III-V Nitrides for Electronic and Optoelectronic Applications

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Continued development and commercialization of optoelectronic devices, including light-emitting diodes and semiconductor lasers produced from III-V gallium arsenide-based materials, has also generated interest in the much wider bandgap semiconductor mononitride materials containing boron, aluminum, gallium, and indium. The majority of the studies have been conducted on pure gallium nitride thin films having the wurtzite structure, and this emphasis continues to the present day. However, recent research has resulted in the fabrication of p-n junctions in cubic boron nitride, the deposition of cubic gallium nitride, as well as the fabrication of multilayer heterostructures and the formation of thin film solid solutions. Chemical vapor deposition (CVD) has usually been the technique of choice for thin film fabrication. However, more recently these materials have also been deposited by plasma-assisted CVD, reactive ionized-cluster beam deposition, and reactive and ionized molecular beam epitaxy. The objective of this paper will be to review the recent developments in all the III-V nitride thin film materials vis à vis electronic and optoelectronic applications.

I. INTRODUCTION

The commercial realization of light emitting diodes and semiconductor lasers in the previous decade generated much interest in thin films of the wider bandgap semiconductor III-V mononitrides, especially GaN. As noted in Table 1, the latter material, in the wurtzite form, has a bandgap of 3.45 eV (near UV region) at room temperature. It also forms a continuous range of solid solutions with AlN (6.28 eV) and InN (1.95 eV). Thus optoelectronic devices having specifically engineered bandgaps with energies from the visible to the deep UV region are theoretically possible with these materials. The wide bandgaps of these materials and their strong atomic bonding also makes them candidates for high-power and high-temperature devices, assuming appropriate doping impurities are available and can be incorporated on the crystal lattice sites.

By contrast, films of cubic (c) BN have been of interest primarily for wear and corrosion resistant, electrically insulating and passivating surfaces which can be used in high temperature and/or corrosive environments. Cubic BN also has considerable applications in the machining of steels where diamond tools cause problems as a result of the transfer of C into the metal following transformation to graphite at the hot interface. Moreover, electrically active, moderately shallow n- and p-type dopants exist for cBN, and considerable interest in this material for microelectronic applications has been stimulated by the recent creation of a p-n junction diode having a portion of its emission spectra in the ultraviolet.

In the following subsections, reviews of the development of thin films of these materials and their current status are presented. The problems which are currently limiting the development of these materials and devices made from them are also discussed.

II. REVIEW AND CURRENT STATUS OF III-V NITRIDES WITH AN EMPHASIS ON ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

A. Cubic Boron Nitride

Boron nitride has no counterpart in nature. By analogy to C, it exists as a soft, hexagonal, graphite-like material; as
an extremely hard cubic form (zincblende structure); and as
an equally hard hexagonal (hBN wurtzite) form [1]. The
graphic form of BN is used as a refractory material and
a lubricant. The cubic form is produced under equilibrium
conditions only at high temperatures and high pressures
[2]. It is used primarily as an abrasive grain. But it is
this material which is now attracting attention in terms of
synthesis at lower temperatures and pressures in a manner
recently developed for diamond. The applications would
be for hard coatings and high-power, high-temperature
electronics.

The first experimental evidence for the fabrication of
either hBN or cBN under nonequilibrium conditions was
reported by Sokolowski [3]. He used a reactive pulse
plasma crystallization technique which involved an electric
discharge between electrodes made of B and Cu contained
in an atmosphere of 3:1 N2 and H2. The plasma reaction
products were thin layers containing B and N which were
deposited on metal substrates held at 300 K. The primary
phase which occurred was hBN. This research was subse-
sequently expanded by Weissmantel and coworkers [4]-[6]
who formed hard films with characteristics of cBN using
both ion beam plating of electron-beam evaporated B and
N2 ions and ion beam deposition using the precursor of
borazine (B3N3H6). The substrates were not heated. These
investigators referred to this material as "i-BN" to indicate
the critical role of ion bombardment in the growth process.
The films were mostly amorphous, but contained 5–20nm
cBN crystallites. Electron energy loss spectroscopy results
confirmed the presence of this crystalline phase. These
investigators also employed a dual ion beam technique
involving (1) a sputtered beam from a B or BN target and
(2) an N ion beam.

Weissmantel et al. [6] noted that the properties of the
films were very dependent upon processing conditions,
however, the relationships were never defined. They sug-
gested that ionic species were essential to the process,
although this was not confirmed experimentally. A criticism
of the techniques is that they were not configured such as to
provide a systematic identification of the species involved in
the reaction, thus making improvements in the film quality
difficult.

Shanfield and Wolfson [7] also extracted ions from a
borazine plasma using a Kaufmann source and accelerated
them to 100 eV onto the substrate. X-ray spectra of the
samples showed peaks of cBN. Auger analysis yielded a
B/N ratio of 1:1. Almost simultaneous with this research
was that of Satou and Fujimoto [8] who employed a
sophisticated combination of the electron beam evaporation
of B and the production of N2⁺ ions. The latter species were
derived from a Penning discharge source used for plasma
generation and accelerated through a magnetic sector for
mass and energy analysis. The N2⁺ ions also passed through
a focusing magnetic lens system and a suppressor which
controlled the secondary electron output from the Ta and
NaCl substrates. The evaporation of the B and the N2⁺
bombardment of the substrates occurred simultaneously.
Their deposition rates were controlled separately using
a thickness monitor for B and by the beam current for
N2⁺. The substrates were maintained at room temperature.
Various N/B ratios were used. The resistivity of the films
increased markedly at a ratio of 1.0. At a ratio of 1.8, N
was incorporated in the form of bubbles, and the films
were amorphous (or extremely fine grained). At a ratio
of 2.5, fairly large grains of hBN (wurtzite) and cBN
were observed by electron microscopy and selected area
diffraction. No information regarding the better substrate
for deposition was noted.

In research conducted by Chopra et al. [9] and more
recently by Lin et al. [10] a modified activated reactive
evaporation (ARE) process was used to prepare coatings
containing cBN via evaporation of H2BO3 in an NH3
plasma. ARE involves the electron beam or resistance
heated evaporation of a metal or a compound in the
presence of a reactive gas. In this case, the B2O3 formed
by the decomposition of H2BO3 was reduced by atomic
H to B which reacted with the atomic N produced in the
plasma to form BN. Various substrates including steel and
fused quartz as well as Si and NaCl single crystals were
used. Microstructural (TEM and selected area diffraction),
optical (UV-IR transmission spectra and optical band gap
measurements) and hardness studies indicated the existence
of the zincblende [9] or a simple cubic (a most unusual
form) [10] structure of cBN in the polycrystalline films.
No hexagonal phase was detected.

Inagawa and coworkers [11] have borrowed from the
research of the previous investigators in their use of electron
beam evaporated B (with either a standard 270° deflection
type gun or a hollow cathode discharge gun) and plasma
activated N to deposit cBN on substrates RF biased in the
range of 0 to -600 V. The schematics of this equipment
are shown in Fig. 1. The simultaneous addition of Ar into
the N plasma considerably assisted the formation of cBN,
as shown in Figs. 2 and 3. At an Ar/N2 ratio of 4:1, the
films contained virtually 100% of the cubic phase.

A more recently published study of cBN deposition using
electron beam evaporation and an electrical arc to create
a plasma (reactive ion plating technique) has been that of
Ikeda et al. [12]. The Si substrate was held at 725 K. An RF
bias was also applied to the substrate. It was determined
that the bias potential played an important role in the formation
of the cBN films. Infrared spectra revealed the presence of
cBN, and TEM showed that the microstructure consisted of
100 Å average diameter grains of cBN deposited on an
amorphous BN layer located on the substrate surface.

Wiggins et al. [13] and Seidel et al. [14] have used RF
reactive sputtering. The structure of the film was not deter-
ned in the former study, however cBN was obtained in the
latter research. Sharp diffraction rings were obtained in
TEM when the bias potential was increased to a maximum
of -33% in combination with an increase in the partial
pressure of N2 to a maximum of 1.3 x 10⁻² mbar (P_total =
2 x 10⁻² mbar). This corresponded to nearly stoichiometric
films. The films consisted of microcrystals with diameters
in the range from 50-to-1000Å. Calculation of the lattice
parameter from the diffraction patterns corresponded to the
3.61 Å for cBN. It was estimated that nearly the whole film consisted of cBN microcrystals. Raising the substrate temperature from ambient to 573 K did not markedly change the microstructure or the diffraction patterns of the films.

As noted in the first paragraph of this subsection, cBN is a nonequilibrium phase at the temperatures and pressures used in the experimental programs described above. As such, nonequilibrium routes which imparted additional internal and activation energies to both the B and especially the N₂ have been used to ensure that a higher energy phase would be deposited. Successful deposition of cBN has been attained. However, as pointed out in a recent review by Arya and D'Amico [15] concerning the preparation, properties, and applications of BN, the films have been polycrystalline and mixed with other amorphous or hexagonal phases of BN.

The one apparent exception to the last statement is the recent work of Doll et al. [16]. These investigators used laser (KrF) ablation of hot pressed or pyrolytic BN (both forms have the graphitic structure) in an ultrahigh purity N₂ environment (1-10⁻⁷ Torr) to achieve the first successful heteroepitaxial growth of pure cBN. The laser operating conditions included a fluence of 1.5J/cm², pulse length of 22 ns, power density of 0.2 gigawatts/cm² and a frequency of 6 kHz. The optimum temperature for the Si (001) substrates was 673 K. Numerous 20-40 μm diameter pinholes in the films at this temperature may have some strain accommodation-related importance regarding the achievement of pure cBN, as they were absent under conditions (higher and lower temperatures) where it did not occur or was present to a limited extent. Electron diffraction showed preferred orientation of the (011) plane of the very small grain size polycrystalline cBN with the Si (001) plane; the planar spacing is such that three times the value for Si is within 1% of twice the value of cBN. X-ray and electron diffraction showed the cBN lattice constant to be 3.615 Å or exactly that expected for this material. They examined the ablated plume with a second laser and found B⁺, B₂, and N₂ but no BN molecules. Apparently the cBN forms and grows at the Si surface. Auger electron spectroscopy indicated a homogeneous nonstoichiometry of B_N0.8; however, the N/B ratio could be increased if NH₃ was used. Device fabrication on these films is being contemplated by the investigators.

At this writing, the only devices in cBN have been recently produced under high-pressure conditions. Mishima et al. [17] have fabricated p-n junctions in cBN single crystals by growing the initial crystal in a solvent of LiCaBN₂ containing the donor dopant of Si under the conditions of 55 kbar and 2075 K (at the cBN seed crystal) using a temperature difference method. The second crystal
surrounded the first and was obtained under the same conditions except that the solvent contained the acceptor species of Be. The resistance of the individual Be-doped and Si-doped crystals at room temperature was $10^2 - 10^3$, and $10^3 - 10^4$, respectively, while that of the undoped crystal was $>10^6$. The temperature dependence of the resistance of each of these materials is shown in Fig. 4 to $\approx 873$ K. The activation energies for the Be- and Si-doped materials, estimated from the slopes of the lines in Fig. 4, are $0.23 \pm 0.02$ eV and $0.24 \pm 0.03$ eV, respectively.

The diode was functional from room temperature to $923$ K [18], as shown in Fig. 5. The measurement became unstable with the onset of a large leakage current at $973$ K. Finally, injection luminescence in the ultraviolet was observed for the first time [18]. As shown in Fig. 6, the total spectra extended from $\approx 215$ nm to the red with a few peaks in the ultraviolet. Curves A and B in Fig. 6 are injection luminescence spectra under forward bias conditions with the junction currents indicated. The two patterns are likely a result of crystal nonuniformity, especially in doping and reproducibility in forming the electrode.

The principal roadblocks to the development of the high pressure technique is the resulting crystal size and the necessity to use the high pressure batch process. In addition, good ohmic contacts to n- and p-type material must be found and suitable insulating materials and methods of dry etching must be developed if high-power, high-frequency, and high-temperature devices are to be realized even from the materials produced at high pressures.

**B. Aluminum Nitride**

The properties of AlN indicate that it has great potential for several applications. The direct band gap of 6.28 eV [19] suggests the possibility of windows which would transmit light in the ultraviolet region of the spectra and, if properly doped, optoelectronic devices which would emit light in the same spectral region. Second harmonic generators have also been proposed to make use of the high nonlinear optical susceptibilities [20]. This material also possesses the highest reported surface acoustic wave velocity (Raleigh $V_R=6-6.2$ km/s, longitudinal $V_L=11-12$ km/s [21]-[23]) reported for any material and a substantial electromechanical coupling coefficient (to 1% [24]). In addition, it is distinguished by high hardness (1800 on Knoop scale), chemical stability, transparency in the visible, infrared (and ultra-violet) ranges, a melting point in excess of $2275$ K [25], high electrical resistivity ($\rho \geq 10^{13}$ cm) and excellent thermal conductivity. These last two properties coupled with a static dielectric constant of $\approx 9.0$ have been commercially exploited in recent years in the manufacture of sintered polycrystalline ceramic heat sinks and substrates for semiconductor chips [29]. The material is also unaffected by electromagnetic radiation, electron and ion bombardment or shock waves (to 59 GPa) [26]. These properties (especially the acoustic) strongly indicate that superior surface acoustic wave devices, operational in aggressive media and under extreme conditions both
as sensors for high temperatures and pressures and as acousto-optic devices [21]-[23], [24] can be developed. However, progress regarding these (and other) applications is hampered by the lack of good single crystals. To this end, several studies have been directed toward the achievement of monocrystalline films of this material.

The research conducted prior to 1975 has been reviewed extensively by Duffy [28]. In brief, reactive sputtering, plasma discharge, sublimation, and chemical vapor deposition (CVD) were used in this earlier period, with CVD being by far the most widely employed. Aluminum nitride films having single crystal character were deposited on Si, α-Al2O3 (sapphire), MgAl2O4, and a-Sic [29]-[37]. Street and coworkers [19] and Callaghan et al. [35] noted that several orientations of AlN with varying degrees of crystalline perfection may be produced simultaneously on (0112)-oriented (R-plane) sapphire substrates by the chloride process. In contrast, AlN films grown by the metal-organic process are (1120)-oriented (A-plane) [34], [36], [37]. This latter orientation is of greatest interest for surface acoustic wave applications. Unfortunately, essentially all the films grown on sapphire using either the chemistries or the crystallographic planes noted above resulted in highly faceted films (see [28] for a collection of micrographs on various sapphire planes).

Liu et al. [37] also deposited films on polished surfaces of previously grown AlN films. However, the microstructure of the original films and those deposited on AlN surfaces were similar in appearance. Numerous morphological features including scale-like structures, ridge-like formations, and “bow-tie” shaped grains were evident. Preliminary results indicated that the interfacial strain extended approximately 1 μm into the AlN film. Surface acoustic properties were also measured and found to strongly correlate with the quality of the AlN films.

Recent AlN deposition programs have used either past techniques with some modifications to the equipment and/or a change in the reactant species or a completely different approach. An example of the latter is the study by Harper and coworkers [38] who used a dual ion beam technique to supply a flux of Al from the Ar+ ion beam (1500 eV, 37 mA) sputtering of an Al target simultaneous with the low energy N2+ (100-500 eV, 8 mA) bombardment of the growing film. All films were deposited on graphite substrates at ambient temperature. In this reactive deposition of AlN, ion-assisted chemistry (i.e., collisionally induced dissociative N2 chemisorption), trapping and preferential sputtering all played strong roles in controlling the film composition. A wide range of arrival rate ratios (0 ≤ N/Al ≤ 1.6) was obtained in each deposition run, producing a composition range of (0 ≤ N/Al ≤ 1.0) across each film. The film composition varied linearly with N arrival flux and saturated at the composition of stoichiometric AlN with the rejection of excess N. For stoichiometric films, the texture and microstructure depended strongly on the N2+ flux and ion energy. For low ion energies (100 eV) and flux, the films formed with the c-axis perpendicular to the film surface, whereas for high ion beam energies (500 eV) the c-axis was close to the plane of the film. All films were polycrystalline. The AlN grain size increased with N2+ energy. The microstructure was found to be determined primarily by chemical driving forces, but was assisted by ion-enhanced diffusion and reaction.

Recently there has been a return to the use of CVD-related techniques but with new reactant materials or with the introduction of plasma. Matloubian and Gershenson [39] used trimethylaluminum (TMA), NH3, and (0001) sapphire and a substrate temperature range of 673-1473 K. Monocrystalline AlN films were only obtained at 1473 K. Itoh et al. [40] deposited AlN films on graphite using RF (13.56 MHz) plasma-enhanced CVD (at 50-500 W) using mixtures of Br2, N2, H2, and Ar and substrate temperatures in the range of 473-1073 K. The deposition rate was strongly dependent on all these parameters as well as the linear flow velocity and the total pressure. Fine grained polycrystalline films were deposited at 973 K under a total pressure of <10 torr. Translucent polycrystalline AlN films having (0001) preferred orientation were deposited in the range 15-40 torr at the same temperature. Finally, Dryburgh [41] has obtained AlN via reaction between Al2Se and N2 in the temperature range 1815-1873 K using a unique CVD reactor. The orientations of sapphire were used as the substrates. Reaction between sapphire and N2 at T>1473 K caused roughening of the surface of the former and partial replacement of Al2O3 by AlN.

Two major related problems with the use of sapphire for the growth of AlN are (a) the significantly different expansion coefficients and (b) the fact that the anisotropies in these coefficients for these two hexagonal crystals are in the opposite senses: for AlN, αLC > αIC while for Al2O3, αLC < αIC. The poor results usually obtained in the attempts to grow smooth, monocrystalline layers of this material are thus explained. The same is true for GaN, the material under discussion in the next subsection.

C. Gallium Nitride

Of all the III-V nitrides, GaN has been the most studied for optoelectronic applications. Films of GaN have been grown from the vapor phase by several techniques including low and high pressure CVD, plasma-enhanced CVD, reactive ionized-cluster beam deposition, and reactive and ionized molecular beam epitaxy. Reactive sputtering of gallium in NH3, N2-NH3, or N2-Ar mixtures and solution growth from Ga or Ga-Bi mixtures have been occasionally used to grow crystalline or amorphous films and small bulk crystals, respectively. Sapphire has been the most widely used substrate, although its lattice parameters and coefficients of thermal expansion are about 23% and about 25% greater, respectively, than those of GaN. Recently, films of cubic β- and wafers of hexagonal α(6H)-SiC and GaAs single crystals have been employed as substrates. The potential applications of GaN include light emitting devices and UV emitting lasers, electrooptic, piezoelectric
and acoustooptic modulators, and negative-electron affinity devices. Two reviews of the deposition methods and luminescent properties of this material have recently appeared [42], [43]. The reader is referred to these references and their bibliographies for a detailed and historical summary through 1988. The following summarizes selected portions of the research since that time.

The recent research regarding pure GaN has been concerned with four main aspects: (1) achievement of the cubic $\beta$-GaN, (2) the use of unusual techniques to deposit the material at low ($< 1300$ K) temperatures, (3) the application of an AlN buffer layer between the substrate (usually sapphire) and the GaN film, and (4) the use of electron beams to achieve p-type material and p-n junctions.

The first reference to the apparent achievement of the cubic (zincblende structure) $\beta$-GaN is to the research of Mizuta et al. [44]. These investigators employed trimethylgallium and hydrazine, as the Ga and N sources, respectively, and GaAs (100) substrates. X-ray precession measurements indicated cubic GaN; however, the diffracted intensity from the extremely thin film was very weak. Moreover, the RHEED data indicated the presence of the common hexagonal structure. Positive evidence for the growth of monocrystalline, epitaxial $\beta$-GaN has been reported by Paisley et al. [45]. This was achieved at 773–973 K using gas-source MBE with thermally evaporated Ga and atomic N and $N_2^+$ derived from a microwave plasma source as the reactants and cubic $\beta$-SiC (100) as the substrate. Transmission electron microscopy studies showed the 170 nm films to be cubic and to contain threading dislocations and microtwins near the interface, the concentration of which decreased rapidly after 25 nm of growth. RHEED patterns confirmed the cubic nature of the films. Auger electron spectroscopy indicated a nominally stoichiometric GaN film. The lattice parameter and bandgap were determined to be 0.454 nm and 3.26 eV, respectively.

More recently, two groups at the University of Illinois, namely Powell et al. [46] and Morkoc [47] have achieved $\beta$-GaN on MgO (100) and GaAs (100), respectively, using modified MBE techniques including an ion source and an electron cyclotron resonance plasma source to produce activated and ionized nitrogen. The material obtained by the former group had a lattice parameter and optical bandgap of 0.4531 nm and 3.30 eV, respectively. The electron carrier concentration also decreased from $4 \times 10^{18}$ to $8 \times 10^{18}$ cm$^{-3}$ with increasing $N_2^+$/Ga flux ratios between 0.63 and 3.9 which supports the common theory that the high donor concentrations are associated with N vacancies. Resistivities $> 10^6 \Omega$ cm were achieved. The latter group [47] has conducted extensive TEM characterization of the cubic films. The lattice constant was reported to be 0.45 nm. TEM revealed a high dislocation density in the GaN due to the large lattice mismatch which extended into the GaAs (probably due to the mismatch in coefficients of thermal expansion and the significant lattice resistance to dislocation motion in GaN at low temperatures). The electrical resistance exceeded 100 $\Omega$ cm. The bandgap was reported to be 3.26 eV, in agreement with the results of Paisley et al. [45].

A plasma technique has also been employed by Humphreys et al. [48] to achieve GaN on (0001) $Al_2O_3$ substrates. Specifically, the procedure consisted of using a remote He gas discharge combined with the down-stream introduction of trimethylgallium and $N_2$. Both cubic [111] and hexagonal [0001] polycrystalline films were obtained, but at different growth temperatures in the range of 673–973 K. As in the previous studies, microtwinning as well as double positioning boundaries and dislocations were observed in high concentrations. The lattice parameter of the cubic phase was measured to be 0.450 $+ 0.002\text{nm}$. Raman spectra were also obtained. Unfortunately this approach has not yet allowed a high resistivity material to be grown, as the electron carrier concentrations were in the $1.0 \times 10^{17}$ to $6.0 \times 10^{19}$ cm$^{-3}$. 

Numerous substrate materials have been used for the deposition of GaN with the most common being (0001) sapphire. However, the surface morphology of these films markedly improved if an AlN buffer layer was initially deposited on the sapphire, as shown initially by Yoshida et al. [49], [50]. More recently Amano et al. [51] and Akasaki and coworkers [52] have shown that the use of the AlN layer reduces microscopic fluctuation in crystallite orientation, to relax the strain between sapphire and GaN and to promote lateral growth of the film due to the decrease in interfacial free energy between the film and the substrate. These investigators have used the positive effects of this layer to grow high quality GaN films in which to produce p-n junctions and light-emitting diodes, as discussed below.

Khan et al. [53], [54] used a metalorganic (MO) CVD process similar to that of Akasaki and Amano but at 76 torr. The AlN buffer layer was 50-nm thick. They reported [53] electron carrier densities as low as $1 \times 10^{17}$ with mobilities in excess of 300 cm$^2$/V·s at room temperature. Photoluminescence linewidths as low as 25 meV were achieved. In addition, they reported [54], for the first time, vertical cavity stimulated emission at room temperature from 1.5-μm thick GaN layers. The gain coefficient was $\approx 10^{3}$ cm$^{-1}$. This represents significant progress towards the achievement of a carrier injection type UV laser based on the Al$_x$Ga$_{1-x}$N system.

Nearly all researchers who have grown GaN by CVD and other processes have also investigated in situ doping with Zn and Mg. Both of these dopants as well as Cd, Be, Ge, and Si compensate for the n-type character of GaN, but until recently, none had been used successfully in the making of p-type GaN. However, electrical measurements following cathodoluminescence studies by Amano et al. [55], [56] showed that low-energy electron-beam irradiation of GaN films (LEEBI) produced distinct p-type conduction. The LEEBI exposure not only produced compensation for the n-type character but increased the p-type conductivity and enhanced the photoluminescence efficiency [55] of the material grown and doped by metal organic vapor phase epitaxy. The hole concentrating and mobility and the resistivity at 293 K were $2 \times 10^{16}$ cm$^{-3}$, 8 cm$^2$/V·s and 35 $\Omega$·cm, respectively. The best GaN was deposited at 1310 K on a 50 nm AlN buffer layer previously deposited on sapphire at...
have fabricated a p-n junction LED which showed strong near-band edge emission due to hole injection from the p-layer into the n-layer at room temperature. Finally, Akasaki and coworkers have reported near ultraviolet stimulated emission from a GaN film [57] at room temperature. These results indicate the increasing likelihood of a current injection UV laser diode in the near future. In other research Khan [58] has indicated that he has also achieved p-type GaN using a self-limiting atomic layer epitaxy process and the primary reactants of triethylgallium and amonia and trimethylzinc as the dopant.

Although a solution to fabricating p-type films has been discovered, they must be deposited on highly mismatched substrates or intermediate layers. These films, as well as those deposited on β-SiC and GaAs, are highly defective in terms of dislocations and stacking faults. The ideal substrate would be GaN, but bulk monocrystalline GaN does not exist despite several attempts with different growth methods. These problems will very likely inhibit the development of GaN-based electronic devices for high power and high frequency applications. Moreover, suitable ohmic and rectifying contacts for n- and p-type GaN do not exist; insulating field and gate materials must be developed for GaN devices, as there is no stable native oxide of Ga. Etchants and etching procedures have not been developed for GaN.

D. AlN/GaN Solid Solutions and Heterostructures

Solid solutions of AlN and GaN have been produced by several methods to achieve bandgap engineering by analogy with the Al_xGa_1-xN (X=Sb, As, and P) systems. The Al_xGa_1-xN solutions have the potential for optoelectronic devices operating in the ultraviolet as a result of the direct gaps between 3.45 and 6.28 eV. Baranov et al. [59] and Hagen et al. [60] were the first to fabricate films of these materials via chloride vapor phase epitaxy. The former group produced films to x=0.45 at 1325 K. The latter investigators showed the existence of complete solid solubility throughout the binary system. This research set in motion a semicontinuous exploration of these materials, primarily in Japan and the United States which is still ongoing.

Yoshida and coworkers [61], a collaborative effort between Khan et al. and Gershenzon [62] and the individual efforts of Gershenzon and his students [63] were the next research teams to produce and characterize these solid solutions. Yoshida et al. produced single crystal films over the entire composition range on (0001) sapphire and (111) Si at 973 K by RMBE using evaporated Ga and Al and NH_3. The variations in lattice constant, electrical properties, energy gap and the energy of the intense peak in the cathodoluminescence spectra are shown in Figs. 7-10. A perusal of these figures show that the lattice constant exhibits a nonlinear dependence on composition. By contrast, the bandgap energy and the cathodoluminescence peaks vary smoothly throughout the compositional range. Similar but less extensive research has been conducted by Khan et al. using triethylgallium, trimethylaluminum (TMA), NH_3 and (0001) sapphire substrates held at a temperature of 1190 K. In contrast to Yoshida, they found that the carrier mobility and the carrier concentration decreased with increasing values of Al concentration.

Quantum well structures consisting of 0.2 μm layers of Al_xGa_1-xN surrounding the GaN well (10-30 nm) have been produced by Khan et al. [65]. This assembly was also deposited via MOCVD on an AlN buffer layer previously deposited on sapphire at 1273 K. The photoluminescence spectra of samples having different well thicknesses were measured and compared to theoretical solutions for the quantum well. The difference between peak emission from GaN bulk and quantum well structures consisted of a large constant offset (35.5 meV) and a smaller shift due to quantum size effects. The magnitude of the constant offset...
is consistent with the disappearance of band tails in the well and/or strain-induced band shifts due to the lattice mismatch between AlGaN and GaN.

In a related study, Khan et al. [66] have reported a substantial increase in mobility in single GaN (300 nm)/Al$_{0.10}$Ga$_{0.90}$N (50 nm) heterojunctions (1155 cm$^2$/V·s (23 K) and 460 cm$^2$/V·s (77 K)) relative to bulk GaN (56 cm$^2$/V·s (23 K) and 19 cm$^2$/V·s (77 K)), again produced via MOCVD using sapphire coated with AlN. The high mobility values were attributed primarily to the presence of a two-dimensional electron gas at the interface similar to that reported for GaAs/Al$_{1-x}$Ga$_x$As heterojunctions [67]. The band discontinuity was estimated to be 0.25 eV. Evidence for the presence of the two-dimensional electron gas was obtained from a multiple (18) heterojunction structure. The mobility in this structure increased more than two-fold relative to a two-layer assembly.

Heterostructures of AlN and GaN have been fabricated by Yoshida et al. [49, 50] and Sitar and coworkers [68]. In the research of the former group, (0001) GaN was deposited directly on (0001) sapphire or, as noted above, on $\approx$300 nm of (0001) AlN previously deposited on sapphire. The substrate temperatures for all depositions of AlN and GaN were 1373 K and 973 K, respectively. The GaN deposited on the AlN showed a three-fold increase in Hall mobility to $\approx$34 cm$^2$/V·s which was independent of the film thickness. Moreover, the GaN cathodoluminescence peak at 360 nm (valence band-to-conduction band transition) was sharper and much more intense for the material deposited on the AlN. This intensity increased with an increase in thickness of the GaN, especially beyond 0.2-0.4 μm for all films due to the enhanced quality of the films. A decrease in the luminescence intensity was noted when the thickness of the AlN layer was less than 200 nm.

Multiple AlN/GaN bilayer heterostructures having individual periods of 1.5-40 nm and total numbers of periods per deposition of 20-200 have been grown at NCSU on (0001)-oriented sapphire and 6H-SiC substrates containing a 140 nm GaN buffer layer within the temperature range of 773-1025 K using gas source MBE in the ionized mode [68]. Standard effusion cells were used as sources of Al and Ga. An MBE compatible, electron cyclotron resonance (ECR) plasma source produced activated/ionized nitrogen prior to deposition. Auger, X-ray diffractometry, and TEM analyses showed the interfaces to be compositionally, structurally, and microstructurally sharp. Figure 11 shows a TEM image of 5-nm thick layers of each compound. The (1011) diffraction pattern (inset), taken only from the layered structure confirms the monocrystalline nature of this assembly. Coherent interfaces (no relaxation by misfit dislocations) were observed for bilayer periods less than 6 nm. By contrast, completely relaxed individual layers of GaN and AlN with respect to each other were present for bilayer periods above 20 nm. Cathodoluminescence revealed a shift in the position of the principal emission
E. Indium Nitride

Of all the III-V nitride compounds, InN has been the least studied. All the aforementioned problems associated with GaN, i.e., high equilibrium N₂ vapor pressure, high electron carrier concentration and low mobility are found in InN [69]. As in the case of GaN, the poor semiconducting properties have been associated with the presence of N vacancies and therefore the high vapor pressure of this component. (The argument of self-compensation to explain the lack of p-type character in InN and GaN has never been used even though it apparently accounts for this phenomenon in ZnO and ZnSe.). As such, several low temperature film deposition methods have been employed over the years with varying results.

Hovel and Cuomo [70] were apparently the first to reactively RF sputter InN. They employed an In target, pure N₂ and (0001) sapphire and (111) Si heated in the range of 300-873 K. The resulting films were polycrystalline, preferentially oriented and highly conducting n-type with an electron concentration of \(7 \times 10^{18} \text{cm}^{-3}\) and a Hall mobility of \(250 \pm 50 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1}\). The achievement of InN films at \(T=873 \text{ K}\) is proof that although the equilibrium vapor pressure of N₂ is extreme, that of atomic nitrogen is much more moderate and can be used to successfully grow InN (and probably all other III-V nitrides) at higher than expected substrate temperatures. Extensive characterization of the reactive sputtering process of InN and related materials has been conducted by Natarajan et al. [71]. In additional reactive sputtering research, Tansley and Foley [72] have reported a direct correlation between fully nitrided targets and high electron mobilities (and low electron concentrations). These authors have reported the most favorable data to date for these parameters (\(\mu=3000 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1}\) and \(n=(2-10) \times 10^{16} \text{ cm}^{-3}\)). However, sputtering from an incompletely nitrided target produced films with lower mobilities and higher \(n\) values (\(>10^{17} \text{ cm}^{-3}\)). This relationship between poorly nitrided targets and higher electron concentrations has been apparently confirmed in research by Sullivan et al. [73].

Electron beam evaporation of In, a pulsed nitrogen plasma and (0001) sapphire substrates at \(T=300-650 \text{ K}\) have been used by Trainor and Rose [74]. Typical growth rates ranged from 1.0-1.2 \(\mu\text{m}^{-1}\) h. The best material had a Hall mobility at 300 K of 20 \(\text{cm}^{2}\text{V}^{-1}\text{s}^{-1}\) and a carrier concentration in the \(10^{19} \text{ cm}^{-3}\) range. These electronic results are similar to those of Marasina et al. [75] who employed the interaction of InCl₃ and NH₃ on (0001) sapphire. The former authors also found that annealing InN in N₂ at 773 K caused rapid decomposition; however, this did not occur even within an hour at \(10^{13} \text{ torr}\) in the presence of atomic nitrogen. Similar research has more recently been conducted by Masaki et al. [76]. Their primary alteration was the use of an ion gun instead of a direct plasma to provide the reactive nitrogen species. Silicon and glass were additional substrate choices. The films were deposited at room temperature; however, In-N bonding was observed by infrared absorption only after heating the deposited film to 450 K. Defects and/or impurities dominated the electrical characteristics, especially at and below room temperature.

III. Summary

The potential of III-V nitride thin films for applications in high-power and high-frequency electronic devices and optoelectronic devices over a broad range of wavelengths is considerable—but this has been recognized for many years without truly viable materials or devices being produced. The lack of a suitable substrate, with the possible exception of SiC for AlN, is a problem of considerable magnitude. This is compounded by the presence of shallow donor bands in GaN and InN which are apparently caused by N vacancies. The question of whether these vacancies occur (if they do) as a result of intrinsic or extrinsic (as a result of deposition) nonstoichiometry has not been answered. The recent advances of Akasaki and his coworkers [55]-[57] in the fabrication of p-type GaN and a p-n junction light emitting diode via the electron beam stimulation of the Mg dopant is very encouraging and may considerably advance the technology of this material. This would indicate that self-compensation effects, similar to those observed in ZnO and ZnSe, may not be present in the III-V nitrides,
since cBN, AlN, and now GaN have been reportedly doped both n- and p-type. It is also encouraging that several routes to lower temperature processes have been successful. However, if the number of workers in the field continues to be small, the commercial reality of devices from these materials, individually, as solid solutions and/or as heterostructures may be several years away.

ACKNOWLEDGMENT

Deepest appreciation is expressed to Z. Sitar and M. Paisley who contributed to this manuscript.

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DVIS: III-V NITRIDES FOR APPLICATIONS


Robert F. Davis, for a photograph and biography please see page 598 of this issue.