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Structural and electronic properties of group-III nitrides

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We present first-principles calculations of structural and electronic properties of group-III nitrides in wurtzite and zinc-blende structure. For a most accurate treatment of these wide-band-gap semiconductors within local density approximation we employ our self-interaction- and relaxation-corrected pseudopotentials together with Gaussian-orbital basis sets. The results for BN, AlN, GaN, and InN are in good agreement with a host of experimental data yielding a consistent theoretical description of this class of technologically important semiconductor compounds. [S0163-1829(97)05119-9]

Group-III nitrides are currently investigated very intensively worldwide. The large interest originates from their promising potential for short-wavelength light-emitting diodes, semiconductor lasers and optical detectors, as well as for high-temperature, high-power, and high-frequency devices.[1,2] The very basis for these important applications is the specific electronic properties of the nitrides. A quantitative description of their bulk electronic structure would be extremely useful, therefore, and would constitute a most reliable starting point for bulk defect, alloy, surface, and interface investigations, at the same time.

Large theoretical efforts to properly describe structural and electronic properties of this important class of materials have been made and considerable progress has been achieved in recent years. Yet, a fully consistent picture is still lacking (see, e.g., the compilation of pertinent results in Ref. 3). Among the theoretical studies, *ab initio* local density approximation (LDA) calculations employing all electron linear muffin-tin orbital,[3–6] orthogonalized linear combination of atomic orbitals,[7] full-potential Korringa-Kohn-Rostocker[8] and pseudopotential[9–12] (PP) methods, GW quasiparticle calculations,[10–12] and Hartree-Fock (HF) calculations[13] have been reported. Some of them treat the Ga and In semicore d electrons as inert core electrons while others explicitly include them in the valence shell. The calculations correspondingly find cationic s and p conduction bands, as well as lower N $2s$ and mostly N $2p$ derived upper valence bands. In addition, semicore d bands are obtained for GaN and InN. The importance of these d bands for binding properties and their influence on the band gaps has been addressed as well.[3,4,7] But there remain a number of open questions related to (a) the calculated band-gap energies, (b) the energetic position of the semicore d bands, (c) the width and energetic position of the N $2s$ bands, as well as their hybridization with the semicore d bands, and (d) the width of the N $2p$ bands.

In this paper, we report the results of recent applications of new pseudopotentials[14,15] to group-III nitrides that allow one to largely overcome the problems identified above. These pseudopotentials incorporate self-interaction-corrections (SIC), as well as self-interaction and relaxation corrections (SIRC) in an approximate but very efficient way. The justification and construction of this type of pseudopotential has been discussed in depth in Ref. 15 and they were shown to be extremely useful for a quantitative description of II-VI compounds, as examples.

Standard LDA calculations, in general, fail to correctly describe energy gaps and semicore d bands originating from highly localized states. These shortcomings, although well known, remain a nuisance after all. In the case of group-III nitrides the band-gap underestimates range from some 30% for BN up to more than 100% for InN. As a matter of fact, for InN even a ''negative gap'' (i.e., the energy of the Γ_{1c} state is below that of the Γ_{15v} state) of up to -0.4 eV is obtained (cf. Ref. 8), as opposed to the measured gap energy of 1.9 eV. Obviously, bulk defect calculations for InN would strongly be hampered when standard LDA were to be employed. HF calculations,[13] on the contrary, yield much too large gaps. For wurtzite GaN, e.g., a gap energy of 10.5 eV was reported in marked contrast to the experimental value of 3.5 eV. Only the GW quasiparticle calculations (cf. Ref. 11) yield gap energies in reasonable agreement with experiment. But they did not yield semicore d bands since d electrons have not explicitly been included in the valence shell. In addition, the width of the N $2p$ bands and the dispersion of the N $2s$ bands resulting from these calculations may not be appropriate since p-d and s-d hybridization has not been taken into account. Standard LDA calculations retaining the d electrons in the valence shell[3–7,9] certainly obtain semicore d bands but these results are roughly 3 eV too high in energy, as compared to experiment. As a matter of fact, the calculated d bands in GaN, e.g., were obtained as fully resonant with the N $2s$ valence bands, in marked contrast to experiment. As a consequence, the calculated energetic position and dispersion of the N $2s$ bands are not correctly described. Only the HF calculations[13] yield the energetic order of the semicore d bands and the N $2s$ bands in accord with experiment (Ga $3d<$N $2s$) but the calculated absolute energy positions of the respective bands deviate from experiment by as much as 6 eV.

Our SIC and SIRC pseudopotential approach[14,15] is able to overcome these obstacles to a large extent, as is shown below. Its usefulness derives from the fact that group-III nitrides are strongly ionic wide-band-gap semiconductors very much like the II-VI compounds. Their main characteristics, namely, the dominance of strongly localized orbitals and their large ionicities, are precisely of the same nature as the obstacles that had hampered accurate band-structure calcula-

TABLE I. Calculated structural parameters a,c (in Å) and the internal parameter u of ZB and W configurations of group-III nitrides in comparison with experimental data (see Ref. 3).

		PP	SIC−PP	Exp.
$\mathrm{BN}^{\mathrm{ZB}}$	a	3.57	3.68	3.62
$\mathrm{AlN}^{\mathrm{ZB}}$	a	4.29	4.36	4.37
AlN^{W}	a	3.05	3.10	3.11
	c	4.89	4.97	4.98
	u	0.382	0.381	0.385
$\mathrm{GaN}^{\mathrm{ZB}}$	a	4.45	4.56	4.50
GaN^{W}	a	3.15	3.22	3.18
	c	5.13	5.26	5.17
	u	0.372	0.371	~ 0.375
$\mathrm{InN}^{\mathrm{ZB}}$	a	4.97	5.05	4.98
InN^{W}	a	3.53	3.59	3.53
	c	5.72	5.81	5.69
	u	0.378	0.378	~ 0.375

tions for II-VI compounds for a long time.

In our PP reference calculations, we employ for N, B, and Al the nonlocal, norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter[16] and respective PP's for Ga and In that have been constructed according to the prescription of Hamann.[17] These PP's enter, as well, the construction of the necessary SIC- and SIRC-PP's (see Refs. 14,15). All pseudopotentials are transformed into the separable Kleinman-Bylander form[18] and we use the Ceperley-Alder[19] exchange-correlation potential as parametrized by Perdew and Zunger.[20] As basis sets we employ 80 Gaussian orbitals per unit cell for the zinc-blende (ZB) and 160 Gaussian orbitals per unit cell for the wurtzite (W) compounds, respectively, with appropriately determined decay constants. These basis sets yield well-converged results. For cubic GaN, e.g., our standard PP calculations with 80 Gaussian orbitals per unit cell yield virtually the same band-structure energies as obtained by Wright and Nelson[9] using 9400 plane waves per unit cell. Brillouin-zone sums are carried out at six or ten special **k** points for the W or ZB compounds, respectively.

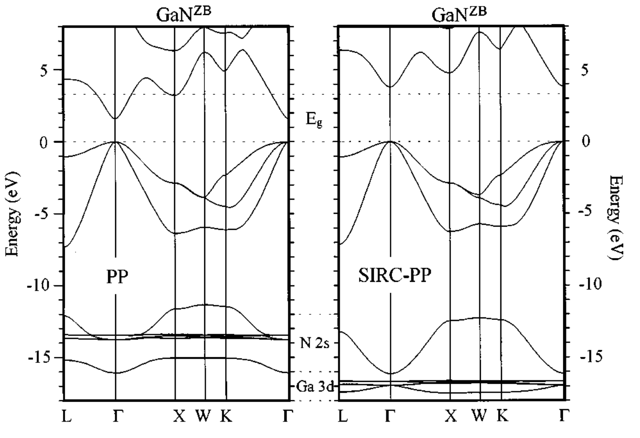

FIG. 1. LDA bulk band structure of ZB GaN as calculated using standard PP's (left panel) and SIRC-PP's (right panel). The horizontal dotted lines indicate the measured gap, as well as the widths of the measured N $2s$ and Ga $3d$ bands.

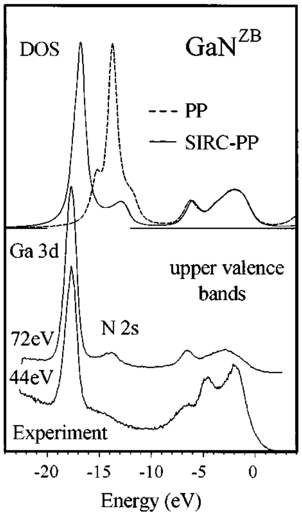

FIG. 2. Bulk density of states of ZB GaN as calculated using standard PP's (dashed line) and SIRC-PP's (full line) in comparison with ARPES data (Ref. 21). The data have been taken with 44-eV and 72-eV photon energy, respectively.

The structural parameters obtained from our SIC-PP calculations are compiled in Table I. As ground-state properties they are not subject to relaxation corrections (cf. Ref. 15). We observe that the lattice constants resulting from our SIC-PP calculations are some 2% larger than those resulting from our standard PP calculations and they agree with experiment roughly within 1% in most cases.

Let us now discuss the results of our electronic structure calculations employing the SIRC pseudopotentials. To allow for a more meaningful comparison with experiment and with theoretical literature data they have been carried out at the experimental lattice constants. We first address the bulk band structure of ZB GaN. The left panel of Fig. 1 shows our standard PP results, revealing very clearly the above-mentioned shortcomings. The band gap is underestimated by about 50% and the Ga $3d$ bands result at -13.6 eV fully resonant with the N $2s$ valence band. As a consequence, an inappropriately strong s-d hybridization splits the N $2s$ band

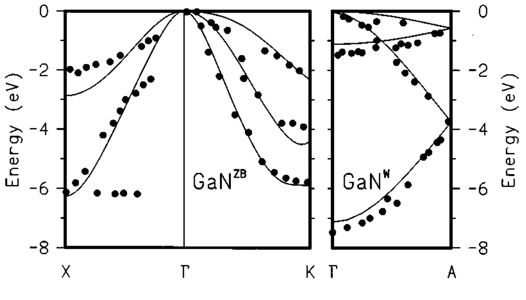

FIG. 3. Comparison of measured (Refs. 21 and 23) upper valence bands of ZB (left panel) and W (right panel) GaN with our SIRC-PP band structures.

TABLE II. Measured energy gaps E_g, d-band positions E_d and N $2p$ valence-band widths W_p (in eV) of some group-III nitrides in comparison with GW results (Refs. 10 and 11) and our PP and SIRC-PP results.

		PP	GW	SIRC−PP	Expt.
BN$^{\mathrm{ZB}}$	E_g	4.4	6.3	6.1	6.1[a]
	W_p	10.8	12.1	11.5	
AlN$^{\mathrm{ZB}}$	E_g	3.2	4.9	5.2	
	W_p	5.9	6.7	5.9	
AlN^{W}	E_g	4.2	5.8	6.7	6.3[b]
	W_p	6.1	6.9	6.0	6.0[b]
GaN$^{\mathrm{ZB}}$	E_g	1.6	3.1	3.8	3.3[b]
	W_p	7.3	7.8	7.1	
	E_d	−13.6		−16.7	−17.7[c]
GaN^{W}	E_g	1.7	3.5	4.0	3.5[d]
	W_p	7.3	8.0	7.1	7.4[e]
	E_d	−13.6		−16.7	−17.1[f]
InN^{W}	E_g	−0.4		1.6	1.9[d]
	W_p	6.1		6.0	
	E_d	−13.4		−15.2	−16.7[g]

[a] Reference 26.
[b] Reference 3.
[c] Reference 21.
[d] Reference 24.
[e] Reference 23.
[f] Reference 6.
[g] Reference 25.

TABLE III. Electron effective masses (in m_0) of some group-III nitrides, as calculated using standard PP's and SIRC-PP's in comparison with measured values (Ref. 24). For the W compounds we give the arithmetic average of the masses.

	PP	SIRC-PP	Expt.
GaN$^{\mathrm{ZB}}$	0.15	0.27	
GaN^{W}	0.16	0.28	0.22−0.28
InN^{W}	0.06	0.16	0.11

into two sections, one above and one below the Ga $3d$ bands, and falsifies its dispersion accordingly. The SIRC-PP band structure in the right panel, on the contrary, yields the d bands around −16.7 eV, in much better agreement with experiment. They now reside below the N $2s$ band so that the s-d hybridization is correctly described and the dispersion of the N $2s$ band is no longer falsified. Concomitantly with the downward shift of the Ga $3d$ bands, the mostly N $2p$ derived upper valence bands are no longer pushed up in energy in an unphysical way and the gap opens up drastically, now being in good accord with the measured gap.

To make the improvements in the description of the Ga $3d$ and N $2s$ bands by our SIRC-PP approach more transparent, we show in Fig. 2 a direct comparison of our calculated densities of states (DOS) for cubic GaN with the angle-resolved photoelectron spectroscopy (ARPES) spectra of Ding *et al.*[21] Our DOS has been Lorentzian broadened by 0.5 eV to ease the comparison with the spectra. The latter were recorded in normal emission with photon energies of 44 and 72 eV, respectively, showing differences in the N $2s$ and $2p$ valence-band regions that are clear indications of matrix element effects. We observe an almost perfect agreement of our SIRC-PP DOS with the 72-eV spectrum, let alone the fact that the experimental spectra are observed some 1.0 eV lower in energy. This rigid shift could be related to problems involved in the experimental determination of the valence-band maximum, as discussed in Ref. 21. The Ga $3d$ bands in Fig. 2 clearly reside below the N $2s$ band and the latter has a width of about 4 eV. In the mostly N $2p$ derived upper valence-band region we find close agreement of our DOS with the 72-eV spectrum. The 44-eV spectrum shows a third peak in this energy region, in addition, which is in very good accord with the weak shoulder in our SIRC-PP DOS. A comparison of our respective DOS, as calculated with standard PP's, shown by the dashed line in Fig. 2, clearly reveals the inappropriateness of that calculation. The PP DOS shows two weak features above and below the d-band peak stemming from the split N $2s$ band that are not observed in experiment. In addition, the respective d-band peak grossly deviates from experiment by about 3 eV. Note that the upper valence bands are described almost equally well in both calculations. For W GaN we find very gratifying agreement of our results with the data reported by Lambrecht *et al.*[6] and by Stagarescu *et al.*[22] In that case the calculated d-band peak in the DOS agrees with the spectra within 0.4 eV.

To compare the mostly N $2p$ derived upper valence bands of GaN in some more detail with ARPES data, we show in Fig. 3 small sections of our SIRC-PP band structures of ZB (left panel) and W (right panel) GaN in direct comparison with the data.[21,23] The general agreement is very good indeed.

We have obtained similar improvements in calculated electronic properties for all group-III nitrides considered. These occur, as well, for BN and AlN although no semicore d bands are involved. This is due to the fact that the self-interaction and relaxation corrections incorporated in our new pseudopotentials sensitively depend on the localization of the involved atomic states so that they are significantly different for s, p, and d electrons, respectively. For the sake of brevity, we only address a few important key quantities. In Table II we have compiled respective PP and SIRC-PP results in comparison with GW results[10,11] and with experimental data.[3,6,21–26] Our SIRC-PP calculations yield grossly improved d-band energies, which are now in reasonable accord with experiment. The remaining deviations are most pronounced for ZB GaN and W InN. It should be noted in this context that the samples used in the respective experiments[21,25] were thin films epitaxially grown on lattice-mismatched GaAs(100) and (110) or Si(100), respectively. Furthermore, we recognize in Table II that the SIRC-PP's yield considerably improved gap energies. Zinc-blende BN and AlN result as indirect while zinc-blende and wurtzite

GaN and InN result as direct semiconductors from our calculations in full accord with experiment. For wurtzite AlN we find an indirect gap with a value of $E_g = 6.7$ eV while the direct gap at the Γ point has a value of 7.0 eV. The SIRC-PP results clearly describe InN as a wide-band-gap semiconductor. In addition, the band gap of W GaN is found to be 0.2 eV larger than that of ZB GaN, in agreement with experiment.

Finally, we have calculated electron effective masses for a few nitrides. Those resulting from our SIRC-PP's are in better agreement with experiment than those that we have obtained from our standard PP calculations (see Table III).

In summary, we have presented lattice parameters, bulk band structures, densities of states, and effective masses of group-III nitrides as calculated using standard PP's, SIC-PP's, and SIRC-PP's. The SIC- and SIRC-PP results are in good agreement with available experimental data. We have thus arrived at a most quantitative description of structural and electronic bulk properties of group-III nitrides on the basis of effective one-particle Hamiltonians. Since our approach is not more involved than any standard LDA calculation it can readily be applied to investigations of bulk defects, alloys, surfaces, or interfaces of group-III nitrides.

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