Anomalous relaxations and chemical trends at III-V semiconductor nitride nonpolar surfaces

Alessio Filippetti

Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Cagliari, Italy
and Department of Physics, University of California, Davis, California 95616

Vincenzo Fiorentini

Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Cagliari, Cagliari, Italy
and Walter Schottky Institut, Technische Universität München, München, Germany

Giancarlo Cappellini

Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Cagliari, Cagliari, Italy

Andrea Bosin

TECHSO S.p.A., Zona Industriale Est, Cagliari, Italy
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Relaxations at nonpolar surfaces of semiconductor III-V compounds result from a competition between dehybridization and charge transfer. First-principles calculations for the (110) and ($10\bar{1}0$) faces of zinc-blende and wurtzite AlN, GaN, and InN reveal an anomalous behavior as compared with ordinary III-V semiconductors. Additional calculations for GaAs and ZnO suggest close analogies with the latter. We interpret our results in terms of the larger ionicity (charge asymmetry) and bonding strength (cohesive energy) in the nitrides with respect to other III-V compounds, both essentially due to the strong valence potential and absence of p core states in the lighter anion. The same interpretation applies to Zn II-VI compounds. [S0163-1829(99)00211-8]

I. INTRODUCTION

The III-V nitrides GaN, AlN, and InN are of enormous current interest[1] in blue optoelectronics and high-power devices technology. Among the relevant problems in this area, there is the high density of threading dislocations and domain boundary defects occurring during growth. These boundaries often coincide geometrically with the nonpolar surfaces of the material, so that accurate characterizations of these surfaces are of interest, and first-principles calculations in this area are timely. Although wurtzite nitrides are usually grown along the (0001) polar direction, other possible growth orientations are being examined, such as the nonpolar ($10\bar{1}0$) and ($11\bar{2}0$) surfaces. Also, thin films of zinc-blende GaN were grown on various substrates,[2] typically along (110) (one of the cleavage faces of zinc blende).

Earlier papers suggest that the nitrides behave quite differently than the ordinary III-V semiconductors such as GaAs or GaP in several respects: the classic gap-cohesive energy relation,[3] structural properties,[4] dielectric,[5] and piezoelectric[6] constants. Recent papers[7,8] have pointed out the unusual surface relaxations of GaN as a further point of difference. The latter ''anomaly'' would reflect a stronger ionic character of GaN, making it similar to the II-VI oxide ZnO, commonly considered as highly ionic. First-principles calculations[9,10] for the ($10\bar{1}0$) surface of ZnO gave smaller rotations and larger contractions than in GaAs and in other II-VI's [in view of the similar morphology and electronic structure of the (110) and ($10\bar{1}0$) surfaces, considerations about the relaxation mechanism are quite valid for both]. In the present paper we take up this problem for the nitrides,

studying the wurtzite ($10\bar{1}0$) and zinc-blende (110) surfaces of GaN, AlN, and InN, and reexamining the properties of the homologous surfaces of ZnO and GaAs as reference systems. We discuss the results in terms of increased ionicity and increased cohesive energy of the nitrides as compared to other III-V compounds. Our interpretation also fits the situation of II-VI compounds, and is compatible with the presence of the ''anomaly'' only for O and N compounds.

The present first-principles calculations are based on density-functional theory[11] in the local density approximation for the exchange-correlation energy functional, for which we adopt the Ceperley-Alder[12] form as parametrized by Perdew and Zunger.[13] Ultrasoft pseudopotentials[14] have been employed for all the elements involved in the calculations. A plane-wave basis is used with a cutoff at 25 Ry. For Ga, In, and Zn, we explicitly include the semicore d electrons in the valence. Slab supercells were used to simulate the surfaces. The results presented here for zinc-blende (wurtzite) surfaces were obtained with symmetric slabs encompassing 8 (9) layers, i.e., 16 (18) atoms, whereby all atomic coordinates were relaxed to obtain forces below 1 mRy/bohr. A mesh of 10 irreducible special **k**-points (obtained by downfolding the bulk mesh) is used for both the zinc-blende and the wurtzite surface. All calculations are performed at the theoretical lattice constants: $a=6.00$ bohr, $c/a=1.613$, $u=0.376$ for ZnO; $a=10.60$ bohr for GaAs; $a=5.81$ bohr, $c/a=1.619$, $u=0.380$ for AlN; $a=6.04$ bohr, $c/a=1.634$, $u=0.376$ for GaN; $a=6.66$ bohr, $c/a=1.627$, $u=0.377$ for InN (see Ref. 6 for details on the optimization procedure).

The results for the structural parameters of the zinc-blende and wurtzite surfaces are presented in Secs. II and III,
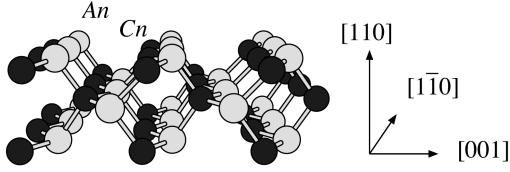
FIG. 1. Side view of (110) zinc-blende surface for III-V semiconductors. White spheres are anions (An), black ones are cations (Cn).

respectively; those for the energetics and electronic structure are discussed in Sec. IV. In Sec. V we discuss our findings on the basis of simple chemical concepts.

II. (110) ZINC-BLENDE SURFACES

The relaxations typical of the (110) surface of most III-V and II-VI compounds have been generally interpreted[15,16] as driven by a loss of sp^3 hybridization towards anion p and cation sp^2-like character. Upon cleavage, charge is transferred from the cation dangling bond into the anion dangling bond. The plane containing each anion-cation chain running along $[1\bar{1}0]$ rotates with respect to the ideal surface (see the sketches in Figs. 1 and 2). In each surface dimer, the cation shifts downwards, so as to lay nearly in the plane of its three neighbors, and rehybridizes to sp^2-like. The anion shifts upward and is bound to its neighbors by p-like back bonds, while it fills up its low-laying s-like state.

The relaxations are usually expressed via a combination of the layer rotation angle θ, the bond rotation angle ω, and the bond contraction C_B (see Fig. 2). Notice that θ and ω are independent parameters, since the dimers can stretch or shorten besides rotating. Only if $C_B = 0$, θ and ω are related by $\sqrt{3}\sin\omega = \sin\theta$. In Table I we list our results for AlN, GaN, InN, and GaAs, in comparison with the data of Ref. 7 and (only for GaAs) experiments.[16] The values for GaAs are in very good agreement with experiment. For nitrides, we do indeed confirm an anomalous behavior: the rotation angles are nearly a half than for GaAs, and the bond contractions are appreciable, as opposed to negligible for GaAs. If (see the discussion in Sec. V) we interpret small bond rotations and large bond contractions as a measure of ionicity, we see that the latter grows along the sequence InN→GaN→AlN, i.e., inversely with the cation size. While qualitatively similar, our results differ somewhat from those of Ref. 7 for GaN. The main difference to our study is of course that the
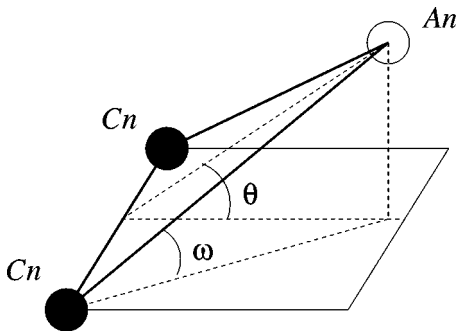
TABLE I. Surface dimer rotation angles θ and ω (see Fig. 2), and relative bond contraction C_B for zinc-blende (110) surfaces. θ^a, ω^a, and C_B^a are from Ref. 7. For GaAs experimental values are also shown (Ref. 15).

	AlN	InN	GaN	GaAs
θ	11.7°	14.4°	14.3°	30.1°
θ^a			2.06°	24.3°
$\theta^{Expt.}$				31.1°
ω	5.8°	7.4°	7.3°	16.5°
ω^a			1.0°	13.4°
ω^{Expt}				16.7°
C_B	5.9%	4.3%	4.9%	0.9%
C_B^a			6.5%	1.3%
C_B^{Expt}				2%

calculations in Ref. 7 are based on the Hartree-Fock approximation. Additional technical issues that may explain the discrepancy are the smaller cells and limited relaxations (first layer only) in Ref. 7.

In Table II the atomic displacements of first- and second-layer atoms are listed for GaN and GaAs ($\hat{x} = [001]$, $\hat{z} = [110]$). For GaN the largest shifts are those of the surface cation, whereas the other atoms shift only slightly and almost rigidly. In GaAs, the displacements along $\hat{z}$ are much more relevant for both anion and cation. They move far away from each other, their vertical distance $[d = 0.25 a_0 (1 - 0.01\ C_B)\sin\omega]$ being 0.69 Å in GaAs against 0.23 Å of GaN, on account of a more than double rotation angle, and of course of the 20% larger lattice constant.

III. $(10\bar{1}0)$ WURTZITE SURFACES

Wurtzite is the most stable phase of III-V nitrides. Its $(10\bar{1}0)$ surface is sketched in Fig. 3. At variance with zinc-blende (110), symmetry only allows dimers rotation in the plane containing the $[10\bar{1}0]$ and $[0001]$ directions, i.e., orthogonally to the surface plane. Thus, there is only one rotation angle: $\theta = \omega$. The chemical picture closely resembles that of the (110). Instead of GaAs, we now consider ZnO $(10\bar{1}0)$ as reference system. ZnO is one of the most ionic II-VI semiconductors, and it allegedly exhibits the same kind of relaxation anomaly[9] under examination here for the nitrides; thus, it represents a suitable, if extreme, case for comparison.

Our results for the relaxations of wurtzite $(10\bar{1}0)$ (Table

FIG. 2. Dimer rotation at (110) surface; θ and ω are two independent parameters.

TABLE II. Displacements from ideal positions (in Å) of anions (An) and cations (Cn) in first and second layer of GaN and GaAs (110). $\hat{x} = [001]$ and $\hat{z} = [110]$.

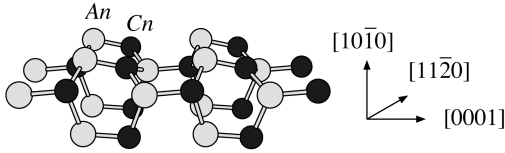|	GaN		GaAs	
	Δx	Δz	Δx	Δz
An_1	−0.04	0.05	0.15	0.42
Cn_1	0.17	−0.18	0.37	−0.27
An_2	−0.05	0.02	0.06	0.13
Cn_2	−0.03	0.07	0.08	0.23

FIG. 3. Side view of the relaxed $(10\bar{1}0)$ surface. White spheres are anions (An), black ones cations (Cn).

III) basically confirm the findings for the zinc-blende (110) surfaces, with angles and bond contractions of the same order of magnitude (angles are somewhat smaller and, consistently, contractions are a bit larger). For GaN, previous calculations[8] gave comparable, in fact somewhat smaller rotation angles. For ZnO our values can be compared with theoretical[9] and low-energy electron diffraction results,[17] and are seen to agree well with the latter. Among the important features we note the close similarity between GaN and ZnO and the highly ionic character of AlN (see Sec. V); also, the ''ionicity'' trend InN→GaN→AlN is confirmed.

In Table IV we list the atomic displacements in the first- and second-surface layer for GaN and ZnO. For GaN, the first-layer anions move upward, the cations downward. The separation along $\hat{z}$ is 0.36 Å against 0.22 Å of Ref. 8. As a consequence our θ is $\sim 40\%$ greater. Also, we find that even the second-layer cation moves upward sizeably, whereas in Ref. 8 changes in the second layer are moderate. Finally, for ZnO both surface atoms go down, but their distance along $\hat{z}$ (0.36 Å) equals that of GaN.

IV. SURFACE ENERGIES AND ELECTRONIC STATES

In Table V we report the surface formation energies of all compounds studied. σ is the surface energy per atom of the fully relaxed structure, and $\Delta\sigma$ the energy gained upon relaxation. Our results agree well with previous data for GaN $(10\bar{1}0)$ (Ref. 8) and GaAs (110).[15] The formation energy per atom may be roughly understood as the energy needed to break a single bond, i.e., 1/4 the cohesive energy per atom: indeed, at least for the cases in Table V, σ is close to $E_{coh}/4$.

σ is also reported in Fig. 4 to make trends easily detectable. For the nitrides, the (110) surfaces energies are $\sim 60\%$ larger than in GaAs. This difference is enhanced by relaxations, that strongly reduce the surface energy of GaAs. For the $(10\bar{1}0)$ surfaces, energy differences range in an interval

TABLE III. Dimer rotation angle (θ) and relative bond contraction (C_B), for $(10\bar{1}0)$ surfaces. Labels a and b refer to results from Refs. 8 and 9, respectively. Experiments are from Ref. 17.

	AlN	InN	GaN	ZnO
θ	7.5°	11.0°	11.5°	11.7°
θ^a		7°		
θ^b				7°
θ^{Expt}				11.47° ± 5°
C_B	7.5%	5.3%	6.0%	6.0%
C_B^a		6%		
C_B^b				8%
C_B^{Expt}				−0.9%

TABLE IV. Atomic displacements of first (An$_1$ and Cn$_1$) and second (An$_2$ and Cn$_2$) layer from ideal positions (in Å) for the $(10\bar{1}0)$ surface of GaN and ZnO. ($\hat{x}=[0001]$ and $\hat{z}=[10\bar{1}0]$). An and Cn indicate anion and cation, respectively. Superscript a indicates results from Ref. 8.

	GaN				ZnO	
	Δx	Δx^a	Δz	Δz^a	Δx	Δz
An$_1$	0.04	0.01	0.08	0.02	0.02	−0.13
Cn$_1$	−0.15	−0.11	−0.28	−0.20	−0.14	−0.50
An$_2$	0.04	0.05	−0.02	0.05	−0.02	−0.09
Cn$_2$	0.05	0.05	0.15	0.05	0.03	−0.09

of ~ 0.2 eV. Noticeably, σ grows along the same pattern of ionicity observed previously for bond contractions (InN →GaN→AlN). Finally, the (110) and $(10\bar{1}0)$ surface formation energies of a given compound are similar, although the relaxation energy is larger for the latter.

It is overall evident that as far as nonpolar surfaces are concerned, the nitrides are closer to a highly ionic compound such as ZnO than to GaAs. Similar conclusions have been drawn from recent studies on spontaneous polarization and piezoelectric constants of bulk nitrides;[6] indeed, all the data suggest that the nitrides are even more extreme in their deviation from typical III-V behavior than ZnO compared to typical II-VI's. It is appropriate to check if such a behavior is also mirrored in the electronic properties. Indeed, while no surface states are present in the gap at the (110) surfaces of GaAs and GaP (Ref. 16) because of dimer rotation, for ZnO the occupied dangling-bond surface state has been predicted to lay in the gap.[9] A previous calculation[8] for GaN $(10\bar{1}0)$ found the occupied anionic surface state to lay slightly (~ 0.1 eV) below the valence band top. We find similar results, reported in Fig. 5, with the anionic surface state touching the valence top but still remaining within the band edge at Γ. Similar results are found for the other nitrides. In agreement with the detailed analysis of Ref. 9 for ZnO, the empty surface state corresponding to the remnants of the cation dangling bond, prevailingly s-like. The filled surface state just above the valence band corresponds to the anion p-like backbonds. It should also be mentioned that recent results by Hirsch et al.[18] suggest that the occupied surface states just mentioned lay indeed completely inside the gap. The difference to ours and other previous results should be attributed to an improved treatment of the semicore d states in Ref. 18.

V. DISCUSSION

To describe the relaxation mechanism, it is useful to consider separately three items. *First*, on all the (110) surfaces of binary tetrahedrally coordinated $A_N B_{8-N}$ compounds, a charge transfer occurs from the cation dangling bond into the anion dangling bond of the as-cleaved surface. This is a purely electronic-structure effect, occurring even at zero rotation angle: the cation dangling bond state is much higher in energy, and it fully transfers its electron occupancy into the anion state.

Second, the surface dimer rehybridizes towards a cation sp^2-like/anion p-like configuration. This entails a rotation of

TABLE V. Surface formation energies (σ), relaxation energies ($\Delta\sigma$), and cohesive energies per bond (i.e., $E_{coh}/4$, where E_{coh} is the cohesive energy per atom). Results are in eV/atom.

	AlN	InN	GaN	GaAs	ZnO
			(110)		
σ	1.07	0.84	0.97	0.60	
$\Delta\sigma$	0.23	0.15	0.22	0.34	
$E_{coh}/4$			1.09	0.81	
			$(10\bar{1}0)$		
σ	1.17	0.86	0.99		0.85
$\Delta\sigma$	0.24	0.21	0.39		0.37
$E_{coh}/4$			1.09		0.94

FIG. 5. Band energies of the simulation slab of GaN ($10\bar{1}0$), plotted for **k** running along the diagonal of the irreducible Brillouin zone (shown in the inset). Black circles are anionic (S_N) and cationic (S_{Ga}) surface states.

the dimer (a combined anion-upward, cation-downwards motion). This rotation is accompanied by a lowering of the energy of the occupied anion dangling bond state, and an increase of the energy of the cation empty state. This is precisely the reason why the cation-anion dangling bond occupation transfer is desirable for this rotation to happen. Since this rehybridization is qualitatively a kind of reverse of sp^3 hybridization, it is expected to be most favorable when the hybridization energy gain is low to begin with.

Third, the charge within the surface dimer is asymmetric towards the anion, because of (a) chemical bond ionicity, in the spirit of, e.g., the Garcia-Cohen[19] charge asymmetry, and on top of that (b) the dangling bond transfer. Therefore, the dimer rotation, with the ensuing anion displacement out of, and away from the cation plane, costs electrostatic energy. The energetic cost will be larger, the more asymmetric the charge distribution is (see, e.g., Ref. 20). A key point is now that, in all materials, there is always a *complete* cation-anion dangling bond occupation transfer: therefore, what matters is the *net* anion-cation charge asymmetry, that is largely equivalent to bulk ionicity.[19] The larger this is, the less the rotation is favored. To be precise, the dangling bond charge transfer will increase the local charge asymmetry (hence hinder rotation) more strongly in low-bulk-ionicity compounds: in the latter, the bulk (i.e., precleavage) charge asymmetry is smaller than in more ionic compounds; thus, when the full dangling bond occupation is transferred to the anion, the net asymmetry increases more than in strongly ionic compounds.

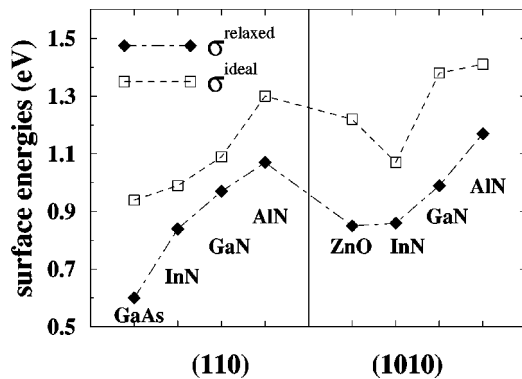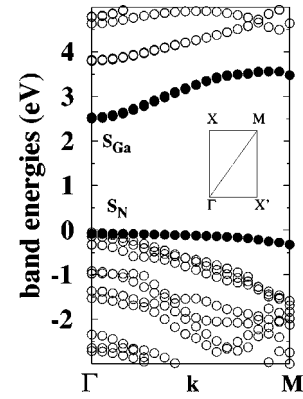We can then rationalize the energetic balance as follows.

FIG. 4. Formation energies σ of (110) and $(10\bar{1}0)$ surfaces.

Rehybridization-plus-rotation is less costly when (a) the gain in the process of sp^3 hybridization is low, i.e., qualitatively when the cohesive energy of the material is small, and (b) when the electrostatic cost of the outward rotation is low, i.e., when charge asymmetry is small, i.e., ionicity is low. The predicted trend is then that materials with small cohesive energies and ionicities will tend to have large rotations, and, vice versa, very ionic and strongly bound solids will tend towards small rotations. While ''small'' is to be understood in a relative sense, e.g., for GaAs compared to GaN, or ZnS compared to ZnO, the nitrides and ZnO are more ionic than all zinc-blende and wurtzite III-V's and II-VI's whatever the ionicity scale.[19,20] This picture agrees nicely with the calculated quantities for the nitrides as compared with other III-V's, as well as with those for ZnO as compared to other II-VI's;[9] both ZnO and the nitrides have both larger cohesion and ionicity (on any scale), and smaller rotation angles than their companion materials. (In the same direction, note that the dimer rotation can be interpreted as a frozen-in zone-center A_1 surface phonon;[21] as all other phonons in the nitrides and ZnO, this mode is stiffer, hence more energetically costly, than in the other III-V's and II-VI's, respectively.)

Indeed, large ionicities and cohesive energies, and hence small rotations, are to be expected for first-row anions. The basic reason is that first-row atoms such as N and O have a very deep potential for the valence p states (and no p core-orthogonality constraint), whence stronger bonding and larger ionicity than with other cations. There is indeed a rather abrupt change in rotation angles (and in other properties too) for first-row anion both in II-VI's (see CdS vs ZnO in Ref. 9) and in III-V's; in this sense selenides are arsenide-like, sulphides are phosphidelike, and ZnO is GaN-like. Interestingly, a similar behavior is observed in the piezoelectric constants,[6] which increase strongly as the anion decreases in size. For the nitrides they are large and positive, against the small and negative values of normal III-V's; for ZnO they are large and positive, against positive and small in other II-VI's (the II-VI–III-V difference is due to a changed balance of the electronic and ionic components).

Note however that one does not expect these trends to hold for any *cation*, in particular small ones. The trend for anions getting heavier and cations lighter is towards an effective exchange of roles (e.g., in boron compounds, this is
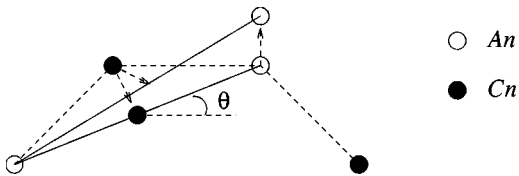
FIG. 6. Side view of the $(10\bar{1}0)$ surface. Dashed line denotes the ideal structure, full lines two possible atomic rearrangements, one with the anion kept fixed in its ideal position, the other with anion shifted upward.

reflected in anomalies of structural transitions under pressure), which blurs the picture somewhat.

Dehybridization and charge asymmetry contrast each other also in geometrical terms, i.e., the larger the layer rotation, the smaller the bond contraction. This can be seen by a simple geometrical argument. In Fig. 6 an idealized picture of the surface profile is shown. The dashed line refers to the unrelaxed surface. If we keep the surface anion fixed and let the cation relax onto the plane formed by first- and second-layer anions (thus undergoing an ideal $sp^3 \rightarrow sp^2$ rehybridization), we have $\theta \approx 35°$ and a bond contraction of $\sim 5\%$. If the surface anion relaxes upwards, i.e., towards a more pure p-like configuration (which indeed it does), then bond contraction tends to be suppressed. This is the case for GaAs, where large rotation angles ($\sim 30°$) and small bond contractions ($\sim 1\%$) indicate that dehybridization dominates (also the case for other III-V's such as GaP). On the contrary, the small rotations in ZnO and the nitrides are accompanied by relatively large bond contractions, consistently with the more critical balance of electrostatic repulsion and dehybridization.

It is barely necessary to confirm explicitly that the nitrides are more ionic than other III-V's. Charge asymmetry increases with the electronegativity gap between cation and anion, commonly used as a measure of compound ionicity. In Fig. 7 we report the experimental values of electronegativity (i.e., one half the sum of atomic ionization potential and electron affinity) and the hardness (i.e., one half the difference of ionization and affinity) for the atoms under consideration. The main feature is that while cations behave quite similarly, this does not hold for anions, nitrogen having much larger values of χ and η. How does this influence

FIG. 8. Charge transfer per dimer given by the electronegativity equalization model.

charge asymmetry in compounds? A semiquantitative estimate is provided by the electronegativity equalization principle,[22] which assumes the compound energy to be simply the sum of the atomic contributions. Upon compound formation, one obtains a charge transfer

$$\Delta N = \frac{\chi_B - \chi_A}{2(\eta_B + \eta_A)}, \qquad (1)$$

which is depicted in Fig. 8. The charge transfer upon nitride formation is much larger, as a consequence of a greater ionicity. Use of other ionicity scales (Phillips, Pauling, etc.) will lead to the same qualitative conclusions. For instance, the charge asymmetry coefficients[19] g are 0.78, 0.79, and 0.85 for AlN, GaN, and InN, respectively, a factor of ~ 2.5 larger than the 0.32 of GaN. Indeed, such huge difference is partially mitigated by the large chemical hardness of N in the denominator of Eq. (1).

VI. CONCLUSION

In summary, nonpolar surfaces of III-V nitrides provide further evidence that the nitrides are closer to the extreme ionic limit (embodied, e.g., by ZnO) than to normal III-V compounds such as GaAs, in agreement with previous results on structural and polarization properties. This strong ionic character causes the prevalence of dehybridization in determining surface relaxations to be less pronounced than in other III-V's. The same reasoning applies to ZnO with regard to other II-VI compounds. In the final analysis, it is the nature of the nitrogen anion, in particular its strong valence potential and the absence of core p states, that sets the nitrides apart from the other III-V's, just as the analogous properties of oxygen cause the major differences of ZnO and other II-V compounds.
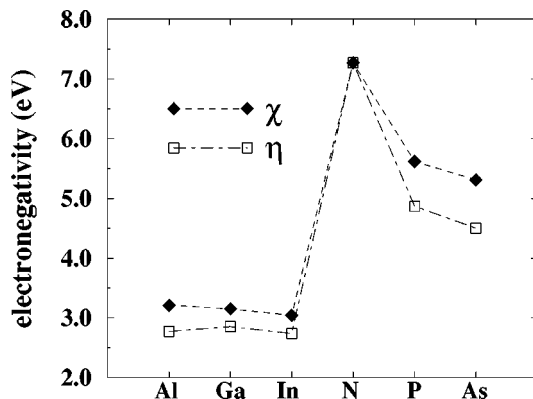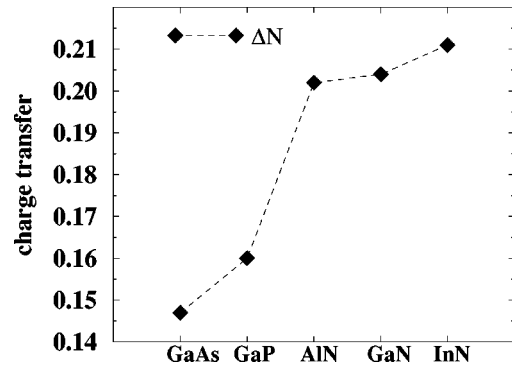
ACKNOWLEDGMENTS

FIG. 7. Electronegativity χ and hardness η for the atomic components of some III-V semiconductors. N is considerably more electronegative than the other anions.

[1] F. A. Ponce and D. P. Bour, Nature (London) **386**, 351 (1997).

[2] *Diamond, Silicon Carbide and Related Wide Bandgap Semiconductors*, edited by J. T. Glass, R. Messier, and N. Fujimori, MRS Symposia Proceedings No. 162 (Materials Research Society, Pittsburgh, PA, 1990); M. J. Paisley, Z. Sitar, J. B. Posthill, and R. F. Davis, J. Vac. Sci. Technol. A **7**, 701 (1989); G. Martin, S. Strite, J. Thornton, and H. Morkoc, Appl. Phys. Lett. **58**, 2375 (1991).

[3] P. Manca, J. Phys. Chem. Solids **20**, 268 (1961).

[4] V. Fiorentini, M. Methfessel, and M. Scheffler, Phys. Rev. B **47**, 13 353 (1993).

[5] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. Lett. **79**, 3958 (1997).

[6] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. B **56**, R10 024 (1997).

[7] J. E. Jaffe, R. Pandey, and P. Zapol, Phys. Rev. B **53**, 4209 (1996).

[8] J. E. Northrup and J. Neugebauer, Phys. Rev. B **53**, 10 477 (1996).

[9] P. Schröer, P. Krüger, and J. Pollman, Phys. Rev. B **49**, 17 092 (1994); J. Pollman (private communication).

[10] J. E. Jaffe, N. M. Harrison, and A. C. Hess, Phys. Rev. B **49**, 11 153 (1994).

[11] R. Dreizler and E. K. U. Gross, *Density-Functional Theory* (Springer, New York, 1990).

[12] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[13] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[15] See, e.g., G.-X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1989).

[16] F. Bechstedt and R. Enderlein, *Semiconductor Surfaces and Interfaces* (Akademie-Verlag, Berlin, 1988).

[17] C. B. Duke, R. J. Meyer, A. Paton, and P. Mark, Phys. Rev. B **18**, 4225 (1978).

[18] The self-interaction relaxation-corrected pseudopotential technique is treated in detail in D. Vogel, P. Krüger, and J. Pollmann, Phys. Rev. B **52**, R14 316 (1995); **54**, 5495 (1996). A further discussion of semicore effects in semiconductors is given by M. Rohlfing, P. Krüger, and J. Pollmann, *ibid.* **57**, 6485 (1998). For the surfaces of GaN, see G. Hirsch, P. Krüger, and J. Pollmann (unpublished).

[19] A. Garcia and M. L. Cohen, Phys. Rev. B **47**, 4215 (1993); **47**, 4221 (1993).

[20] W. Mönch, *Semiconductor Surfaces and Interfaces*, Springer Series in Surface Science Vol. 26 (Springer, Berlin, 1993).

[21] Y. R. Wang and C. B. Duke, Surf. Sci. **205**, L755 (1988); P. Santini, L. Miglio, G. Benedek, U. Harten, P. Ruggerone, and J. P. Toennies, Phys. Rev. B **42**, 11 942 (1990).

[22] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).