

THE PREPARATION AND PROPERTIES OF VAPOR-DEPOSITED SINGLE-CRYSTALLINE GaN

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Single-crystalline, colorless, GaN has been prepared by a vapor-phase growth technique previously used to prepare GaAs, GaP, and GaSb. These crystals are the first reported specimens of GaN suitable for good electrical and optical evaluation of this compound. It has been determined that GaN has a *direct* energy bandgap of 3.39 eV, and that undoped crystals prepared by this method have a very high inherent electron concentration, typically above $10^{19}/\text{cm}^3$, which is probably related to a high density of nitrogen vacancies. Conducting *p*-type specimens have been prepared using Ge as the dopant; but this result has been difficult to reproduce, and the samples have been electrically inhomogeneous.

A large amount of work has been expended for the preparation and characterization of III-V compounds having bandgaps corresponding to the spectral range from the infrared to the middle of the visible spectrum. In general, this involves compounds formed from the Group V elements As, P, and Sb. In contrast, for the nitrogen-containing compounds which have relatively large bandgaps (extending through the visible and into the ultraviolet) very little work has been reported despite their potential for use as photoconductors, in both cathodo- and electroluminescent devices, and for high-temperature applications.

One nitride of particular interest is GaN, since its bandgap corresponds to the edge of the ultraviolet and, therefore, could be applicable to the entire visible spectrum. The work that has been reported has, in general, described the preparation and properties of polycrystalline deposits, usually prepared by the reaction of NH_3 with Ga,¹ Ga_2O_3 ,² or GaP.³ The only report of single-crystalline material involves small needles, only a few microns in length.⁴ It is significant that very little reported work deals with the growth of GaN from the vapor phase. In contrast, vapor-phase growth techniques have played an important role in the preparation and characterization of GaAs,⁵ GaP,⁶ and GaSb.⁷ In particular, a compatible method^{7,8} has been developed for the preparation of these compounds in which the respective hydrides AsH_3 , PH_3 , and SbH_3 serve as the sources of the Group V elements, and Ga is transported as its subchloride via a reaction with HCl gas. This technique has now been further extended for the preparation of GaN by using NH_3 as the source of nitrogen.

The apparatus used in this study is essentially identical to that described previously,⁸ with the exception that NH_3 is used in place of the other Group V hydrides. It is primarily comprised of a straight tube through which the pertinent gaseous species flow to provide chloride transport of metallic gallium, and subsequent reaction of these transport products with ammonia to form GaN on a substrate surface.

With the exception of the ammonia⁹ and $\langle 0001 \rangle$ -oriented sapphire single-crystalline substrates,¹⁰ the materials employed in this study are as described previously.⁶ The sapphire substrates were mechanically polished¹⁰ to a flat mirror-smooth finish, and then heat-treated in hydrogen at 1200°C , prior to their introduction to the growth apparatus. Typical substrate dimensions were about 2 cm^2 in area and about 0.25 mm thick.

The growth procedure also closely follows that described previously.⁸ Freshly heat-treated substrates are inserted into the deposition zone of the growth chamber and heated in hydrogen at a rate of about $20^\circ\text{C}/\text{min}$. When the final growth temperature is reached, the NH_3 flow is started and, after a 15-min period to allow the NH_3 concentration to reach a steady-state value, the HCl flow is started to provide transport of the Ga and deposition of GaN.

The flow rates of pure HCl and NH_3 are about 5 and $400\text{ cm}^3/\text{min}$, respectively, and an additional 2.5 liters/min of hydrogen is used as a carrier gas. With these flow rates, a substrate temperature of 825°C , a Ga-zone temperature of 900°C , and a center-zone (that region between the Ga and deposition zones) temperature of 925°C , growth rates of about $0.5\text{ }\mu/\text{min}$ are obtained under steady-state conditions. Typical thicknesses for these deposits have been in the range of $50\text{--}150\text{ }\mu$. Doping is accomplished, during the growth process, by introducing the dopant to the growth apparatus, either as its hydride or by direct evaporation of the element into a hydrogen-carrier gas.

X-ray analysis by the Debye-Scherrer technique indicates that these layers are single phase, hexagonal GaN, having the wurtzite structure and lattice parameters $a = 3.189\text{ }\text{\AA}$, $c = 5.185\text{ }\text{\AA}$, at room temperature. The lattice parameter is presented as a function of temperature in Fig. 1 for the range $300\text{--}900^\circ\text{K}$. These data were obtained by means of powder patterns taken every 100°K with a Unicam high-temperature camera. From these data, a mean coefficient of thermal expansion for the a direction is determined to be $5.59 \times 10^{-6}/^\circ\text{K}$ for the entire

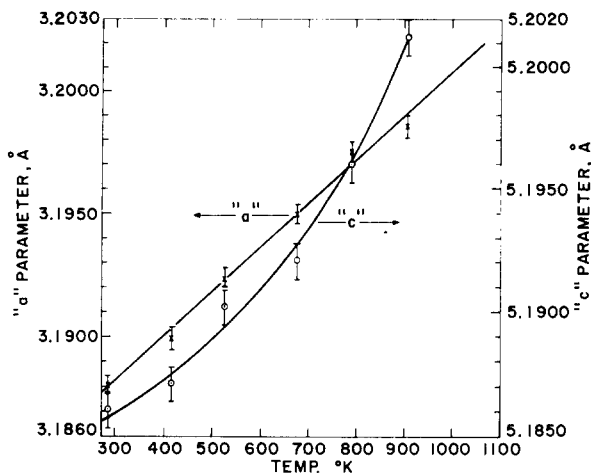


Fig. 1. Dependence of the lattice parameters of GaN on temperature.

temperature range investigated, while for the c direction, values of 3.17×10^{-6} and $7.75 \times 10^{-6}/^\circ\text{K}$ are approximated for the temperature ranges 300–700 $^\circ\text{K}$ and 700–900 $^\circ\text{K}$, respectively. Laue back-reflection patterns show this material to be single-crystalline and epitaxial, having a (0001) orientation.

The GaN prepared by this technique was found to be insoluble in H_2O , acids, or bases at room temperature. It dissolves slowly in hot alkalis, a sample weighing 150 mg taking 24 h to completely dissolve in boiling NaOH. Emission spectrographic and mass spectrometric analyses indicate a total impurity content of less than 10 ppm and less than 1 ppm of any one impurity.

Room-temperature optical-absorption measurements on undoped GaN reveal a very sharp absorption edge, as shown in Fig. 2, and on the high-energy side of this edge, the absorption coefficient obeys the general relationship

$$\alpha = \alpha_0(E - E_g)^n,$$

where E is the photon energy, and E_g is the energy of the bandgap.¹¹ From the absorption data, E_g and n were determined to be 3.39 eV and 0.62, respectively. The value of 0.62 is indicative of a *direct* transition across the energy gap and is consistent with values obtained for other direct bandgap III-V compounds.¹² The value for E_g of 3.39 eV obtained in this study is slightly larger than the previously reported value of 3.26 eV.¹³

These epitaxial layers were examined by conventional Hall coefficient and resistivity measurements. Undoped samples are n -type, having typical electron concentrations in the range of 1 to $5 \times 10^{18}/\text{cm}^3$ and room-temperature mobilities of between 125 and 150 $\text{cm}^2/\text{V sec}$. These high mobility values for such high carrier concentrations also support the contention that GaN is a direct bandgap semiconductor. Since the total impurity content of these crystals is at least two orders of magnitude

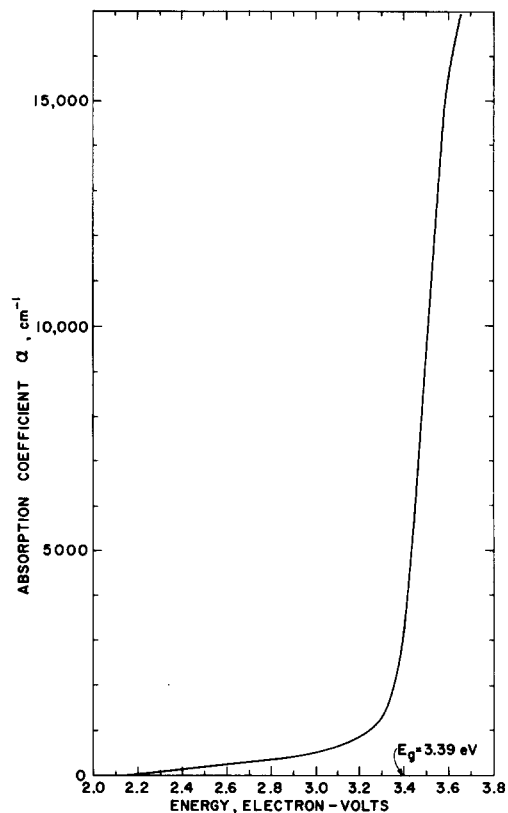


Fig. 2. Dependence of the absorption coefficient on energy for GaN.

too low to account for the high inherent donor concentration, it is suspected that the donor is related to a native defect, probably a nitrogen vacancy. In this regard, it should be noted that GaN dissociates to liberate nitrogen at temperatures as low as 600 $^\circ\text{C}$.²

Preliminary experiments have been carried out in an effort to dope these GaN layers with acceptor impurities. The impurities studied to date include, Zn, Mg, Hg, Si, and Ge. Both Zn and Mg produce high-resistivity material ($\rho > 10^9 \Omega\text{-cm}$) and color the normally colorless GaN orange and yellow, respectively. Evidently, both of these impurities are introduced as deep acceptor states. Hg-doped samples remained highly conducting n -type, undoubtedly due to a relatively limited solubility of Hg in GaN at the growth temperature. Emission spectrographic analysis revealed that Hg had not been incorporated in the GaN in concentrations greater than 30 ppm.

Consistent with the hypothesis that these GaN layers have a very high density of nitrogen vacancies, the Group IV elements, Si and Ge, are attractive candidates as p -type dopants, since they are readily introduced to the growth apparatus in the form of their hydrides, and as substitutes for nitrogen sites, should behave as acceptor states. Indeed, the best success was achieved with these impurities. In the case of Si, substantial compensation

was achieved without introducing a color to the GaN, indicating that Si is probably a shallow acceptor. However, to date, although the carrier concentration has been reduced to as low as $3 \times 10^{18}/\text{cm}^3$, Si-doped samples have all been *n*-type.

With Ge doping, conducting *p*-type behavior has been achieved. Two layers have been prepared with resistivities of 0.01 and 0.94 $\Omega\text{-cm}$ for hole concentrations of 6×10^{19} and $6 \times 10^{18}/\text{cm}^3$, respectively. While this result is encouraging since it demonstrates that a fundamental mechanism does not exist which prevents amphoteric doping of this compound, it has been very difficult to reproduce and the layers are nonuniform, with some regions of the sample being *n*-type.

This aspect of the research of GaN will be continued to provide a more detailed description of the role of acceptor impurities in this compound, and will be the subject matter of a later publication.

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SUPERCONDUCTING PROPERTIES OF NIOBIUM-TITANIUM-NITRIDE THIN FILMS*†

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A series of Nb-Ti-N films have been prepared, with various Nb/Ti ratios, by a high purity, reactive sputtering process. A maximum in transition temperature (at $\sim 15.5^\circ\text{K}$) has been obtained for a composition of $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{N}$. Critical field and critical current measurements indicate a degradation in these properties with increasing titanium content, contrary to results reported previously.

Superconducting critical temperatures up to about 18°K have been reported for a number of the B1 structure (rocksalt) compounds based upon the Group IV and Group V transition metals.^{1,2} In bulk form, these compounds exhibit lower critical current densities J_c and smaller values of upper critical field H_{c2} than high T_c compounds of the well-known A15 structure (β -W). We recently found, by careful attention to purity, that thin films of NbN can be made with T_c around 15°K , which is equal to the bulk material T_c . Moreover, we have found that the high-field properties of NbN are greatly im-

proved when prepared in thin film form.^{3,4} In this paper, we report on the superconducting properties of thin films in the Nb-Ti-N system.

The films in this investigation were prepared by a high-purity sputtering technique similar to that previously used for the deposition of NbN films.³ This technique involves deposition in a system with a total background pressure, prior to sputtering, of 5×10^{-10} Torr or less, and the use of high substrate temperatures (500°C). To obtain films of various compositions, flat sputtering cathodes were used, made either from a Nb-Ti alloy or from pure niobium and titanium welded together into a single cathode. The compositions of the films were estimated either from the composition of the Nb-Ti alloy, or from the location of the substrates, when the two-section niobium and titanium cathode was used.

In our experiments the addition of titanium to

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