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Origin of optical anisotropies of nonpolar GaN surfaces

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We investigate the origin of optical anisotropies of the nonpolar GaN (110) and $(10\bar{1}0)$ surfaces. Using semiempirical tight-binding calculations, we analyze in detail the main optical signature of each surface. The origin of the optical spectra is discussed in terms of the main surface electronic states and of the specific surface atomic rearrangement. Results of the surface dielectric function, and reflectance anisotropy spectra, are presented.

Nitride semiconductors are visible light emitters and detectors that have gained importance due to their real and potential applications. Actually, there exists a tremendous research activity of nitride semiconductor compounds motivated, of course, by expectations in the optoelectronic industry.[1] This research covers topics from growth and characterization to device processing. Among nitrides, GaN has been extensively studied due to its physical properties: a wide-band gap, two crystalline equilibrium phases (wurtzite and zinc blende) each one with a direct electronic gap (3.2 and 3.5 eV), efficient electron-hole recombination coefficients, high thermal conductivities, and hardness.

Although much theoretical work has been done to determine electronic and optical properties of both bulk phases of GaN,[2] only a few attempts have been made to characterize their surfaces.[3–7] Furthermore, most of these theoretical studies did not provide a way of comparing with experiments, and it is impossible to elucidate which atomic models are closer to reality. Until now, there is no consensus on the physical characteristics of the main GaN surfaces. However, the continuous development of nitride growth and nanostructure technologies makes evident the need for a detailed theoretical understanding of their surfaces. For example, the study of optical properties of thin films has been stimulated by applications that cover a wide spectrum of systems and tools, ranging from lasers to the characterization of film growth. Within this context, characterizations using optical spectroscopies in semiconductor surfaces have become extremely useful due to their nondestructive character and *in situ* potentiality.[8] Unfortunately, this tool has not been used to understand GaN surfaces.

In this paper we present a detailed study of the optical properties of nonpolar GaN surfaces. The main features of the optical spectra we obtain are analyzed in terms of transitions between electronic states that are inherent to each surface atomic rearrangement. This analysis allows us to identify the surface electronic states and their role in the physical properties of each surface.

To calculate the optical properties of GaN surfaces, we performed calculations using a well, known tight-binding procedure.[9] First, the electronic-level structure of a slab, corresponding to each surface, is generated using an sp^3s^* atomiclike basis that provides a good description of valence and conduction bands of semiconductors. The parameters used here for GaN were reported previously for wurtzite[6] and cubic[10] phases. Once the electronic-level structure of each slab is obtained, we calculate the average slab dielectric function $\epsilon_{\text{slab}}(\omega)$. We first obtain the imaginary part of the average slab polarizability, in terms of the transition probability between eigenstates induced by an external radiation field. For each surface, we take an average over 4900 **k** points distributed homogeneously in the irreducible two-dimensional Brillouin zone (2DBZ). The real part of the average polarizability is calculated using the Kramers-Kronig relations. The surface dielectric function is obtained by considering a surface thickness of about two atomic layers, and then subtracting the bulk dielectric function to $\epsilon_{\text{slab}}(\omega)$. The details are fully explained in Ref. 11.

We also performed calculations of the optical properties using a first-principles method based on density-functional theory (DFT).[7,14] As is well known, the DFT does not accurately describe conduction states. In general, we found the same physical behavior of the DFT results and the calculations reported and discussed in this paper. However, the energies at which the main optical transitions occur do not correspond to the real ones. In this regard, the tight-binding method, used here, gives better results.

The surfaces were modeled using a slab, yielding a free relaxed surface on each face of the slab. Periodic boundary conditions were employed parallel to the surface. The wurtzite $(10\bar{1}0)$ relaxed surface has a slab of 16 atomic layers, with 32 atoms in total. The zinc-blende (110) relaxed surface has a slab of 12 atomic layers, with 24 atoms in total. In both cases, the thickness of the slab is large enough to decouple the surface states at the top and bottom of the slab.

For the $(10\bar{1}0)$ surface, the X and Y axes on the surface plane correspond to the $[\bar{1}2\bar{1}0]$ and $[0001]$ crystalline directions, as shown in Fig. 1. The atomic coordinates of the relaxed surfaces were taken from those reported by Northrup and Neugebauer.[4] The surface atomic rearrangement of the $(10\bar{1}0)$ surface presents a bond rotation of the surface atoms of about $\omega = 6°$, and a length contraction of the bond between surface atoms of $\Delta d = 6\%$, with respect to the bulk bond length. On the other hand, for the (110) surface, the X and Y axes on the surface plane correspond to the $[\bar{1}10]$ and $[001]$ crystalline directions, as shown in Fig. 1. An atomic relaxation similar to the $(10\bar{1}0)$ surface was found for the (110) surface. In this case, $\Delta d = 5\%$ and $\omega = 14°$, as reported

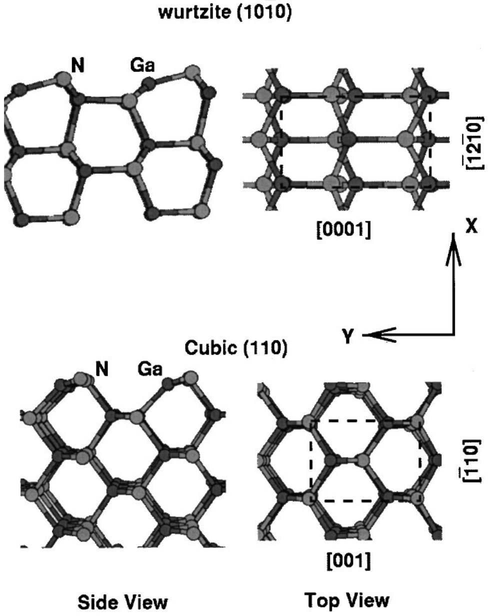

FIG. 1. Side and top views of (a) $(10\bar{1}0)$, and (b) (110).

by Filippetii *et al.*[5] Similar atomic rearrangements have also been reported by other groups, where the physical origin of the surface relaxation was fully explained.[12,13]

In Fig. 2, we show the calculated electronic band structure along high-symmetry directions in the irreducible 2DBZ. On the right-hand side panels, we show the total and projected electronic density of states (DOS) in the first, second, and third layers. For the $(10\bar{1}0)$ case we observed two electronic bands C_3 (cation) and A_5 (anion) within the projected bulk band gap. These bands are surface states that belong to dangling bonds located in the Ga and N atoms at the surface. C_3 is an empty surface band corresponding to the Ga atoms in the first layer. The energy of the C_3 band is about 2.5 eV from the top of the valence band, and it has a very small dispersion along the 2DBZ, which gives rise to a large contribution to the DOS within the projected bulk gap. It was previously reported[6] that the position of the C_3 band is quite susceptible to the atomic position of the surface atoms. On the other hand, A_5 is an occupied electronic band located in the N atoms in the first layer. A_5 also shows a small dispersion in the 2DBZ, that also gives rise to a large contribution to the DOS. The A_5 band is located at an energy of about 1.5 eV below the top of the bulk valence band between the X and M points. When the band approaches the Γ point, this band disappears inside the projected bulk valence band. In general, we found good agreement of our results with those previously reported.[4]

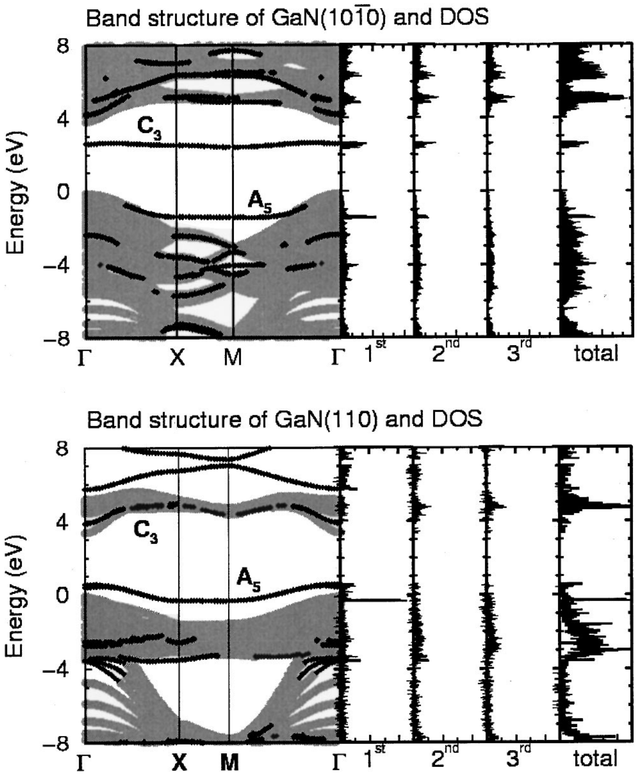

FIG. 2. Electronic band structure and the total and projected DOS in the first, second, and third atomic layers. Surface states are shown by black dots, and projected bulk states by gray dots.

Northrup and Neugebauer[4] performed DFT calculations, where for the $(10\bar{1}0)$ surface they found an occupied electronic band due to the dangling bonds of the N atoms located in the first layer. These authors found that this band is at an energy of about 0.1 eV below the top of the bulk valence band, and shows a very small dispersion when it approaches the M point. They also reported an empty surface band due to the dangling bonds of the Ga atoms in the first layer. They found that the location of this band is inside the projected conduction band at the Γ point, shows a large dispersion from Γ to halfway to M, and then becomes almost flat at the M point. In our calculation, C_3 is in the middle of the bulk gap. The differences in energy between our calculations and their results, especially for the empty states, are expected, since they used a different formalism than the one we employed here. Within DFT calculations, quasiparticle corrections must be done to remedy its deficiency. It has been found for bulk electronic states that these corrections should consist of an almost rigid shift of energy of the unoccupied electronic states. However, for unoccupied electronic states inherent to the surface, this shift could not be of the same magnitude of energy as in the bulk. For example, in the case of the Si(111)-2×1 surface,[17] the amount of energy shift for the unoccupied surface states is 1/3 of the shift for the bulk states. Therefore, it is difficult to compare our results directly with those reported by Northrup and Neugebauer,[4] where no corrections to the DFT calculations were made. Another source of discrepancy may be the tight-binding parameters used here, which were obtained for the bulk and then extrapolated for the surface, using Harrison's rule. Furthermore, due to effects of additional orbital confinement on the surface, we should expect an extra modification in the surface of these parameters.[14] However, we have to take into account that the simultaneous calculation of consistent atomic positions and band-structure parameters in this kind of tight-binding calculation, is quite a difficult task.

In Fig. 2 we observe for the (110) surface two electronic bands also labeled C_3 and A_5. These bands are also due to the dangling bonds located at the first layer Ga and N atoms, respectively. In this case, the empty band C_3 is at the edge of the bottom of the bulk conduction band, and shows a dispersion of 1 eV in the 2DBZ, which does not contribute significantly to the DOS. The occupied surface band A_5 located 0.5 eV above the bulk valence band at the Γ point, shows an energy dispersion of 0.7 eV from Γ to the X point, and is flat between the high-symmetry points X and M. This fact gives rise to a large contribution to the DOS, showing that A_5 is totally located in the N atoms in the first layer. Again, we have found a very good agreement of our results with those reported by Grossner *et al.*,[13] where the C_3 and A_5 surface electronic bands of the (110) surface have also been found. They reported that the physical origin of these bands arises in the dangling bonds of the first-layer Ga and N atoms. In this case, differences in energy between our calculations and their results were also found. Since Grossner *et al.*[13] also performed DFT calculations, those discrepancies are expected for the same reasons discussed above. Furthermore, it may be that additional orbital confinement effects of the electrons belonging to surface become important for those atoms with low atomic numbers, where valence electrons are close to the nucleus, such as those electrons in N atoms. For example, for the C(111)-2×1 surface, an additional orbital confinement of about -2.3 eV was found for the orbital, pointing out the surface of the C atoms at the first layer.[11] In the case of the GaN(110) surface this effect may be responsible for the discrepancy in energy of 0.5 eV of the A_5 band between our calculations and the DFT results found in Ref. 13. However, the reported behavior and dispersion of the surface bands in Ref. 13 are in very good agreement with our results.

We can conclude from the electronic band structure that even when both surfaces show the same kinds of surface states, those states have different physical behaviors. For example, C_3 is a flat band for the $(10\bar{1}0)$ surface, while it shows a large dispersion for the (110) surface. Therefore, one can expect that these differences would also be evident when other physical properties, such as their optical behavior, are measured or calculated. Taking into account the limitations of the tight-binding method used here, the following discussion of the optical properties is valid only qualitatively.

The imaginary part of the surface dielectric function of the $(10\bar{1}0)$ and (110) surfaces is presented in the top panels of Fig. 3. The surface dielectric function for light polarized along the main surface crystalline directions X and Y are shown by solid and dotted lines, respectively. For the $(10\bar{1}0)$ surface we observe that electron transitions start at an energy of 2.5 eV, while for the (110) surface they start at slightly higher energies. In both surfaces, at those energies, the transitions for light polarized along the Y axis are more intense than those transitions for X polarization. On the other hand, at higher energies the transitions along X are always the most intense, except at some energies where both signals are comparable. Now let us analyze the surface dielectric function in detail using Fig. 3, where electron transitions of $\epsilon^{\alpha\alpha}_{\text{slab}}(\omega)$ have been decomposed in transitions from surface to surface electronic states (s-s), from surface to bulk (s-b), from bulk to surface (b-s), and from bulk to bulk (b-b). Note that the discussion of the optical spectra can be done only qualitatively, due to the limitations of the tight-binding method. These limitations were discussed above.

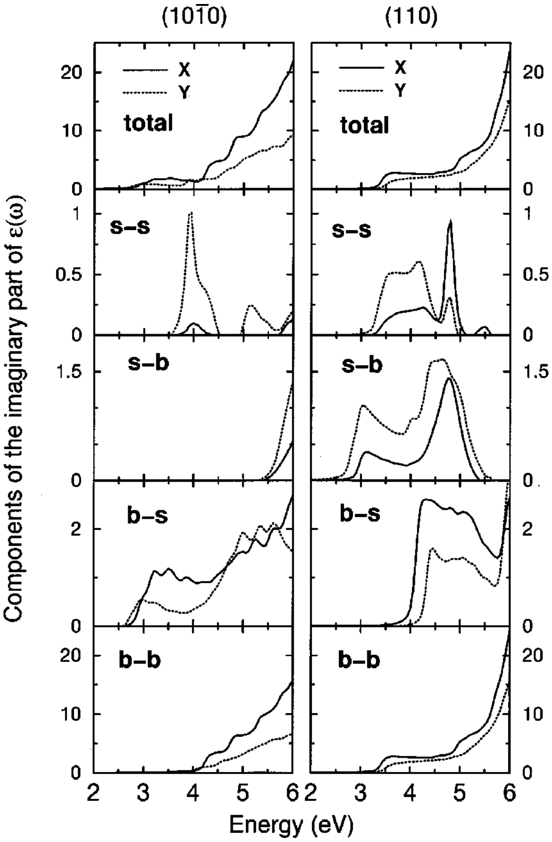

FIG. 3. Imaginary part of the surface dielectric function and the components of $\epsilon^{\alpha\alpha}_{\text{slab}}(\omega)$, with $\alpha = X$ shown by the solid line, and $\alpha = Y$ shown by the dashed line.

First, we analyze the case of the $(10\bar{1}0)$ surface, where electron transitions start below the bulk band gap at about 2.5 eV, and these are mainly b-s transitions. We can see that this b-s contribution involves occupied bulk electronic states around the Γ point and the empty surface electronic states labeled as C_3. At low energies, from 2.5 to 3.0 eV, the spectrum is more intense for Y polarization than for X. However, this situation changes from 3 eV to above 4.5 eV, where now the intensity is larger along X. From 3.6 to 4.5 eV, we have also found s-s contributions to the optical spectrum. These s-s transitions are always more pronounced for Y polarization. If we look at the electronic band structure, we can see that the s-s transitions have their physical origin in the A_5 occupied surface band and the C_3 empty band. These s-s transitions become more significant between the X and M points in the electronic band structure, where those surface bands are almost flat. This fact gives rise to a large contribution to the DOS, and therefore to the intensity of the corresponding electron transitions. We can also see that s-b transitions do not contribute to the surface dielectric functions at energies below 5.5 eV. Also, contributions from b-b transitions dominate the spectrum at energies above 4 eV. Clearly, we can see that the optical response of the surface is anisotropic. We have explained this anisotropy as a consequence of the physical behavior of the electronic states. Recall that the discussion about the main optical properties is qualitative, and the energies at which electron transitions occur can be different from the real transitions.

For the (110) surface the physical origin of the optical anisotropy is completely different. While for the $(10\bar{1}0)$ surface the s-b contributions are negligible, for the (110) surface these are very pronounced. The s-b electronic transitions start at 2.6 eV and finish at about 5.5 eV. This s-b contribution is due to transitions among the occupied A_5 surface band to bulk empty states. The s-b contribution becomes important at an energy of 4.5 eV, which corresponds to the fact where the A_5 surface band is almost flat between the X and M points in the 2DBZ. This physical effect in the DOS explains why the intensity of the optical response is larger for Y polarization at low energies than for X polarization. Also for this (110) surface, the s-s contribution is significant at energies below or equal to the bulk gap. These s-s transitions, from 3 to 5.5 eV, involve surface states that belong to A_5 and C_3. From 3 to 4.6 eV, the intensity of the s-s transitions is largest for light polarized along Y. Again, this fact is due to the small dispersion of the A_5 band between the X and M points. At about 4.8 eV the situation changes, and now the intensity along X is the largest. This originates in the region of the 2DBZ where the C_3 band is flat enough to give rise to a large contribution to the DOS. This situation corresponds to the region between Γ and X, close to the X point. The b-s contributions start almost at 4 eV, and extend up to 6 eV. These transitions are always more intense for X polarization than for Y polarization. At 4 eV, the empty surface states involved in the b-s transitions are those associated with the C_3 band, while for energies about 6 eV, the surface states involved are those located at 5.8 eV at the Γ point. These empty surface states are due to back bonds between Ga and N atoms in the surface. Finally, b-b contributions to the optical spectrum start at 4 eV, and dominate at higher energies. We conclude that the optical response of the cubic nonpolar surface is also anisotropic.

The physical origin of the optical anisotropy of the (110) surface is very different from that found for the $(10\bar{1}0)$ surface. In both cases we have identified the physical cause of such anisotropy, and we have found that it is completely different for each surface. For example, let us suppose that the bonds of N atoms at the surface can be saturated with hydrogen without change in any other electronic property. In this case, one would expect that the A_5 band of both surfaces would reduce its energy considerably. Now the optical spectra for each surface will change in a different way. For example, for the $(10\bar{1}0)$ surface the b-s contributions to the optical response will not be modified, and we should not expect changes to the optical spectrum for energies below 4 eV. On the other hand, the s-s and s-b contributions to the optical spectrum of the (110) surface will be suppressed at energies below 4 eV, modifying the optical response. In conclusion, in a different way we could manipulate the optical response of each surface be performing the same type of atomic modification.

Now, using the above results, let us briefly present calculations of reflectance anisotropy spectra (RAS) for the (110) surface. The RAS calculations can be directly compared with experimental measurements. We believe that the theoretical results presented here could motivate one to perform future RAS measurements. Optical techniques calculations of like RAS, have been widely used to explore the rearrangements of the surface atoms. However, RAS are useful for cubic crystals where the optical response of the bulk is isotropic, and, for this reason, we present RAS results for the (110) surface only. Note that other spectroscopies, such as electron-energy loss spectroscopy (EELS), can also be employed to obtain information in the same range of energies as optical spectroscopies, and in the case of EELS, this is not limited to handle isotropic optical media only.[15] Results of EELS for nonpolar GaN surfaces have been reported elsewhere.[16]

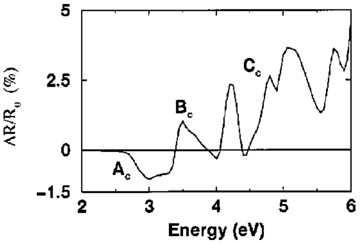

FIG. 4. RAS of GaN(110).

In Fig. 4, we present RAS results of the (110) surface for light at normal incidence. RAS are given by $\Delta R/R_0 = [\Delta R/R_0]_X - [\Delta R/R_0]_Y$, where R_0 is the reflectivity calculated by the Fresnel formula, and $\Delta R = R - R_0$ is the difference between R_0 and the actual reflection coefficient. In Fig. 4, the labels A_c and B_c correspond to peaks which are located at 3.0 and 3.5 eV, respectively. The third label, C_c, corresponds to the peak at 4.2 eV and to the structure from 4.5 to 5.5 eV. Peak A_c is due to s-b transitions. It also has s-s contributions that start at 3 eV, and it is more intense along the Y direction up to energies about 4.5 eV. For both transitions, the intensity for Y polarization is larger than for X polarization, and this fact gives rise to the negative value of A_c. Peak B_c comes from a strong b-b contribution, which is more significant for X polarization than for Y polarization. The latter gives a change in the sing of the spectrum, where now the structures have positive values. Finally, the structures labeled by C_c are related to b-s transitions, which are also more intense for light polarized along the X direction, starting at 4 eV. Also, at these energies the b-b contribution becomes very substantial.

In summary, we have presented a detailed microscopic study of the optical properties of nonpolar GaN$(10\bar{1}0)$ and (110) surfaces. We have found that both optical spectra are anisotropic, and we have identified their physical origin. We conclude that even though the atomic relaxations of both surfaces are quite similar, their optical responses are very different. We have explained the main features of each spectra in terms of their corresponding surface electronic structure. We presented our results of the surface dielectric response in each case, and for the (110) surface we also presented reflectance anisotropy spectra (RAS). In conclusion, we have described RAS in terms of the main features of the optical response of the surface, and we have studied the physical origin of the spectrum. We believe that RAS and other spectroscopies yet to be will be very helpful to better understand the physical properties of this promising material.

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