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Pressure studies of gallium nitride: Crystal growth and fundamental electronic properties

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Results of experimental and theoretical studies of the fundamental electronic properties of GaN are presented. Single crystals of GaN grown by means of an equilibrium high-pressure technique have been used for the determination of the energy gap E_g, refractive index n, and their pressure dependences. The electronic band structure of GaN has been calculated by means of the self-consistent linear-muffin-tin-orbital method. It has allowed us to determine the pressure variation of the measured electronic properties of GaN and to reexamine the character of E_g (direct or indirect). A satisfactory agreement between the experimental and theoretical results has been obtained, and it is found that GaN is a direct-band-gap semiconductor. The pressure dependences of E_g and n have been used also for comparison of GaN with other semiconductors and to examine the validity of some semiempirical schemes used for the classification of semiconductor compounds.

I. INTRODUCTION

Gallium nitride, together with aluminum nitride and cubic boron nitride, belongs to an interesting subgroup in the III-V family. The specific role of nitrogen consists of forming short bonds (with the length of about 80% of those existing in GaAs), which results in the exceptionally small atomic volumes characterizing these compounds. Consequently, many of the physical properties of the considered nitrides are similar to those characterizing diamond. It concerns the large magnitude of the forbidden gap ($E_g > 3$ eV), a considerable hardness and high thermal conductivity. All of the above-mentioned properties make the nitrides interesting and very useful. For example, the extremely hard cubic BN competes with the diamond as an abrasive powder, and the high thermal conductivity makes AlN an ideal substrate material for microelectronics. In addition, the nitrides are potentially useful as short-wavelength (green, blue, and ultraviolet) electroluminescent devices. In this respect, GaN is considered to be a particularly promising material.

In spite of the prospects of nitrides for various applications, experimental data on their microscopic parameters are surprisingly scarce. This is mainly due to the lack of high-quality single crystals. Moreover, the understanding of the properties of these materials from the theoretical point of view is far from being satisfactory. The results of calculations concerning the electronic band structure often contradict each other [see example, data on GaN (Refs. 1–5) as well as BN (Ref. 6)]. The small amount of experimental data available makes it difficult to verify and test different theoretical predictions.

In this paper we will concentrate on GaN, taking the model of the successful growth of GaN single crystals.[7] Usually, GaN is grown on foreign substrates by the use of several techniques based on chemical-vapor deposition including metal-organic chemical-vapor deposition (MOCVD) and molecular-beam epitaxy (MBE). The properties of GaN heteroepitaxial layers are strongly influenced by the substrates, due mainly to the large lattice mismatch. For the most popular substrate material, sapphire, the mismatch is as large as 8.3%. Therefore, despite the fact that the electrical properties of pressure-grown single crystals are, generally, not better than those of the layers, the use of bulk, single-crystalline samples is crucial for proper material characterization.

We will start from the description of the high-pressure growth of nitrides—a unique method that has assured the equilibrium conditions for obtaining the high-quality single crystals of GaN [and also AlN (Ref. 8)]. Then the experimental data concerning such basic electronic properties of GaN as the band gap and the refractive index (the electronic part of the dielectric constant) will be presented. Next, the pressure dependence of these parameters up to 6 GPa will be described in detail. The purpose of the latter measurements was twofold:

First, we hoped to solve by this means the ambiguity concerning the character of the main energy gap. Although the existing experimental data have been interpreted in the past with the assumption that GaN is a direct-band-gap semiconductor, very recent theoretical work[5] claimed it to be indirect-band-gap material. The pressure behavior of the observed absorption edge could be used here to select which of the two possibilities is the proper one.

Secondly, the pressure coefficients of the parameters considered could be used for examination of the validity of classification schemes used in unified descriptions of semiconductor compounds. Many physical properties of semiconductors can be scaled with material parameters such as atomic volume and ionicity. The theory proposed by Van Vechten[9] was based on this, and gave a qualitatively good classification of a large number of fourfold-coordinated semiconductors. This approach also includes pressure effects. From this point of view, it is interesting to investigate the pressure behavior of GaN, which is one of the most ionic semiconductors in the III-V group [0.43 (Ref. 10) or 0.5 (Ref. 9) on the Phillips scale[11]] and has a very small atomic volume, about 11 Å^3, which is one-half that of GaAs.

For the purpose of discussing the postulated chemical trends in detail as well as for interpreting our experimental results in terms of microscopic parameters of GaN, we have decided to perform self-consistent first-principles calculations of the electronic band structure of GaN by means of the self-consistent linear muffin-tin orbital (LMTO) method within the local-density approximation (LDA). Since the main experimental results of this work concern the pressure variation of the electronic properties of GaN, the band-structure calculations are performed here for different values of hydrostatic pressure.

The most important results of this paper are the following: (i) growth of single crystals of GaN by means of an equilibrium high-pressure technique, (ii) obtaining a good agreement between experimental and theoretical results concerning the basic electronic properties and their pressure coefficients. In particular, it has been found that the main energy gap is direct. (iii) As may be expected, GaN differs essentially from the other III-V semiconductors. These differences are reflected in the characteristic short bond length. This parameter, together with the ionicity, is important in the discussion of chemical trends as introduced by Van Vechten.[9] Various simplified approaches using only the ionicity should be treated with caution.

The data presented in this paper that characterize basic electronic properties of GaN are complementary to the results of previous studies of the crystal lattice dynamics and stability.[12]

II. CRYSTAL GROWTH

Until now, GaN has not been obtained in the form of large single crystals, since its thermodynamical properties preclude the use of any standard growth technique leading to bulk high-quality material (like Czochralski melt growth technique). The value of the melting temperature is not known with sufficient accuracy. Both theoretical[9] and experimental[13,14] evaluations give values significantly exceeding 2000 °C. Moreover, the equilibrium pressure of nitrogen over GaN is extremely high at elevated temperatures, which is illustrated in Fig. 1. The diagram shows the GaN stability field evaluated by the three-phase equilibrium studies performed up to 2300 °C and 6 GPa.[13] Although the increase of N_2 pressure with temperature is moderated by the nonideal behavior of compressed nitrogen, the pressure of 2 GPa is needed to have a stable compound at the temperature of 1600 °C, which is still quite far from the melting point. Therefore, even at such extreme conditions, GaN cannot be grown from the melt.

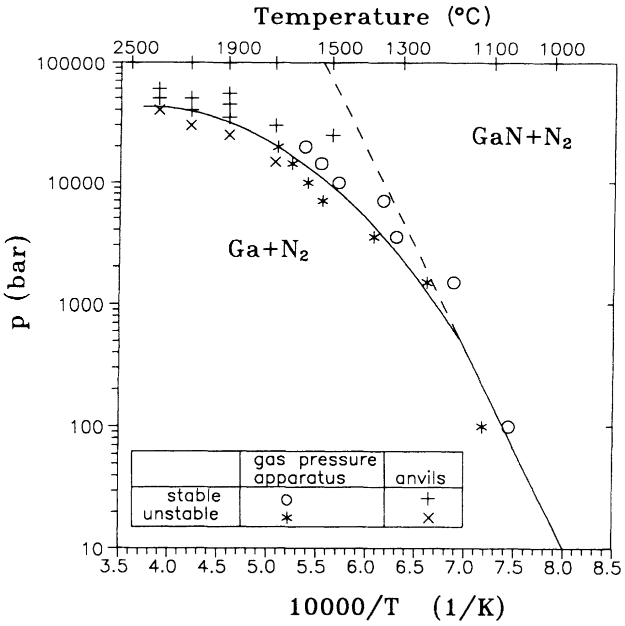

FIG. 1. Equilibrium N_2 pressure over GaN (Ref. 13). The dashed line was calculated for the ideal-gas approximation.

The rise of the solution temperature from 1200 °C allows us to increase the nitrogen concentration in the liquid gallium from 10^{-2} to 1 at. %.[13,15] Such an increase of nitrogen solubility is crucial for the stable growth of good-quality crystals from a high-temperature solution.[16]

The GaN crystals used in this work were grown by the method resulting from the considerations above in the internally heated gas pressure chamber at an N_2 pressure up to 2 GPa. A temperature gradient of the order of 50 K/cm was applied to create the supersaturation in the cooler part of the solution. After processing for a few h, the excess gallium was removed by chemical etching (GaN is unaffected by boiling concentrated acids) and a number of GaN crystals (up to few mm) grown on the internal surface of GaN polycrystalline crust covering the sample were obtained. The shapes of the crystals are strongly dependent on growth temperature and pressure. Platelike samples result from the choice of (P,T) values from the vicinity of the equilibrium line and needlelike samples are obtained for P and T lying deep in GaN stability range region. Typical samples are shown in Fig. 2.

III. EXPERIMENT

A. Energy gap under pressure

The experiment was performed in Merrill-Bassett-type diamond-anvil cell with a 4:1 methanol-ethanol mixture as a pressure-transmitting medium. A GaN platelet of about 100 μm diam and 20-μm thickness was placed in a specially drilled hole in the Inconel gasket. The special shape of the gasket's hole enables the sample to totally

FIG. 2. GaN crystal grown from the solution at N_2 pressure of 1.7 GPa.

cover the area of the hole, and thus no light passes beside the sample.[17] We used a 150-W xenon lamp as a light source. The light was analyzed by a Spex 500-M monochromator and detected by a photomultiplier. The intensity of the passing light was strongly reduced by the absorption in diamonds (yellow diamond), which occurs near the uv region (3–3.3 eV). This caused a decrease in the accuracy of the determination of the gap E_g. All experiments were conducted at room temperature.

B. Refractive index under pressure

The pressure-generation system was the same as that described above. The 150-W halogen lamp light was focused on an 80-μm pinhole. An image of the pinhole was then created on the sample surface. The signal was analyzed by GDM-1000 double spectrometer and detected by a photomultiplier. We performed our measurements in the spectral region from 1.4 up to 2 eV. We chose this region because of strong free-carrier absorption observed below the 1.4-eV energy region.

IV. THEORY

The band structure of GaN was calculated from the first-principles LMTO method in its scalar-relativistic form[18] [i.e., all relativistic effects, except the spin-orbit (so) coupling, were included], in conjunction with the local-density approach. With self-consistent potentials generated in this way, the so interaction was added in a last iteration as a formal perturbation term in the Hamiltonian.[18] We applied here the LMTO method in its simplest form, i.e., the atomic-sphere approximation (ASA).[18] However, we incorporated the "combined correction" terms.[18] Band-structure calculations based on LDA lead to too small values of band gaps, when deduced directly from the LDA eigenvalues. Therefore, we corrected them by the addition of some external potentials,[19] which are sharply peaked at the atomic sites, and which are included in the self-consistent iteration procedure. The details of the LDA-LMTO calculations for zinc-blende-type semiconductors are given elsewhere.[19–21] The wurtzite structure, in which GaN crystallizes at ambient conditions, is somewhat more complicated for this kind of calculation. The unit cell contains four "real" atoms and four so-called "empty spheres."[19–21] The LMTO calculations were optimized by the choice of equal atomic spheres for Ga and N (radius $S=2.08$ a.u.) and different ones for two types of "empty spheres" ($E1$, $S=1.664$ a.u.; $E2$, $S=2.375$ a.u.). The Ga $3d$ states were included as band states. Two energy panels were needed to obtain bands over the entire energy range of interest: panel 1 was composed of the Ga $3d$ band and the N s band, and panel 2 covered the remaining valence states. The calculations were performed under the assumption that the structure was "ideal," meaning that the c/a ratio was taken as being equal to 1.633, whereas the experimental[22] value was 1.627. In the context of the present work the error introduced hereby is negligible.[21]

V. RESULTS

A. Absorption edge

The measured transmission spectra of GaN at room temperature are shown in Fig. 3. The gap energy is taken as the energy where the transmission falls to the level of scattered light. The gap values at ambient pressure vary from 3.41 to 3.46 eV, from sample to sample, probably due to different electron concentrations. This scatter in E_g does not influence the value of the measured pressure coefficient dE_g/dP.

The pressure dependence of the absorption edge is illustrated in Fig. 4. A typical sublinear dependence is found, and it can be well described by the equation $E_g(P)=-0.0018P^2+0.047P+E_g\ (P=0)$, where P is the pressure in GPa and E_g is in eV. Figure 5 shows strictly linear dependence of E_g on the lattice constant. Thus, the sublinearity of the $E_g(P)$ curve originates in the equation of state GaN.[12] The pressure dependence of E_g as given above represents a generalization of

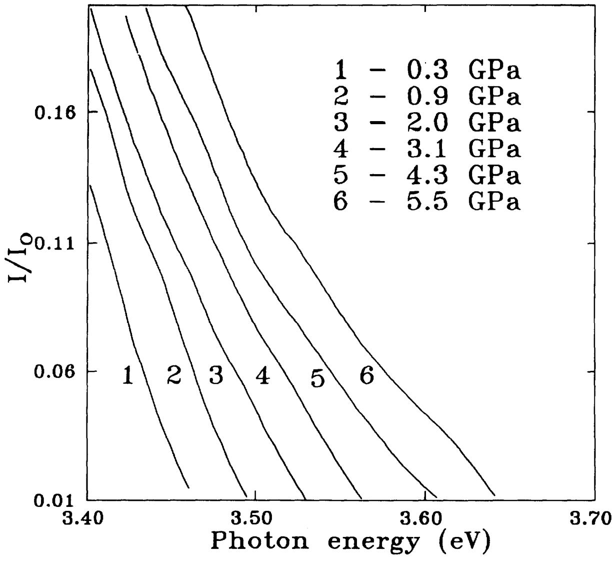

FIG. 3. Transmission spectra of GaN in the region of the absorption edge. The incident light is parallel to the c axis.

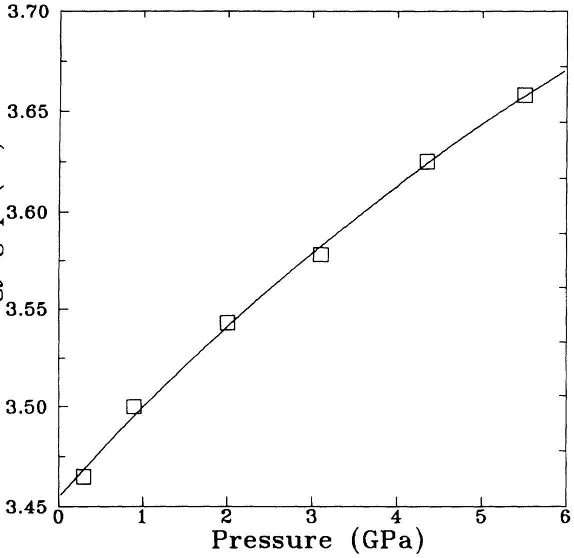

FIG. 4. Pressure dependence of the GaN energy gap showing typical sublinear character ($T=300$ K).

Camphausen's[23] experimental result ($dE_g/dP=0.042$ eV/GPa). The latter experiment, performed for pressures below 1 GPa, allowed only the linear pressure coefficient to be extracted. Due to the large value of the bulk modulus of GaN (245 GPa),[12] more-detailed studies of the pressure dependence require application of much higher pressures.

As has been mentioned briefly in the Introduction, the fact that GaN is the direct-band-gap semiconductor was disputed recently in the theoretical work of Grinayev, Malachow, and Czaldyszew.[5] The authors postulated the existence of two energy gaps, indirect and direct ones (3.0 and 3.4 eV, respectively). As a consequence, at two-feature structure of the GaN absorption spectrum is expected. Thus, with increasing photon energy one should observe a broad tail related to indirect transitions, followed by a stronger and steeper contribution originating in the electron excitation across the direct gap. In this case, application of hydrostatic pressure would modify significantly the shape of the absorption spectrum. For tetrahedrally coordinated semiconductors, pressure causes a shift of indirect transitions towards lower energies, whereas direct transitions exhibit the opposite behavior. The inspection of our experimental data shows that the shape of the absorption spectrum does not change significantly with pressure, and the blue shift of the total spectrum strongly supports the concept that GaN is the direct-band-gap semiconductor. For further studies of electronic properties of GaN, the calculations of its band structure have been performed using the method described in Sec. IV.

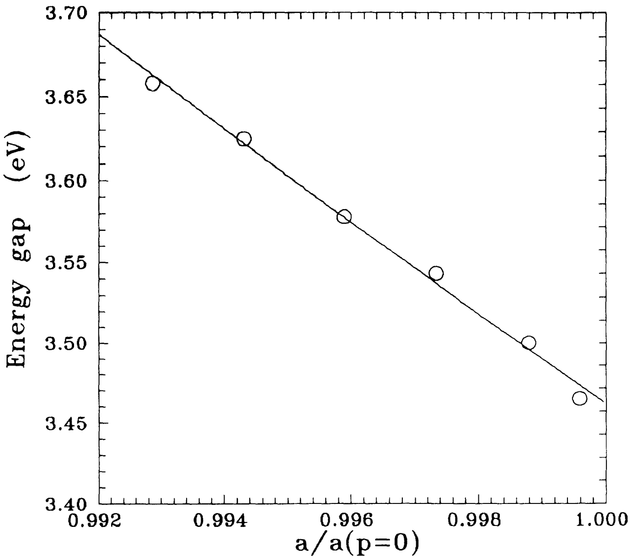

FIG. 5. Energy gap as a function of lattice constant for the GaN crystal ($T=300$ K).

The band structure calculated at the experimental equilibrium volume ($a_0=3.19$ Å) (Ref. 22) is shown in Fig. 6. The band structure of Fig. 6 does not differ significantly from the earlier pseudopotential calculations using a local nonempirical pseudopotential,[1] nonlocal pseudopotential fitted to only the fundamental gap,[2] and empirical local pseudopotential.[4] But there is little agreement with the pseudopotential band-structure calculation performed by using an energy-dependent pseudopotential combined with a muffin-tin atomic potential.[3] The latter calculations led to much flatter valence bands and less flat conduction bands. Comparing our results with the most recent model pseudopotential calculations,[5] we have found that the dispersion curves of the valence states are almost the same, but there is a serious qualitative discrepancy in the conduction-band structure. According to the work of Ref. 5, the absolute minimum of the conduction band is lying on the line L-M in the Brillouin zone (see Fig. 6), so in that case GaN becomes an indirect-band-gap semiconductor with $E_g=3.0$ eV. To support this finding, the following tendency was postulated for gallium compounds: with decreasing anion atomic number, E_g changes from direct to indirect. Accordingly, for the series, GaSb, GaAs, GaP, GaN, the gap character changes for GaP. However, the postulated trend does not agree with existing experimental data.[23] Also, as mentioned above, our experiment does not indicate that

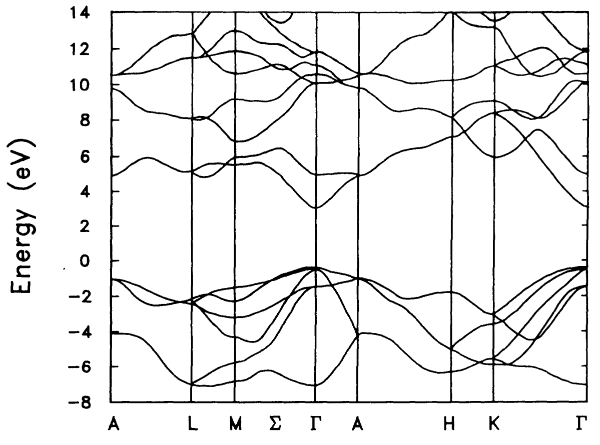

FIG. 6. Calculated band structure of GaN.

GaN could be an indirect-band-gap semiconductor. The absolute minimum of the conduction band resulting from our calculations is situated at the Γ point, and so the band gap is direct and occurs at the center of the Brillouin zone (the valence-band maximum is displaced very slightly in the Σ [110] direction as was suggested earlier in Ref. 3, but this effect is so small that it can be neglected).

For evaluation of the pressure effects we have calculated the total energy and band structure of GaN for several values of the lattice constant. In our calculations we have included the adjusting potentials (see Sec. IV) chosen so that the gaps at zero pressure agree with experiments.[23] From the total-energy dependence on volume and calculated equation of state, we have obtained the volume-pressure relation, the equilibrium lattice constant $a_0=3.16$ Å, and the bulk modulus $B_0=239$ GPa. The band structures obtained at various volumes served for calculating the pressure coefficients and deformation potentials $a=\partial E/\partial \ln V$ for the energy gaps at the points of high symmetry. Calculations confirm the sublinear character of energy-gap variations with pressure, and almost exactly confirm the linear character of volume dependences of energy gaps. The pressure coefficients and deformation-potential constants are given in Table I, together with the values of the corresponding energy gaps. We have calculated the pressure coefficient of the fundamental energy gap to be 0.041 eV/GPa—very close to the value obtained in an earlier experiment (0.042 eV/GPa),[24] and also in a good agreement with our experimental result 0.047 eV/GPa. Camphausen's prediction (0.053 eV/GPa) (Ref. 10), based on the Van Vechten approach, seems to be an overestimate. It might result from the fact that nearest-neighbor distance scaling used by Camphausen is not very precise, since its value is extremely small in GaN. Additionally, at the time of Camphausen's work, the bulk modulus of GaN was not known very accurately. Camphausen assumed the value of B_0 to be equal to 200 GPa, whereas the recent experimental[12] value is 245 GPa.

B. Refractive index

The refractive index and the dielectric constant, together with the energy gaps, are the most important parameters characterizing electronic properties of semiconductors. We performed our experiment in the energy range well below the gap energy and at the same time above the energy of phonons and the plasma frequency. In this region the dielectric function is usually described as $\epsilon(0)$.

TABLE I. Calculated energy band gaps at the points of high symmetry, their pressure coefficients, and corresponding deformation potentials.

	E (eV)	$\partial E/\partial P$ (meV/kbar)	$-a$ (eV)
Γ_v-Γ_c	3.44	4.1	10.1
Γ_v-K_c	6.36	0.4	1.0
Γ_v-M_c	5.97	1.7	4.2
Γ_v-A_c	5.36	3.4	8.5
Γ_v-L_c	5.34	2.0	5.0
Γ_v-H_c	7.22	3.4	8.6
K_v-K_c	9.04	1.6	4.0
M_v-M_c	7.03	2.2	5.5
A_v-A_c	5.95	3.7	9.3
L_v-L_c	7.37	2.8	7.0
H_v-H_c	8.88	4.1	10.2

Making use of the fact that our high-pressure crystal-growth technique gives us the possibility of controlling the morphology, we grew GaN samples in the form of perfect plane-parallel platelets, and thus we could easily apply an interference method to measure the refractive index of the material. If light passes through a plane-parallel platelet, one can observe oscillations in the transmission, where the maxima are given by $2dn=a\lambda_a$. Here d is the thickness of the sample, α is the order number of the maximum considered, and λ_α is a wavelength corresponding to this maximum. We determined the value of α by making a least-squares fit do the relation $\alpha=2dn/\lambda$. Knowing the absolute numbers α of the interference maxima, we could establish the relation $n(\lambda)$ and thus the dispersion of dielectric constant. Figure 7 illustrates the dispersion of the dielectric constant ϵ. The solid line represents a simple one-gap model of ϵ given by the expression

$$\epsilon=1+\frac{A}{E_0^2-E^2}\,, \tag{1}$$

where E_0 is the average gap in the Penn model[25] and A is proportional to $1/V$ (V is the atomic volume). The best fit to experimental results is obtained for $A=385$ and $E_0=9$ eV, which is in agreement with the value of the average gap predicted by Van Vechten.[9] It is seen from Fig. 7 that in view of the simplicity of the model, the fit is fairly good. Determination of the absolute value of n requires a good knowledge of the sample thickness d. Our microscopic method of measuring d had 10% accuracy (2 μm), so extrapolating n with the use of expression (1) we obtained the value of n at the low-frequency limit

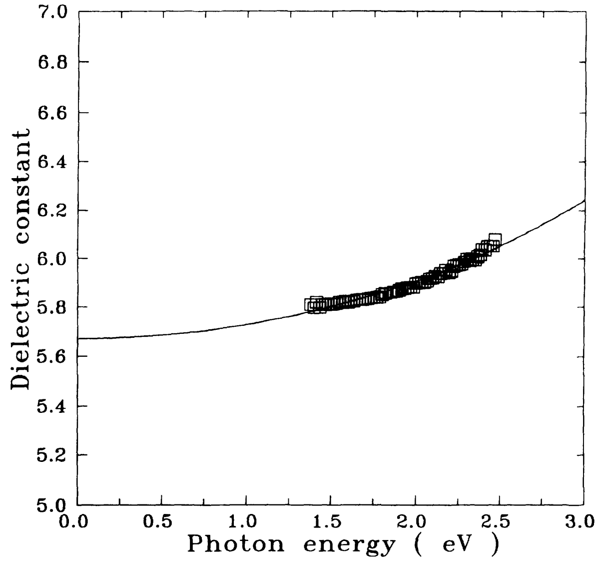

FIG. 7. Dispersion of the refractive index of GaN ($T=300$ K).

equal to 2.4±0.2.

If the refractive index changes under pressure, that also shifts the positions of every interference maximum and the distance between maxima as well. It is much easier, however, to determine the absolute shift of a given maximum than the changes in the exact distance between two of them. Therefore, the pressure dependence of the energetic position of an arbitrarily chosen interference maximum was used for the determination of $n(P)$. The change in the sample thickness is included in calculations with the use of the equation of state of GaN determined in Ref. 12. Figure 8 shows the pressure dependence of the refractive index. We can see that n decreases as in the majority of other compounds. The linear pressure coefficient $(1/n)(dn/dP)$ is equal to $(-0.30\pm0.04)\times10^{-2}\,\mathrm{GPa}^{-1}$.

Now we can estimate the theoretical value of the pressure coefficient of the refractive index in terms of the Penn model based on the results of our LMTO band-structure calculations. Expression (1) for $E=0$ leads to the following formula for the pressure derivative:

$$\frac{1}{n}\frac{\partial n}{\partial p}=\tfrac{1}{2}(1-\epsilon^{-1})\left[K-2E_0^{-1}\frac{\partial E_0}{\partial p}\right], \qquad (2)$$

where K is the isothermal compressibility. We notice that the value of this coefficient results from the contributions of two mechanisms: The first represents compressibility, which causes an increasing in the value of n, and the second one is given by the average change in the band structure induced by pressure, which, if $\partial E_g/\partial P$ is positive, causes n to decrease with pressure. Following the considerations by Tsay, Mitra, and Bendow,[26] we assume that the average Penn gap occurs at the Σ point midway between Γ and M of the Brillouin zone (see Fig. 6). The calculated energy gap at this point is 7.4 eV, in reasonable agreement with the value obtained from refractive index dispersion data, and its pressure coefficient is 0.037 eV/GPa. With these values we obtain $(1/n)dn/dP=-0.24\times10^{-2}\,\mathrm{GPa}^{-1}$, which is in very good agreement with the value obtained experimentally. But it differs significantly from the value $-0.05\times10^{-2}\,\mathrm{GPa}^{-1}$ predicted by Camphausen.[10]

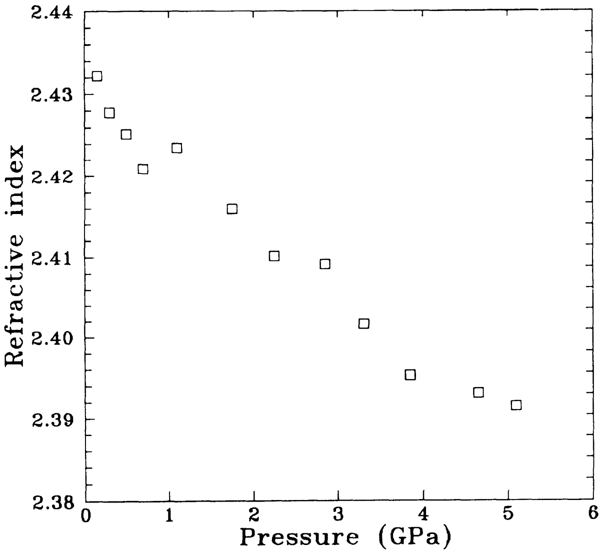

FIG. 8. Pressure dependence of the refractive index of GaN ($T=300$ K).

VI. DISCUSSION AND CONCLUSIONS

In this paper we present results of an examination of the electronic properties of GaN. Detailed experimental studies were possible thanks to the improvement in GaN single-crystal-growth technology. It turned out that the idea of applying high pressure for this purpose became very fruitful.

Very good agreement is obtained between theory and experiment for the value of the pressure coefficient of the main energy gap as well as for the pressure coefficient of the refractive index. We believe that this illustrates the quality of the employed theoretical approach to the electronic band structure of GaN. The study of the pressure behavior of material properties provides a sensitive test of the theoretical models used.

We find that the pressure coefficient of the energy gap of GaN does not fit the previously shown ionicity-dependence trend.[27] In Fig. 9 the dependence of dE_g/dP on ionicity for III-V and II-VI compounds is illustrated. We extended Fig. 15 of Ref. 27 by adding more III-V compounds (those with heavier anions), some representative of II-VI compounds and two nitrides, GaN and AlN. The value of the pressure coefficient for GaN is taken from the present work, and that for AlN is given by the very recent theoretical calculations.[28] The solid line shows the trend postulated in Ref. 27 for III-V compounds. One can see from the figure that there is strong

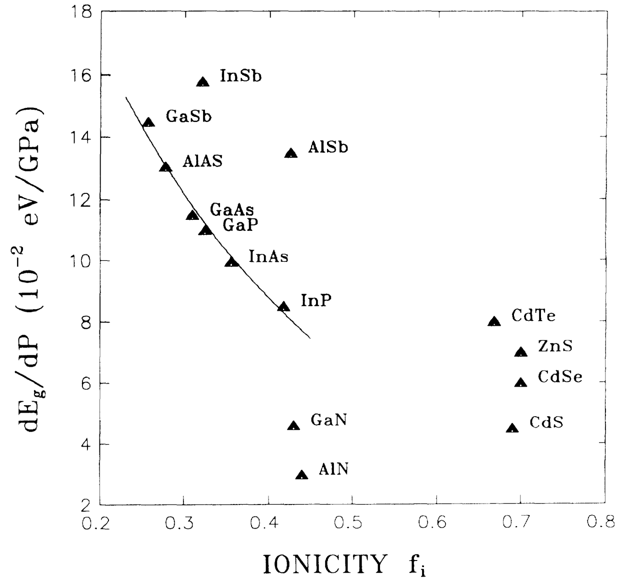

FIG. 9. Ionicity trend in dE_g/dP for various III-V and II-VI semiconductors (data for II-VI semiconductors and GaSb, Ref. 27; AlSb, theoretical value, Ref. 10; GaN, this work; AlN, Ref. 28; other data, Ref. 29). The solid line shows the trend suggested by Ref. 27.

deviation from the proposed trend for the compounds with much heavier or much lighter anion atoms. This once again proves the importance of other parameters, such as the atomic volume.

Considering the pressure dependence of the refractive index, it can be concluded that our work contradicts some suggestions concerning the trend in the value of the pressure coefficient of the refractive index. Previous theoretical calculations predicted a negative value of dn/dP for III-V compounds, a positive value for II-VI compounds, and a value of nearly zero for GaN, which is intermediate in an ionicity scale. Our results, both theoretical and experimental, do not confirm the latter result for the GaN crystal. It is worth noting that for tetrahedrally coordinated semiconductors all experimental dn/dP values known to us are negative.

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[1] S. Bloom, J. Phys. Chem. Solids **32**, 2027 (1971).

[2] D. Jones and A. H. Lettington, Solid State Commun. **23**, 815 (1972).

[3] J. Bourne and R. L. Jacobs, J. Phys. C **5**, 3462 (1972).

[4] S. Bloom, G. Harbeke, E. Meier, and I. B. Ortenburger, Phys. Status Solidi B **66**, 161 (1974).

[5] S. H. Grinayev, W. J. Malachow, and W. A. Czaldyszew, Izv. Vuz. Fiz. (USSR) **29**, 69 (1986).

[6] A. Zunger and A. J. Freeman, Phys. Rev. B **17**, 2030 (1978), and references cited therein.

[7] S. Porowski, I. Grzegory, and J. Jun, in *High Pressure Chemical Synthesis,* edited by B. Baranowski and J. Jurczak (Elsevier, Amsterdam, 1989).

[8] I. Gorczyca, N. E. Christensen, P. Perlin, I. Grzegory, J. Jun, and M. Bockowksi, Solid State Commun. **79**, 1033 (1991).

[9] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969); **187**, 1007 (1969); Phys. Rev. B **4**, 1479 (1973).

[10] D. L. Camphausen, G. A. Neville Conell, and W. Paul, Phys. Rev. Lett. **26**, 184 (1971).

[11] J. C. Phillips, Phys. Rev. Lett. **20**, 550 (1968).

[12] P. Perlin, C. Jauberthie-Carillon, J. P. Itie, A. San Miguel, I. Grzegory, and A. Polian, High Pressure Res. **7**, 96 (1991).

[13] J. Karpinski, S. Porowski, and J. Jun., J. Cryst. Growth **66**, 11 (1984).

[14] J. Grzegory, M. Bockowski, J. Jun, and P. Figurny, High Pressure Res. **7**, 284 (1991).

[15] R. Madar, G. Jacob, J. Hallais, and R. Fruchart, J. Cryst. Growth **31**, 197 (1975).

[16] D. Elwell and H. J. Scheel, *Crystal Growth from High-Temperature Solutions* (Academic, London, 1975).

[17] T. Kobayashi, Rev. Sci. Instrum. **56**, 255 (1985).

[18] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[19] N. E. Christensen, Phys. Rev. B **30**, 5753 (1984); M. Cardona, N. E. Christensen, and G. Fasol, *ibid.* **38**, 1806 (1988).

[20] G. B. Bachelet and N. E. Christensen, Phys. Rev. B **31**, 879 (1985).

[21] N. E. Christensen and O. B. Christensen, Phys. Rev. B **33**, 4739 (1986).

[22] H. Shultz and K. H. Thiemann, Solid State Commun. **23**, 815 (1977).

[23] I. Gorczyca and N. E. Christensen, Solid State Commun. **80**, 335 (1991).

[24] D. L. Camphausen and G. A. N. Conell, J. Appl. Phys. **42**, 4438 (1971).

[25] D. R. Penn, Phys. Rev. **128**, 2093 (1962); E. Tosatti and G. P. Parravicini, J. Phys. Chem. Solids **32**, 623 (1970).

[26] Y. F. Tsay, S. S. Mitra, and B. Bendow, Phys. Rev. B **10**, 1476 (1974).

[27] S. Adachi, J. Appl. Phys. **58**, R1 (1985).

[28] I. Gorczyca and N. E. Christensen (unpublished).

[29] *Numerical Data and Functional Relationships in Science and Technology,* edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein, New Series, Vol. 17 (Springer-Verlag, Berlin, 1982).

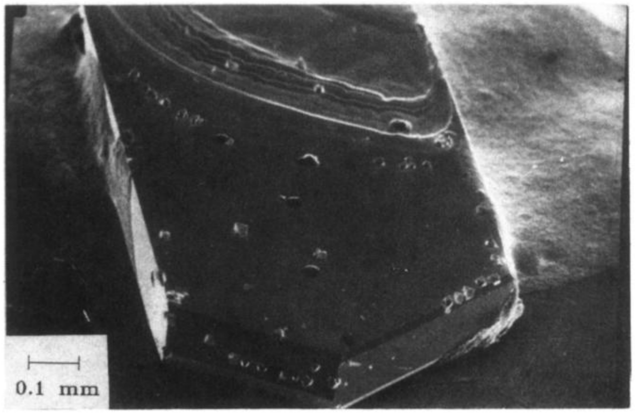

FIG. 2. GaN crystal grown from the solution at N_2 pressure of 1.7 GPa.