with a cohesive energy of 5eV makes these N adatoms thermodynamically unstable against evaporation as N_2 [28]. If the dimer forms, it will be a precursor state of the N_2 molecule with very small activation energy. Despite a global N-rich growth environment and some stable N-rich structure as theoretically predicted, there would exist a local deficiency in N atoms on the surface, which eliminates the pathway to form these structures. In addition, formation of N-dimers is not expected to be energetically favorable process due to the very short N-N bonding length (1.8 Å) of the N_2 molecule compared to the in-plane lattice constant of 3.2 Å of the GaN. Dimerization will cause significant bond distortion and should be very energy costly. To increase the N corporation and reduce the N-vacancies commonly observed in the nitrides, one may need to use N-rich condition. However, as discussed above, it is difficult to occur in the case of the MBE growth. As a result, use of surfactants to manipulate growth kinetic process or alter surface energy may become more promising as suggested both theoretically and experimentally [28, 29]. This fact may also explain why the MBE is less successful for nitride film growth than MOCVD where the H might play an important "surfactant" role.

On the other hand, with a stable growing front surface, it is not surprising to observe a smooth surface morphology with larger Ga atom diffusivity under Ga-rich condition [24, 27, 30]. Under even very Ga-rich condition, a stable and atomically flat

Ga-fluid, which consists of 3 to 4 layers Ga, can form [15, 17]. This phase is floating on the growing front so that the surface could survive from roughening. This point is radically different from what occurred on the conventional III-V surfaces. For example, in the case of the GaAs surface, excess As flux is always necessary to achieve a smooth morphology and thus a quality thin film. Growth under excess Ga may lead to Ga-clustering and formation of Ga-droplets, which drives the growth to non-stoichiometric deposition as well as surface roughening. Therefore, our present study clearly shows that, due to the very unique surface property of the GaN, the kinetic process in its MBE growth is rather different from that for the traditional III-Vs.

As for the atomic structure of the surfaces, as we discussed above, the N-dimer does not look like a candidate structural motif. We don't observe STM images that seem to support formation of the Ga-dimer either. The reason may arise from the fact that the Ga-Ga nearest neighboring distance in the bulk Ga is very close to the bonding length in a Ga-dimer. The energy gain expected from the dimer formation should be small. And at the same time, on the (0001) surface of GaN, which is equivalent with the (111) cubic surface in structure, the 1x1 Ga dangling bonds are parallel to the surface normal so that the steric restriction for dimerization is more significant than that on the cubic (001) surface. For these reasons, we assign the main features observed on the STM images to be tunneling from the Ga-adatoms. Under this scheme, one can easily find that the number of the surface reconstructions that satisfy the electron counting model is very limited. If it is the case, for the structures to which the electronic counting is not applicable, the surface Ga atom/adatom dangling bonds will be partially occupied. Therefore, to understand the stable structures observed, one has to consider some other mechanism in addition to those well-established for the conventional III-V surfaces. As a result, the collective electronic effects are found to come into play, as discussed in the cases of the 5x5 and $5\sqrt{3}x2\sqrt{13}$ phases. Details will be reported elsewhere [31].

4. SUMMARY

A series of phases belonging to the GaN (0001) surface, such as 2x2, 4x4, 5x5 and $5\sqrt{3}x2\sqrt{13}$, have been documented and discussed with high resolution STM images. The results are summarized as follows:

(1) On the Si-terminated (0001) and C-terminated $(000\bar{1})$ substrates of the 6H-SiC, the GaN/AlN epitaxial films take the (0001) and $(000\bar{1})$ surface polarities, respectively.

(2) All ordered surface phases are found to be Ga-rich and their structures can be understood by the Ga-adatom scheme. No stable N-rich phase has been observed. Theoretically predicted N-rich phases might be difficult to realize kinetically.

(3) Auto-compensation, one of the guiding rules for conventional III-V compound semiconductor surface reconstructions, may not be strictly satisfied on the GaN surface. In order to describe energy minimization process of the GaN and other wide bandgap semiconductor surfaces, other mechanisms, such as the collective electronic effects, should be considered.

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