Phys. Soc., London 3, 59 (1970).
[11]F. Forstmann and J. B. Pendry, to be published.
[12]S. Wakoh, J. Phys. Soc. Japan 20, 1894 (1965).
[13]G. A. Burdick, Phys. Rev. 129, 138 (1963).
[14]B. Segall, Phys. Rev. 125, 109 (1962).
[15]H. D. Hagstrum and G. E. Becker, Phys. Rev. Letters 16, 230 (1966).
[16]H. D. Hagstrum, Phys. Rev. 150, 495 (1966).
[17]H. Ehrenreich and H. R. Philipp, Phys. Rev. 128, 1622 (1962).
[18]U. Gerhardt, Phys. Rev. 172, 651 (1968).
[19]A. N. Bloch and S. A. Rice, Phys. Rev. 185, 933 (1969).
[20]F. M. Mueller and J. C. Phillips, Phys. Rev. 157, 600 (1967).
[21]P. M. Edwards and J. Mathon, in Proceedings of the Solid State Conference of the Institute of Physics, Manchester, England, January 1970 (unpublished).
[22]L. M. Liebermann, D. R. Fredkin, and H. B. Shore, Phys. Rev. Letters 22, 539 (1969).

OPTICAL ABSORPTION AND VACUUM-ULTRAVIOLET REFLECTANCE OF GaN THIN FILMS

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Optical absorption of GaN thin films shows previously unreported structure at 3.8 eV, which is interpreted as the excitonic "knee" due to transitions across the fundamental direct energy gap previously thought to occur at an energy of about 3.4 eV. We also give the first report of the specular reflectance of GaN; peaks were observed at 6.8, 9.5, and 10.7 eV.

Until very recently, there have been no published optical-absorption or specular-reflectivity data on GaN, largely because no macroscopic single crystals could be made. Early values for the energy of the fundamental edge, ranging from 3.25 to 3.4 eV, have been obtained or inferred from diffuse reflectivity on GaN powder, from the highest-energy light emitted in photoluminescence or cathodoluminescence, and from photoconductivity on very small GaN crystals.[1] Recently work was reported of absorption measurements made on thick (50-100 μm) layers of GaN single-crystal films deposited pryolytically on Al_2O_3 or SiC substrates.[2] In this work, the authors fitted a curve of the type $(E-E_g)^n$ to their experimental data, obtained $E_g = 3.39$ eV, $n = 0.62$ as the best fit, and used this as evidence for a direct energy gap ($n = \frac{1}{2}$ in the simple one-electron model). However, the analytical function used to fit the absorption data neglects electron-hole interaction commonly needed to explain the shape of direct-gap absorption edges.[3]

The films used in this work for absorption and visible reflectance measurements were grown epitaxially on Al_2O_3 substrates by evaporating Ga in the presence of nitrogen activated by a microwave discharge.[4] In all these samples, the hexagonal GaN c axis was oriented perpendicular to the substrate, and essentially parallel to the direction of the incident light. A value of 2.03 ± 0.05 for the index of refraction was obtained at 1.6 eV for a thick sample from the ratio of the transmittance at an interference maximum to that of an adjacent minimum, knowing the index of refraction of the Al_2O_3 substrate.[5] From this value, the thicknesses of all films were obtained from measured interference fringes.

The transmittance in the absorption-edge region was measured, and using the known thickness the dependence of the absorption coefficient on photon energy was determined for each film. The reflectance was assumed constant for the wavelength range of this measurement, and the absorption coefficient was taken as $\alpha(\omega) = -(1/d) \ln t/t_0$, where t was the measured transmittance and t_0 the average transmittance in the visible part of the spectrum, where the film was transparent. For each film, the smallest α plotted was $\alpha \approx 0.25/d$, since smaller values are subject to considerable error. The results of these measurements are shown in Fig. 1. A shoulder appears in the absorption curves at about 3.8 eV for all the films measured.

In Fig. 1 we show also an absorption curve due to Vlasenko[6] for a polycrystalline thin film of cubic ZnS. This material is known to have a direct energy gap at 3.8 eV.[7] The strong resemblance between the shape of the ZnS and GaN absorption curves suggests that the shoulder in the GaN curve is caused by a direct energy-gap absorption, occurring at about 3.8 eV. Structure such as shown in the absorption curves of Fig. 1 is of a form which can be interpreted as due to a transition across a direct energy-gap minimum under conditions that the exciton peak is broadened and no peak is resolved. The analytic form

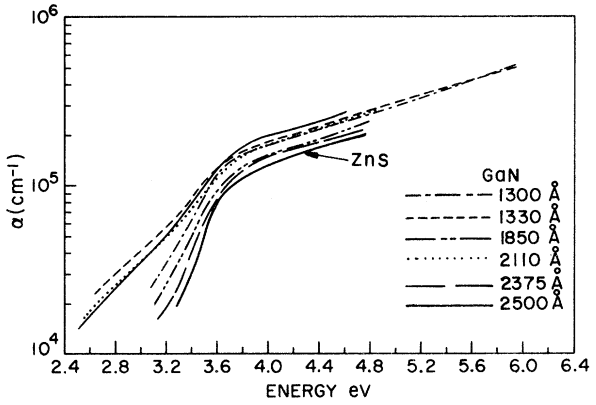

FIG. 1. Absorption constant versus photon energy for six GaN films, measured at 300°K. Also shown is a curve for ZnS from Ref. 6.

of the absorption coefficient between simple, parabolic energy bands, including electron-hole interaction, is given by[3]

$$\alpha = \frac{2\pi e^2\hbar}{m^2 c}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}|P|^2\frac{\epsilon_{ex}^{1/2}}{n\epsilon}\frac{\exp z}{\sinh z}, \quad \epsilon > \epsilon_g, \quad (1)$$

$$z^2 = \pi^2\epsilon_{ex}/(\epsilon-\epsilon_g),$$

where $\epsilon = \hbar\omega$ is the energy of the incident light, ϵ_g is the direct gap energy, m^* is the density of states reduced mass, n is the index of refraction, and $|P|$ is the momentum matrix element at the energy gap minimum. The quantity ϵ_{ex} is the excitonic binding energy, which is given in the weakly bound (hydrogenic) case as $\epsilon_{ex} = (m^*/m)(1/\kappa^2)$ Ry, where κ = the relative dielectric constant. Unlike the absorption coefficient obtained when electron-hole interaction is ignored,[3] Eq. (1) predicts a nonzero absorption at the energy gap (where $\exp z/\sinh z = 2$). We can estimate the magnitude of this absorption coefficient expected for GaN. Using the effective-mass theory of Kane[8] and assuming (1) an energy gap of about 3.8 eV, (2) negligible spin-orbit splitting in the valence band,[9] and (3) a value of the momentum matrix element between the conduction and valence bands which is comparable for direct transitions at the center of the Brillouin zone for all III-V zinc-blende compounds,[10] we obtain electron and hole effective masses $m_c^* \approx 0.19m$ and $m_n^* \gtrsim 0.6m$. The exciton binding energy expected is therefore about $\epsilon_{ex} \approx 0.16$ eV, using $\kappa \approx n^2$. Using the above values and the experimental absorption coefficient at the band edge in GaAs,[11] which has the largest direct energy gap of all III-V compounds extensively studied, the absorption coefficient predicted at the GaN energy gap is about $\alpha(\epsilon_g) \approx 2\times 10^5$ cm^{-1}. In view of the assumptions regarding the effective masses, dielectric constant, and matrix element, the close agreement of this number with the absorption coefficient on the shoulder of the measured curve is probably fortuitous. However, the agreement can at least be taken to show consistency in the interpretation of this shoulder as excitonic structure of a direct energy gap.

It might be expected that considerable sharpening of such excitonic structure would occur on cooling[11]; however, no appreciable change was noticed in the shape of spectra taken at about 100°K for either GaN or ZnS[6] thin films. The negative result in both cases may be due to large internal strains in the films caused by differential contraction between the film and substrate during cooling from the growth temperature (600°C for GaN films). It should be pointed out again that there is little doubt that the shoulder observed in the ZnS absorption curve is caused by transitions across the fundamental, direct gap in this material. Therefore, the lack of temperature dependence in the GaN absorption curve should not in itself disqualify the interpretation of the shoulder as due to direct-gap absorption.

The epitaxial samples discussed above had a slight surface roughness[4] which rendered them unsuitable for uv reflectance measurements. Therefore, we used several polycrystalline GaN films, which were deposited on fused quartz and which appeared smooth surfaced, to measure near-normal reflectance spectra from 4 to 12 eV. In Fig. 2 we show the uv reflectance spectra for two polycrystalline films of GaN. Peaks are seen at 6.8, 9.5, and 10.7 eV and are indicated by solid arrows. The rise in reflectance as the energy is decreased from about 5 to 4 eV may be the high-energy side of a peak occurring near 3.8 eV, where structure was observed in absorption. No reflectance measurements were taken for energies below 4 eV since for lower energies film transmission becomes appreciable and reflectance from the film-substrate interface begins contributing significantly to the measured reflectance.

The absolute magnitudes of the reflectances of these two samples differ somewhat and are significantly less than the reflectances reached by other III-V compounds. This lower reflectance and the difference between samples is believed due to surface irregularity and the resul-

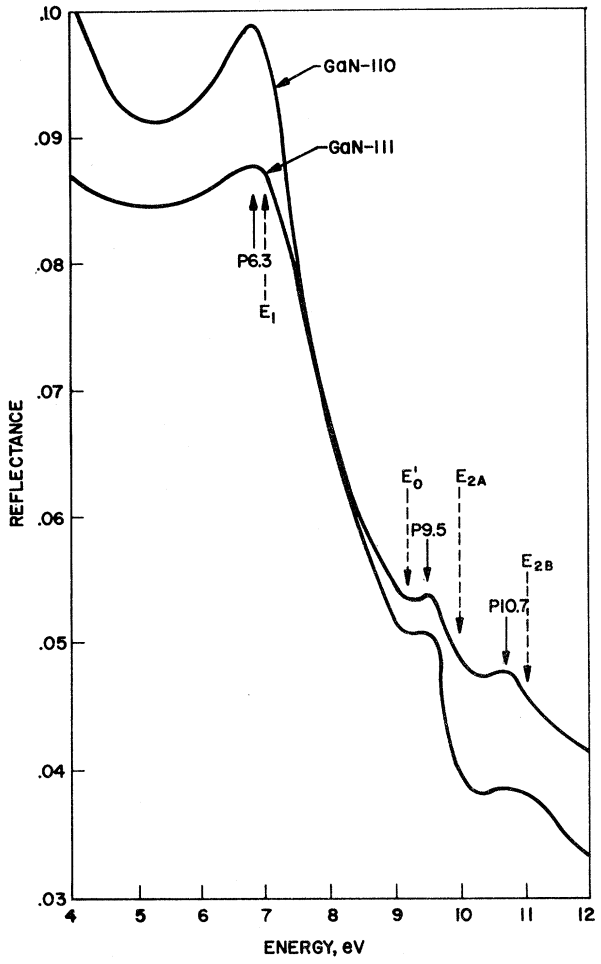

FIG. 2. Reflectance versus photon energy for two GaN films, measured at 300°K. Transitions corresponding to the labels are as follows: E_1, $L_{5,v} \rightarrow L_{3,c}$; E_0', $\Gamma_{1,v}\Gamma_{6,v} \rightarrow \Gamma_{1,c}\Gamma_{6,c}$; E_{2A}, $K_{3,v} \rightarrow K_{2,c}$; E_{2B}, $K_{2,v} \rightarrow K_{2,c}$.

tant diffuse scattering of some of the incident light. Although the absolute magnitude of the reflectance spectra measured on these samples is probably less than that which would be measured on bulk GaN, it is reasonable to expect that any structure seen in reflectance of these samples would also be characteristic of bulk GaN; in particular, the polycrystalline samples showed the same shoulder in absorption at 3.8 eV as seen for the epitaxial samples of Fig. 1, although at a slightly smaller value of absorption coefficient ($\sim 0.8 \times 10^5$ cm^{-1}).

The structure observed in the reflectance spectrum of GaN may be compared with direct-gap energies at different points in the Brillouin zone which have been predicted by means of the dielectric theory of electronegativity.[12] The predicted gap energies for all but the lowest energy gap are indicated by broken arrows in Fig. 2, together with the label indicating the symmetry of the valence and conduction band. It is seen that the structure observed in reflectance occurs near predicted gap energies. We have identified the structure seen in absorption at 3.8 eV with the lowest energy gap (E_0, or $\Gamma_{1,v}\Gamma_{6,v} \rightarrow \Gamma_{1,c}$), even though this gap is predicted to lie at considerably larger energy (4.8 eV).[12] In spite of this quantitative disagreement, however, the structure seen at 3.8 eV clearly seems to be of a form expected from a direct transition, and both the predictions and the structure measured in reflectance seem to indicate that the next higher direct gap transition occurs at much larger energy (6.8-7.0 eV).

The above discussion suggests that the lowest direct energy gap in GaN occurs near 3.8 eV. The possibility remains that the fundamental energy gap may be indirect, at lower energy than 3.8 eV, and undetected by our absorption measurements. However, the qualitative agreement between the energies of the theoretically predicted structure and the measured structure strengthens our confidence in the theory and its prediction that the fundamental energy gap is direct.[12]

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[1]E. Kauer and A. Rabenau, Z. Naturforsch. 12a, 942 (1957); H. G. Grimeiss, R. Grath, and J. Maak, Z. Naturforsch. 15a, 799 (1960); H. G. Grimeiss and H. Koelman, Z. Naturforsch. 14a, 264 (1959).

[2]H. D. Maruska and J. J. Tietjen, Appl. Phys. Letters 15, 327 (1969).

[3]T. P. McLean, in *Progress in Semiconductors*, edited by A. F. Gibson, R. E. Burgess, and F. A. Kroger (Wiley, New York, 1960), Vol. V, p. 53.

[4]B. B. Kosicki and D. Kahng, J. Vac. Sci. Technol. 6, 593 (1969).

[5]J. C. Burgiel, Y. S. Chen, F. Vratny, and G. Smolinsky, J. Electrochem. Soc. 115, 729 (1968).

[6]N. A. Vlasenko, Opt. i Spektroskopiya 7, 511 (1959) [Opt. Spectry. (USSR) 7, 320 (1959)].

[7]D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Status Solidi 9, 645 (1965).

[8]E. O. Kane, J. Phys. Chem. Solids 1, 239 (1957).

[9]R. Braunstein and E. O. Kane, J. Phys. Chem. Solids 23, 1423 (1962).

[10]H. Ehrenreich, J. Appl. Phys. 32, 2155 (1961).

[11]M. D. Sturge, Phys. Rev. 127, 768 (1962).

[12]J. A. Van Vechten, Phys. Rev. 187, 1007 (1969).