Spectroscopic theoretical study of the atomic reconstruction of GaN $(10\bar{1}0)$

Cecilia Noguez
Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, México Distrito Federal 01000, Mexico
(Received 1 June 1998)

We study the atomic reconstruction of the GaN $(10\bar{1}0)$ surface calculating electron-energy-loss (EEL) spectra and optical properties. The unreconstructed and three different atomic reconstructions are considered. We show that the optical properties are very sensitive to the atomic reconstruction. Results are presented and discussed in terms of differential EEL spectra that will allow to compare with experiments. Experiments are proposed to unambiguously determine the surface-atomic reconstruction of this important surface. [S0163-1829(98)01844-X]

The study of the optical and electronic properties of GaN has gained importance due to its potential application in near-ultraviolet optoelectronic devices.[1,2] GaN has a direct gap of 3.4 eV and at ambient conditions it crystallizes in the wurtzite structure, or in some cases, like thin films of GaN, the zinc-blende structure is obtained.[3] The bulk-electronic and optical properties have been known for some time now. Bloom *et al.*[4] measured the reflectivity and calculated the band structure and reflectivity using an empirical pseudopotential method. It is important to characterize the properties of GaN-based materials, in particular the electronic and optical properties of films. The precise structure of these GaN films and their electronic properties are not known. One type of defect appears to be stacking mismatch boundary in which the local atomic structure could be similar to that expected on the $(10\bar{1}0)$ GaN surface. Although there are some theoretical studies, there is not a consensus of the $(10\bar{1}0)$ GaN atomic reconstruction.

It was not until very recently that systematic studies of the surface reconstruction of GaN have been done.[5–7] Jaffe *et al.*[5] studied the anomalous surface relaxation of GaN $(10\bar{1}0)$ and (110), using an *ab initio* Hartree-Fock method (CRYSTAL92). Total-energy calculations were done using linear combinations of Gaussian orbitals to construct a localized atomic basis. These calculations were performed using a six-layer slab. The total energy was minimized within approximately 1 meV/atom. They found a relaxation characterized mainly by a surface bond-length contraction of $\Delta l_0 \sim 7\%$, and very small surface bond rotations of $\beta \sim 1.45°$ (see Fig. 1).

Northrup and Neugebauer[6] also performed *ab initio* calculations within the local-density approximation. They employed the Perdew and Zunger exchange and correlation energy function.[8] Forces and total energies were determined using an optimized plane-wave code similar to that described by Stumpf and Scheffler.[9] The plane-wave cutoff was 60 Ry and four **k** points were used to sample the two-dimensional Brillouin zone. In this calculation, a slab of eight layers was used. The bond contraction was of $\Delta l_0 \sim 6\%$ with respect to that calculated for the bulk, and similar to that found by Jaffe *et al.*[5] The vertical displacements were found to correspond to a bond rotation of $\beta \sim 6°$.

Surface reconstruction has also been calculated by Fillippeti *et al.*,[7] using an *ab initio* method that uses a plane-wave basis set and ultrasoft pseudopotentials. The cutoff energy was set at 25 Ry. The slab contained eight layers and relaxation forces of up to 1 mRy/a.u. were allowed. Energy calculations were done using a grid of **k** points. The surface reconstruction yielded a bond contraction of $\Delta l_0 \sim 6\%$ like previous papers,[5,6] and a surface bond rotation of $\beta \sim 11.5°$. They also found that the first and second layer atoms have larger vertical displacements.

The three atomic reconstruction calculations described above were obtained from quite different methods. We can observed that in all of these theoretical calculations obtained similar bond contractions of the surface atoms $\Delta l_0 \sim 6\%$. On the other hand, vertical displacements on each calculation are very different and lead to quite different bond rotations β. Additionally, none of these theoretical studies provides a way for comparing with experiments, and it is impossible to elucidate which of these is closer to reality. Not only is it

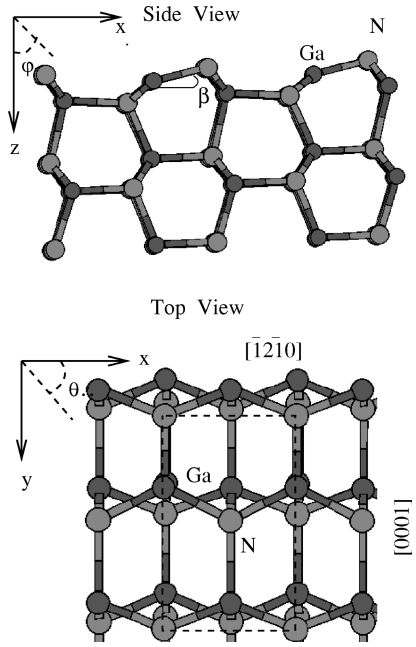

FIG. 1. Side and top views of the GaN $(10\bar{1}0)$ surface. The surface unit cell is shown in dashed line.

TABLE I. Tight-binding interaction parameters for GaN.

V_{ss}	-2.11		
V_{sp}	3.54	V_{ps}	-2.06
V_{pp_σ}	3.95	V_{pp_π}	-1.54
V_{s*p}	1.08	V_{ps*}	-2.94

important to characterize theoretically the surface atomic reconstruction, but also to perform calculations that provide a way to compare with experiments. Only in this way would it be possible to elucidate the atomic reconstruction of this and other important surfaces.

In this paper, we present a realistic microscopic theoretical study of the optical properties of the three different reported atomic reconstructions,[5–7] discussed above. For each reconstruction, as well as for the unreconstructed surface, the surface dielectric response is calculated. Then, the electron-energy-loss (EEL) spectra are calculated using a recent theory for anisotropic systems.[10] Results are analyzed using a differential technique that shows the sensitivity of the optical properties to different bond rotations β. The results presented here will allow to make a detailed comparison with future EEL and optical experiments.

The GaN $(10\bar{1}0)$ surfaces were modeled using a slab of eight bilayers with 32 atoms in total, yielding a free-reconstructed surface on each face of the slab. The thickness of the slab is large enough to decouple the surface states at the top and bottom surfaces of the slab. Periodic boundary conditions were employed parallel to the surface of the slab to effectively model a two-dimensional crystal system. The x axis on the surface plane corresponds to the $[\bar{1}2\bar{1}0]$ crystalline direction, since the y axis corresponds to $[0001]$, as is shown in Fig. 1. We performed the calculations for four different sets of atomic coordinates, corresponding to (i) those of the free-reconstructed surface with no bond rotation and no bond-length contraction, and the atomic coordinates of the reconstructed surfaces reported by (ii) Jaffe *et al.*,[5] (iii) Northrup and Neugebauer,[6] and (iv) Fillipetii *et al.*[7]

To calculate the optical properties of the system, we generate the electronic-level structure of the slab using a well known parametrized tight-binding approach.[11] This method employs a sp^3s^* atomiclike basis that provides a good description of the conduction band of semiconductors. The parameters for the GaN crystal with a wurtzite unit cell were fitted to reproduce the bulk band structure reported previously.[4,12,13] The prodedure to fit the parameters was similar to that employed by Volg, Hjalmarson, and Dow.[14] The values of the orbital energies for N are $\epsilon_s = -10.7806$ eV, $\epsilon_p = 0.8970$ eV, and $\epsilon_{s*} = 11.5150$ eV, and for Ga are $\epsilon_s = -0.5494$ eV, $\epsilon_p = 5.6018$ eV, and $\epsilon_{s*} = 9.1850$ eV. The parameters of tight-binding interactions are listed in Table I. For the surface, we interpolated the parameters using Harrison's rule of $1/d^2$, where d is the bond length of any two first-neighbor atoms.

The optical properties of the system are determined by its dielectric function $\epsilon^{ii}(\omega)$, where the superscripts i denote the diagonal components of the dielectric tensor. We calculate the imaginary part of the average polarizability, which is related to the transition probability between eigenstates induced by an external radiation field. Only two additional parameters to those of the tight-binding Hamiltonian were needed in order to reproduce the bulk dielectric function. These parameters are the so-called intra-atomic sp and s^*p dipoles, with best-fitted values of 0.0634 and 0.565 Å, respectively. Then, the real part is calculated using the Kramers-Kronig transforms. As a test, we first calculated the electronic and optical properties of bulk GaN. The results were reported and discussed elsewhere.[10] In general, the bulk dielectric function shows that electron transitions start at about 3.5 eV, and the anisotropy of the dielectric response is seen at energies above 4.2 eV. These results were in agreement with experiments and previous calculations.[10]

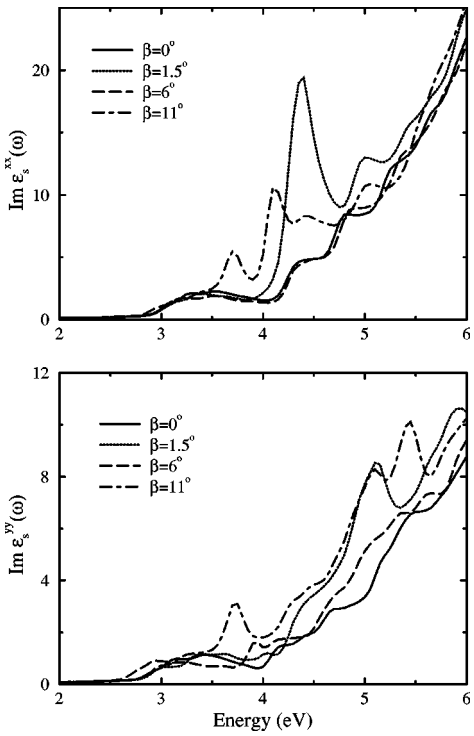

FIG. 2. xx and yy components of imaginary part of the calculated surface-dielectric tensor as a function of energy in eV.

For each set of coordinates, we calculated the imaginary part of the average slab polarizability. For this particular surface, we employed 4900 points distributed homogeneously on the irreducible surface Brillouin zone. The imaginary part of the surface dielectric function is obtained considering a thickness of the surface layer of about 4.5 Å, and subtracting the bulk dielectric function to the slab dielectric function. The details of the calculation are fully explained in Ref. 15.

In Fig. 2 we show the xx and yy components of the imaginary part of the calculated surface dielectric function $\mathrm{Im}\epsilon_s^{ii}(\omega)$. The solid line corresponds to the unreconstructed surface, where $\beta = 0°$ and $\Delta l_0 = 0$, and the the dotted, dashed and dot-dashed lines correspond to the reconstructed models of Refs. 5, 6, and 7, respectively. For all the spectra, we observe that electron transitions start at 2.8 eV for light polarized along the x direction, while for y they start at 2.7 eV. The large sensitivity of the dielectric properties of this surface to small differences of the atomic reconstruction is evident from the figure. In general, we observe that the dielectric response along x is more intense than along y for all energies. The latter means that the surface response is anisotropic for energies below the bulk gap. Thus, any anisotropy

observed experimentally at energies below 4.2 eV are associated to the surface.

From our calculations, we observed that the structure below the bulk gap is mainly due to transitions from bulk to surface states. These surface states are in the bulk gap at an energy of 2.7 eV, from the top of the bulk valence band, and show small dispersion along the irreducible surface Brillouin zone. These surface states are due to the dangling bonds and backbonds of the Ga atoms in the first layer of the surface. The structure of $\mathrm{Im}\epsilon_s^{ii}(\omega)$ from 3.7 to 4.5 eV has also contributions from surface to surface electronic-state transitions, being most intense for the reconstruction with the smallest bond rotation.[5] It is important to notice that $\mathrm{Im}\epsilon_s^{xx}(\omega)$ shows two peaks at 3.7 and 4.1 eV, for the reconstruction with the largest bond rotation $\beta=11°$.[7] There is also a peak at 3.7 for $\mathrm{Im}\epsilon_s^{yy}(\omega)$, for the same reconstruction ($\beta=11°$). These peaks are not observed in the spectra associated to the reconstructions with smaller bond rotations ($\beta=0°$, $\beta=1.5°$, and $\beta=6°$). The particular optical signature associated to each reconstruction is possible to observe experimentally. In the following, we will show results of the calculated EEL spectra for each reconstruction. We will discuss the sensitivity of the spectra to small structural differences.

The energy loss by an electron, within the single-scattering semiclassical theory, can be expressed as

$$W=\int_0^\infty d\omega \int d^2q\hbar\omega\, P(\mathbf{q},\omega), \tag{1}$$

where $P(\mathbf{q},\omega)$ is the electron-scattering probability that an electron loses a quantum of energy $\hbar\omega$ and transfers a momentum $\hbar\mathbf{q}$ in the direction of the surface plane. This probability can be written as the product of a function $A(\mathbf{q},\omega)$ which depends on the lost energy and the transferred momentum of the electron, and the imaginary part of the surface-response function $g(\mathbf{q},\omega)$. The surface-response function of an anisotropic surface on an anisotropic substrate has been recently reported in Ref. 10, where details can be found.

To perform a systematic study of the surface, we propose to analyze EEL spectra experiments using a differential spectroscopic technique. This technique consists of comparing the scattering probability for electron beams impinging at the surface at a fixed angle φ and different angles θ with the scattering probability of an electron beam impinging at the same angle φ but at $\theta=0°$ (see Fig. 1). This is $\Delta P_\theta(q,\omega)=[P_{0°}(q,\omega)-P_\theta(q,\omega)]/P_{0°}(q,\omega)$.

In Fig. 3 we show $\Delta P_\theta(q,\omega)$ for electrons impinging at an angle of $\varphi=45°$, respective to the surface normal. We only consider the specular case. We show the differential spectra for three different plane polarizations, $\theta=30°$, $60°$, and $90°$. As is expected, ΔP_θ increases when the contribution of y component also increases, showing a clear anisotropic behavior of the system at all energies. The spectra correspond to (a) unreconstructed surface with $\beta=0°$, reconstructed surface with (b) $\beta=1.5°$,[5] (c) $\beta=6°$,[6] and (d) $\beta=11°$.[7]

In general, we observe that all the spectra show a peak at about 2.7 eV, where electronic transitions start and belong to the surface reconstruction. This peak is accompanied with a change of sign of the spectra up to about 3.7 eV. At this later energy, contributions from the substrate or bulk are expected. From 2.7 to 3.7 eV, Fig. 3(a) shows an intense peak at about 3.2 eV, while for the reconstruction with $\beta=1.5°$ [Fig. 3(b)] this peak is redshifted. Also, for this reconstruction a structure at about 4.5 eV is observed that comes from

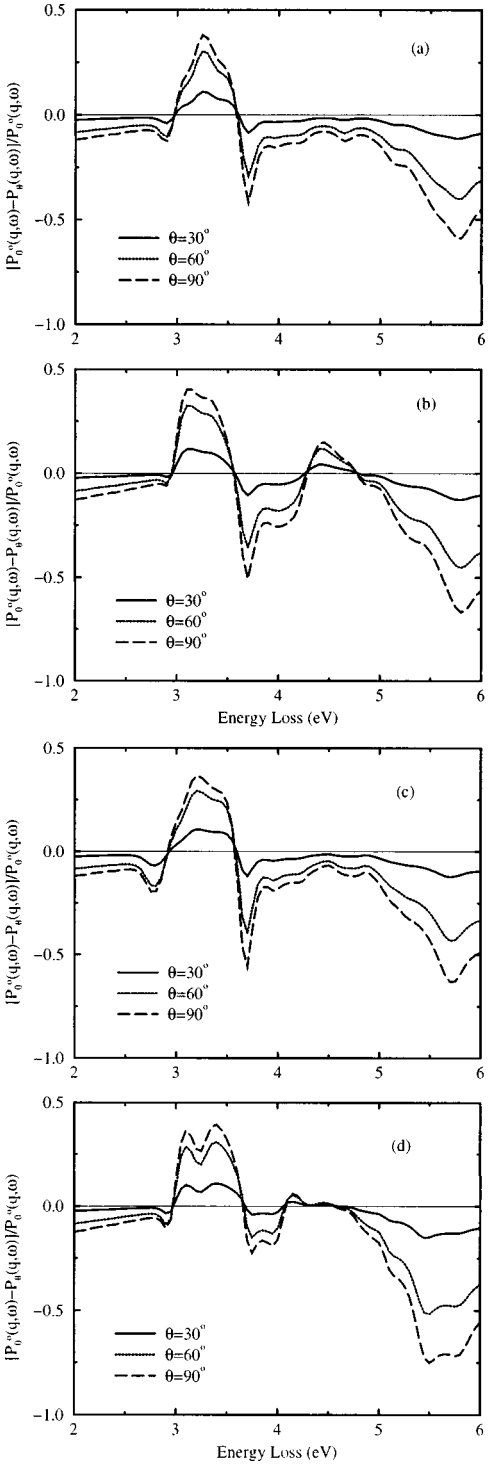

FIG. 3. ΔP_θ as a function of the energy loss, between electrons impinging at an angle of 45° respective to the surface plane. Differences between $\theta=0°$ and three different angles $\theta=30°$, $60°$, and $90°$, are plotted. The spectra correspond to (a) $\beta=0°$, (b) $\beta=1.5°$, (c) $\beta=6°$, and (d) $\beta=11°$.

the intense peak at the same energy shown in $\mathrm{Im}\epsilon_s^{xx}(\omega)$. Notice that this structure is only observed for this particular reconstruction.

On the other hand, ΔP_θ for the reconstruction with $\beta = 6°$ (Ref. 6) [Fig. 3(c)] shows a similar behavior as the ideal spectra. However, for the reconstruction with the greatest bond rotation $\beta = 11°$,[7] additional structures are found. In Fig. 3(d), we observe that the structure between 2.7 and 3.7 eV, as well as the negative peak at 3.8 eV, are split into two peaks. The second peak at about 3.4 eV and the negative peak at 3.8 eV are associated to the structure found about the same energy in the x and y components of $\mathrm{Im}\epsilon_s^{ii}(\omega)$. As mentioned before, this structure was found only for this particular reconstruction. In the same way, the peak at 4.1 eV in $\mathrm{Im}\epsilon_s^{xx}(\omega)$ gives rise to the positive structure at the same energy in Fig. 3(d). From 4.5 eV the spectra for all the reconstructions show a similar behavior, except for Fig. 3(d) with the largest bond rotation, where an additional negative structure at 5.5 eV is observed. This structure is related to the peak in $\mathrm{Im}\epsilon_s^{yy}(\omega)$ at the same energy.

In this paper we demonstrated the sensitivity of optical and EEL spectra to small differences of the atomic reconstruction of the GaN $(10\bar{1}0)$ surface. We did a systematic study for three different atomic reconstructions and for the unreconstructed surface. The results are presented in terms of the surface dielectric function and of the differential scattering probability or differential EEL spectroscopy. It is shown that this later enhances the surface and anisotropy effects. The results are discussed for each reconstruction, in terms of electron transitions involving surface and bulk electronic states.

This work has been supported in part by Grants No. CONACyT-3035PE and No. UNAM-DGAPA-IN104297.

[1] J.H. Edgar, J. Mater. Res. **7**, 235 (1992).
[2] H. Morkoc, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).
[3] G. Martin, S. Strite, J. Thornton, and H. Morkoc, Appl. Phys. Lett. **58**, 2375 (1991).
[4] S. Bloom, G. Harbeke, E. Meiner, and I.B. Ortenburger, Phys. Status Solidi B **66**, 161 (1974).
[5] J.E. Jaffe, R. Pandey, and P. Zapol, Phys. Rev. B **53**, R4209 (1996).
[6] J.E. Northrup and J. Neugebauer, Phys. Rev. B **53**, R10 477 (1996).
[7] A. Filippetti, M. Menchi, A. Bosin, and G. Cappellini, in *III-V Nitrides*, edited by F. A. Ponce, T. D. Moustakas, I. Akasaki, and B. A. Monemar, MRS Symposia Proceedings No. 449 (Materials Research Society, Pittsburgh, 1997), p. 953.
[8] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[9] R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994).
[10] R. Esquivel-Sirvent and C. Noguez, Phys. Rev. B **58**, 7367 (1998).
[11] R. Del Sole, in *Electromagnetic Waves: Recent Developments in Research, Vol. 2: Photonic Probes of Surfaces*, edited by P. Halevi (Elsevier, Amsterdam, 1995), p. 131, and references therein.
[12] M. Palummo, C. M. Bertoni, L. Reining, and F. Finocchi, Physica B **185**, 404 (1993).
[13] K. Miwa and A. Fukumoto, Phys. Rev. B **48**, 7897 (1993).
[14] P. Vogl, H.P. Hjalmarson, and J.D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).
[15] C. Noguez and S.E. Ulloa, Phys. Rev. B **53**, 13 138 (1996), and references therein.