Preparation of GaN and InN for blue light emitting sources

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Semiconductors based on nitrides of Al, Ga and In have gained considerable interest recently for the successful implementation of bright blue and blue-green light emitting sources. Although most of the devices are based on hexagonal (wurtzite) GaN films, cubic (zinc blende) GaN films are of great interest because of possible growth on GaAs. We have prepared GaN and InN from *n*-GaAs and InAs single crystal wafers by NH_3 treatment at 700°C. X-ray diffraction measurements showed both cubic and hexagonal phases of GaN and InN. N_2 plasma treatment of liquid phase epitaxy grown InGaAs at 900°C resulted in growth of separate phases of only cubic GaN and InN. Optical absorption studies on GaN showed a direct band-gap of 3.46 eV. Photoluminescence measurements on GaN showed a defect-related emission band at 2.75 eV.

THERE is now considerable interest in wide-band gap semiconductors for applications in high temperature electronics as well as blue light-emitting sources. The latter are being eagerly sought to increase the density of storage in optical memories since a decrease in wavelength by a factor of 2 from 800 nm to 400 nm is expected to increase the storage capacity by a factor of 4 (ref. 1). Recently Isamu Akasaki[2] and Nakamura *et al.*[3–5] at Nichia, Japan have reported the operation of blue lasers with emission at 400 nm based on gallium nitride (GaN). Pulsed mode operation was first demonstrated[2], followed by cw operation for short durations.

Here we report the first work in India on the preparation of GaN and InN. This was done by treatment of GaAs and InAs single crystals with ammonia at high temperature (700°C).The grown layers were characterized by X-ray diffraction and photoluminescence measurements. Experiments on liquid phase epitaxy (LPE) grown InGaAs by N_2 plasma treatment at 900°C resulted in growth of separate phases of only cubic GaN and InN.

Nitrides are also of interest for high temperature electronics and their preparation and properties have been reviewed by Davis[6]. A programme of work on nitrides was initiated in our laboratory in the late eighties and resulted in the laser deposition of BN[7] and AlN[8] on GaAs and InP. Later the conductor TiN widely used as a diffusion barrier in Si technology was also deposited[9]. The series AlN–GaN–InN is attractive for LED and laser applications as these are all direct gap semiconductors with $E_g = 5.6$ eV, 3.4 eV and 2.07 eV respectively and exhibit complete solid solubility. SiC, on the other hand, with $E_g = 2.6$ eV has an indirect gap resulting in LEDs with much lower efficiencies. The technology of blue sources using the II–VI semiconductor ZnSe is also well developed[1], but the efficiency of GaN-based devices is expected to be higher.

We have prepared GaN and InN from *n*-GaAs and InAs single crystal wafers by NH_3 treatment in a home-made continuous flow reactor which was placed in a muffle furnace whose temperature was controlled to ± 1°C. The temperature of nitridation is critical since As evolution from GaAs and InAs is known to occur above 600°C.

Chemically cleaned GaAs (100) and InAs (100) single crystal wafers were etched and dipped in dilute HF solution. Samples were loaded into the reactor immediately after taking out from the HF solution. The reactor was then purged by nitrogen flow for one hour. Nitridation was then carried out at 700°C for 2 h under NH_3 whose flow rate was 10 cc/min. The colours of GaN and InN films were found to be golden and blackish respectively. From X-ray diffraction measurements using CuK_α radiation ($\lambda = 1.54$ Å) (Figure 1 *a*) three peaks related to GaN were observed at 32.8°, 35° and 39.5°. These peaks represent hexagonal (1010), (0002) and cubic GaN (002) respectively. It is known that under ambient conditions GaN has the wurtzite form and as such is grown on sapphire (Al_2O_3) substrates. However it can be grown with zinc blende structure on GaAs as a strained layer, due to appreciable lattice mismatch, i.e. 4.550 Å vs 5.653 Å. This is desirable for technological reasons since a conducting substrate simplifies device geometry and yields lower series resistance, a non-trivial problem with high band-gap materials.

X-ray diffraction peaks (Figure 1 *b*) at 31°, 51.2°, 60.8° and 35.6° related to InN were observed from the InN/InAs samples. These peaks represent hexagonal (0020), (1100) and (2000) and cubic (200) InN respectively. Attempts to grow GaN on GaAs using NH_3 in r.f. plasma at 250°C were not successful. Next a lattice-matched epitaxial layer of $In_{1-x}Ga_xAs$ ($x = 0.47$) grown on InP (100) by liquid phase epitaxy was taken. The layer had been fully characterized[10] and was 4.5 μm thick with $n = 6.7 \times 10^{16}$ cm^{-3}. When this was heated in a 450 kHz induction furnace at 900–950°C in a nitrogen plasma for 2 h the surface became ash coloured. The X-ray diffraction measurements of the sample showed the formation of both InN and GaN with cubic zinc-blende structures (Figure 1 *c*). The larger diffraction linewidths in Figure 1 *a* are due to smaller grain size. Use of the Scherrer formula shows that the grain size in this case is 95–190 Å compared with 420–540 Å for Figure 1 *b* and 390–514 Å for Figure 1 *c*. This may be attributed to higher bond breaking energy for GaAs compared with InAs and lower tem-

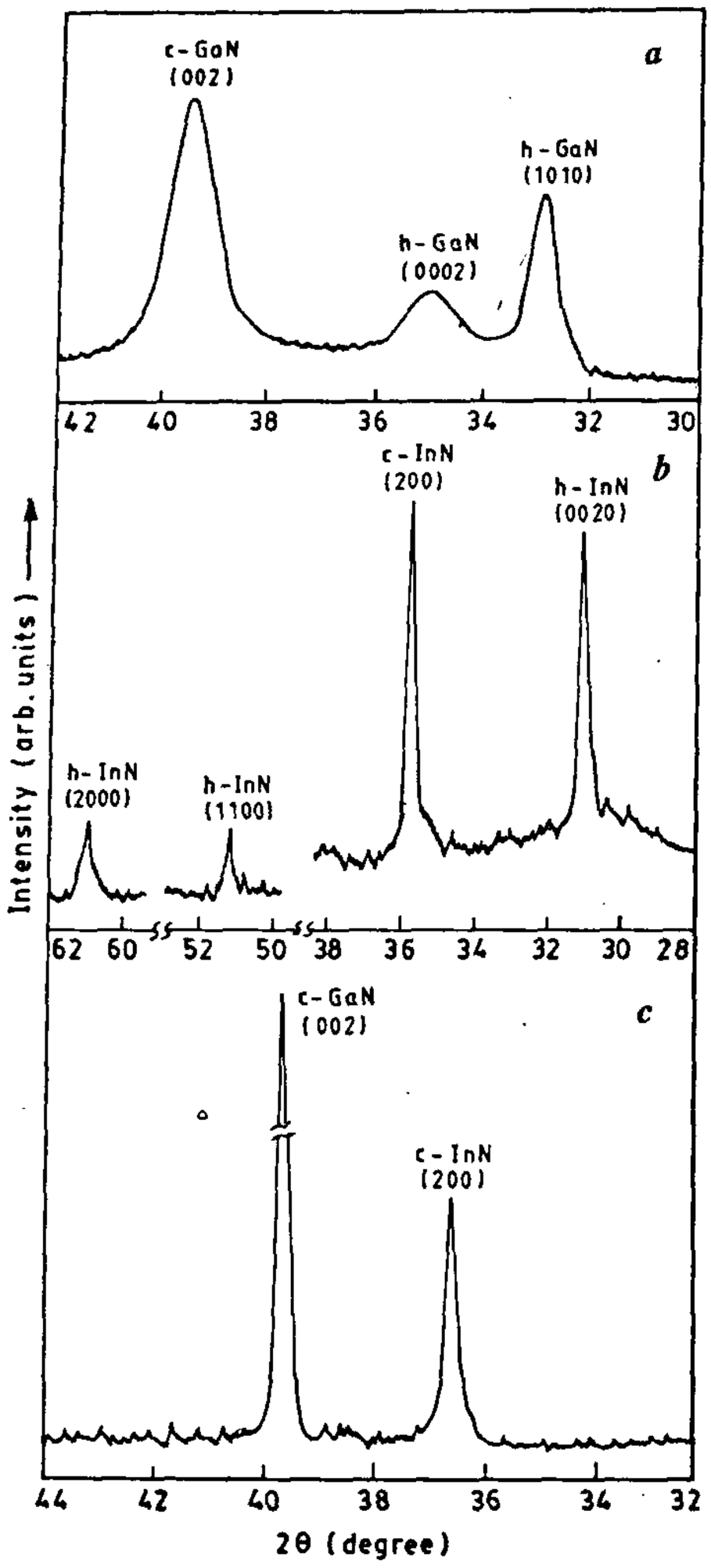

Figure 1 *a–c*. *a*, XRD scans ($\theta - 2\theta$) of GaN obtained from NH_3-treated GaAs. *b*, XRD scans ($\theta - 2\theta$) of InN obtained from NH_3-treated InAs. *c*, XRD scans ($\theta - 2\theta$) of N_2 plasma-treated InGaAs.

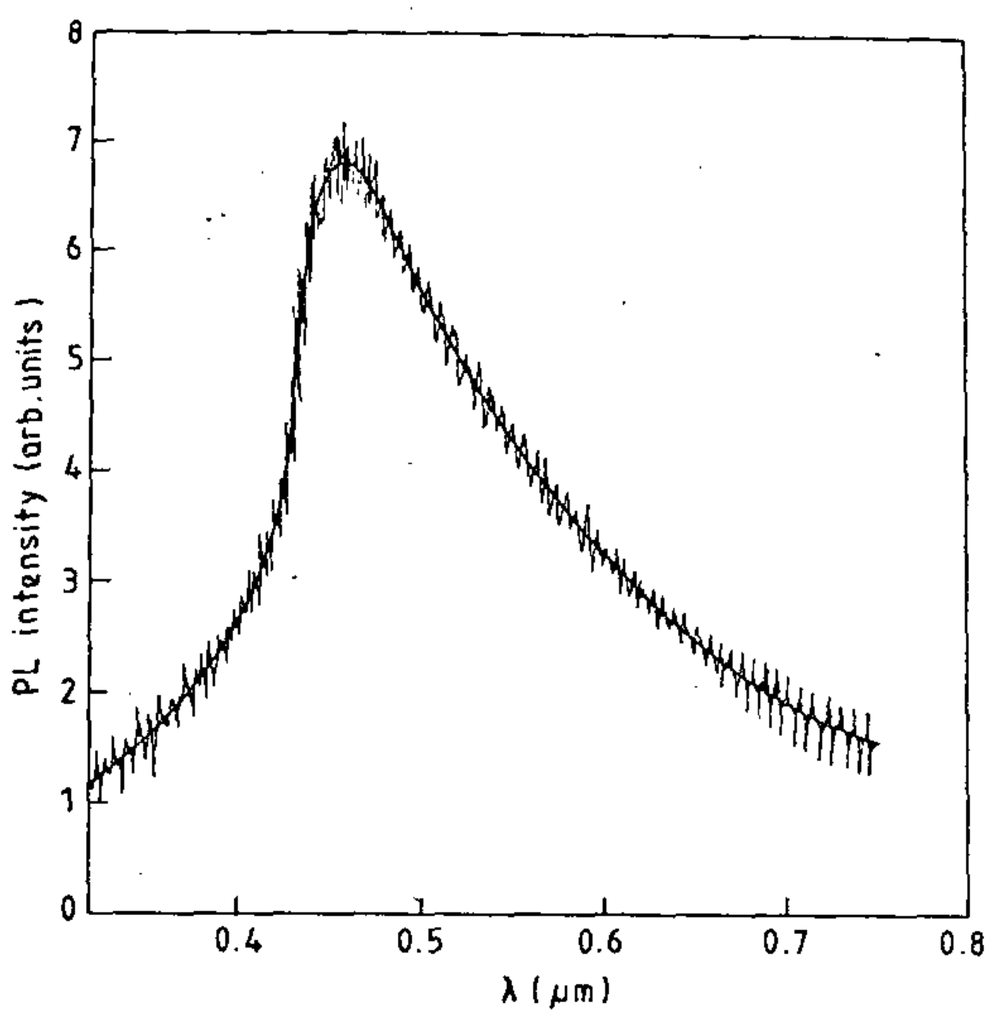

Figure 2. Photoluminescence spectrum of GaN at 300 K.

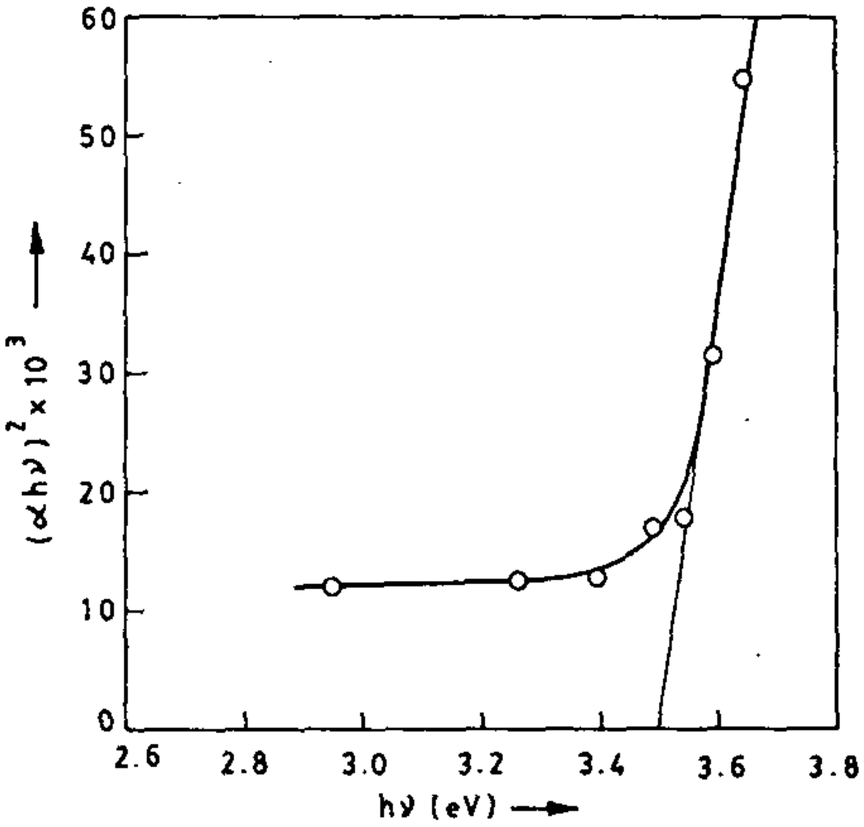

Figure 3. Optical absorption spectra of powder GaN at 300 K.

perature of nitridation, 700°C for Figure 1 *a* compared with 900–950°C for Figure 1 *a*.

Photoluminescence (PL) measurement was carried out on GaN/GaAs and InN/InAs samples at 300 K using 330 nm emission as an excitation source from a tungsten halogen lamp, Jobin-Yvon monochromator and a photomultiplier detector. Only one broad emission band (Figure 2) with peak energy 2.75 eV was obtained. A similar broad band with peak energy 2.9 eV has been observed for polycrystalline GaN films grown on Si at 400°C (ref. 11). No photoluminescence was observed from InN/InAs samples. This is intriguing since InN is considered to have a direct gap of 2.07 eV but no PL measurements have been reported from it[12]. Optical absorption measurements on powder GaN samples (Figure 3) showed a direct band-gap of 3.46 eV.

Summarizing, thermal nitridation on GaAs and InAs in NH_3 formed both cubic and hexagonal GaN and InN respectively while nitridation on InGaAs in N_2 plasma formed only cubic GaN and InN. Photoluminescence measurement on GaN showed a defect-related emission band at 2.75 eV and optical absorption showed a direct band-gap of 3.4 eV.

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Detection of the *lcr* gene in *Yersinia pestis* responsible for the recent outbreak of plague in India

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Rapid detection of plague bacilli is particularly germane to plague epidemiology since untreated bubonic plague can rapidly progress to septicaemic or pneumonic state. A 1.3 kb *Hind*-III/*Xho*-I DNA fragment from the plasmid pCd-1 which codes for the low Ca^{2+} response of *Yersiniae* spp. has been used to screen the isolates of *Y. pestis* obtained from the recent outbreak at Beed and Surat. The probe discriminated *Y. pseudotuberculosis*, diarrhoeagenic *Escherichia coli*, *Klebsiella pneumoniae*, *Salmonella typhi* and *Shigella dysenteria* from *Y. pestis* and *Y. enterocolitica*. Both radioactive and non-radioactive probes gave excellent result.

THE once dreaded bacteria, *Y. pestis* is known to carry three plasmids of 9.5 kb, 70 kb and 95 kb size[1]. While the 9.5 kb (pPst) and 95 kb (pFra) plasmids code for the pesticine and F1 antigen respectively, the 70 kb (pCad) plasmid is responsible for the low calcium response (LCR). Expression of virulence (V-antigen) is controlled by the *lcr* gene[2].

Virulent *Yersiniae* spp. can be detected by the presence of the LCR plasmid which, besides conferring virulence to the microorganism, makes the bacteria dependent on Ca^{2+} for growth at 37°C, expression of novel outer membrane protein called *Yersinia* outer protein (Yop), increased hydrophobicity, increased affinity to crystal violet and congo red, a tendency to agglutinate in media containing mammalian serum or enhanced resistance to bactericidal effects of normal human serum[3]. Although these parameters can be used for *in vitro* detection of the microorganism, they are reported to be not reliable tests[3]. Laboratory screening requires animal passages to isolate a pure culture, phage sensitivity typing, immunofluorescent antibody against fraction-1 (a major capsular antigen), etc. Screening by these methods is expensive and time-consuming. Detection at the nucleic acid level circumvents all the above limitations and provides a rapid and sensitive method for its specific detection.

In the present study, an attempt has been made to detect the presence of *lcr* gene in *Y. pestis* by DNA probe in different human and rodent isolates obtained during the recent outbreak at Beed and Surat districts. The other two virulent non-pestis *Yersiniae*, which include *Y. pseudotuberculosis* and *Y. enterocolitica* and other diarrhoeagenic enterobacteria like *Escherichia coli*, *Klebsiella pneumoniae*, *Shigella dysenteriae* and *Salmonella typhi* were also tested both by radioactive and non-radioactive DNA probes.

The test samples used comprised of 11 clinical isolates of *Y. pestis* from pneumonic patients of Beed district and Surat city: seven isolates from rodents, *Y. pestis* strain no. A-1122 which do not carry the LCR plasmid; *Y. pseudotuberculosis* strain no. 1A which was kindly supplied by May C. Chu, WHO Collaborating Centre at Centre for Disease Control, Fort Collins, USA; the *Y. enterocolitica* strain no. 0:9 IP 383 was kindly provided by Elizabeth Carniel, WHO Collaborating Centre, Institute Pasteur, Paris. Samples of *E. coli*, *K. pneumoniae*, *S. dysenteriae* and *S. typhi*, available in DRDE, were also tested simultaneously.

Bacterial cultures (24 nos) were scraped from agar plates and each resuspended in 100 µl of 0.5 M Tris.HCl (pH 8.0), 0.1 M sodium chloride and 0.01 M ethylene diamine tetraacetic acid (EDTA) in different eppendorf tubes and lysed by lysozyme followed by heat treatment.

The 1.3 kb restriction fragment that has been used as the DNA probe, contained the 3′ end of *lcr-R*, the complete *lcr-G* and part of the *lcr-V* (virulence antigen) gene of the 70 kb LCR plasmid pCD-1. *E. coli* with the recombinant plasmid vector pES6-1, which contains the above as well as the *lcr-H*, *yop-B* and *yop-D* genes