# Enhancement of the direct optical transition in nanocrystallized GaAsN alloys

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(Received 19 March 2001; published 31 August 2001)

Using x-ray diffraction, cross-sectional transmission electron microscopy (XTEM), and infrared absorption techniques, we have investigated the effects of nanocrystallization on the structural and optical properties of $GaAs_{0.99}N_{0.01}$ grown by plasma-enhanced molecular-beam epitaxy. The x-ray diffraction results of postgrowth annealed samples with a protective $Si_3N_4$ cap exhibit significant lattice relaxation, structural inhomogeneity, and apparent nitrogen ''loss,'' indicating the occurrence of phase separation after thermal treatment. High-resolution XTEM confirms the formation of N-enriched GaAsN nanocrystals embedded at the $GaAsN/Si_3N_4$ interface. Infrared absorption study demonstrates that the annealed sample has a strongly enhanced direct optical transition.

DOI: 10.1103/PhysRevB.64.113312 PACS number(s): 78.67.Bf, 61.46.+w, 81.40.−z

Recently, another class of III-V semiconductor alloys, which contain both arsenic and a small fraction of nitrogen in the group-V sublattice, has attracted great research attention due to their interesting physical properties[1–10] and promising applications for optical fiber communications in the 1.3–1.55 $\mu$m wavelength regime.[11] It has been found that incorporation of 1% nitrogen for arsenic in GaAs decreases the room temperature band gap from 1.42 to 1.25 eV, corresponding to an anomalously large and composition-dependent band-gap bowing coefficient of 17 eV.[1,2,8,9] This drastically different behavior has been investigated as due to the formation of spatially separated and sharply localized band edge states around the N atoms.[5–7] However, the application of this material is limited by its poor optical properties. Many studies have shown that annealing can significantly improve its photoluminescence, but the exact origin of this phenomenon is still unclear.[12–14]

Most studies on this material so far have assumed the formation of random alloys. However, calculations based on ordered and disordered alloys have obtained very different band bowing coefficients.[3,5] Also, as indicated by recent optical absorption and Raman studies,[8–10] alloy ordering may play an important role at the dilute limit. In particular, short range ordering such as clustering is highly expected since nitrogen in GaAs has limited solid solubility due to the significant differences in atomic size and electronegativity between As and N.[4] Experimental observations of nitride clustering have been reported for annealed GaInAsN films,[14] as-grown nitrogen atomic-layer-doped planes in GaAs,[15] and GaInAsN/GaAs quantum wells.[16]

In this Brief Report we report the structural and optical properties of postgrowth annealed dilute GaAsN compared with that of the as-grown sample. The as-grown sample shows high structural homogeneity, but have poor optical properties as measured by photoluminescence and optical absorption. The postgrowth annealing procedure is adopted here to promote the formation of short-range ordering or clustering. We found that significant structural changes, which can be attributed as due to the phase separation of N-rich clusters and the dilute alloy matrix, appear after annealing. These structural changes lead to a strongly enhanced band-to-band direct transition probability at a slightly enlarged band gap in the infrared absorption measurements.

The investigated GaAsN sample was grown by electron-cyclotron-resonance (ECR) $N_2$-plasma-enhanced molecular beam epitaxy (MBE) at 565 °C on semi-insulating GaAs(001) substrates and has a ~500-Å-thick GaAs buffer and a ~1500-Å-thick epilayer. The existence of N in the grown layer was confirmed by secondary-ion mass spectroscopy and the exact N concentrations were determined by high-resolution x-ray rocking curves. A 1500-Å-thick $Si_3N_4$ layer grown by plasma-enhanced chemical vapor deposition (PECVD) was used as a protective cap and an excellent diffusion barrier for the annealing procedure. The rapid thermal annealing procedure employed here is a 30 sec annealing at 900 °C (rising time from 30 °C to 900 °C is 1 min). The far-infrared transmittance spectra in the infrared range were measured by a Bruker IFS 120HR Fourier transform infrared spectrometer at different temperatures between 80 and 300 K with resolution better than 1 $cm^{-1}$.

Figure 1 shows (004) double crystal rocking curves recorded from the as-grown and annealed GaAsN samples. The x-ray measurements demonstrate high homogeneity and single phase in the as-grown samples. Also, the in-plane lattice of the epitaxial layers is found to have a coherent tensile strain in order to match the substrate GaAs lattice. Assuming Vegard's law (confirmed by theoretical and experimental studies[4,5,9] for as-grown dilute random alloys) and elastic deformation of the (001) epitaxial layer, the measured perpendicular mismatch $(\Delta a/a)_\perp$ is equal to $(1+2C_{12}/C_{11})x(\Delta a/a)_0 \approx 1.9x(\Delta a/a)_0$, where $C_{11}$ and $C_{12}$ are the elastic stiffness constants, $x$ is the N molar fraction, and $(\Delta a/a)_0=(a_{GaN}-a_{GaAs})/a_{GaAs}$ is the relaxed lattice mismatch of zinc-blende GaN and GaAs.[17] By applying this to the as-grown GaAsN case shown in Fig. 1 for which $(\Delta a/a)_\perp=-0.36\%$ ($\Delta\theta=486$ arcsec, $\theta$ is the Bragg angle) the nitrogen concentration is 0.943%. Upon annealing, the x-ray peak from the epilayer becomes weaker and broader,

 

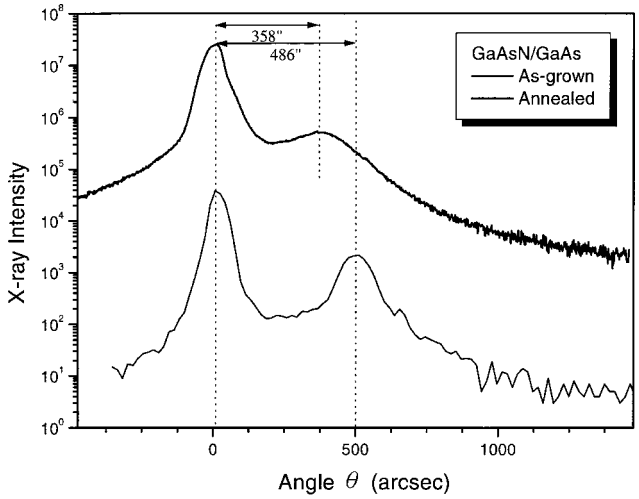


FIG. 1. (004) x-ray diffraction spectra of as-grown and annealed $GaAs_{0.99}N_{0.01}$ films grown on the GaAs(001) substrate.

indicating that this procedure decreases the degree of homogeneity in the samples. Additionally, the measured $(\Delta a/a)_{\perp}$ changes to $-0.266\%$ (GaAsN, N: 0.697%), indicating a significant lattice relaxation along the [001] growth direction. These values of lattice relaxation correspond to an apparent ''loss'' ($\sim$30%) of nitrogen for the annealed GaAsN. Since the sample was capped by $Si_3N_4$, which acts as an excellent diffusion barrier, this relaxation is unlikely to result from the real loss of anion species.

Figures 2(a) and 2(b) show the results of the cross-sectional transmission electron microscopy (XTEM) study on the annealed sample shown in Fig. 1. In addition to the absence of misfit dislocations in the annealed sample, there are clear dotlike features embedded at the $GaAsN/Si_3N_4$ interface [Fig. 2(b) is an image of an individual dot]. We attribute these dots as N-rich regions because their darker contrast is consistent with the expected contrast between N-rich and N-deficient regions as reported in previous XTEM studies on GaAsN/GaAs quantum wells or superlattices (e.g., see Ref. 18). Judging from Fig. 2(a), we can find that the size of these dots is quite uniform with diameters in the range of 10–20 nm and they do not possess a particular crystal shape. The XTEM observations suggest that an embryonic phase separation, i.e., the formation of N-rich nanocrystals occurred during annealing. Also, these nanocrystals have a tendency of out-diffusion toward the $Si_3N_4$ capping.

The optical band gaps of the same set of mixed-anion nitride films were examined by the optical absorption measurements taken in the transmission mode. Typical transmittance spectra of annealed and as-grown samples shown in Fig. 3 (taken at 250 K) indicate that the optical properties of the as-grown film are poor and a significant enhancement in absorption occurred after annealing. At this temperature, the absorption edge of the as-grown GaAsN layer is $\sim$1.2 eV ($\sim$9680 $cm^{-1}$) and that of the annealed GaAsN is $\sim$1.31 eV ($\sim$10566 $cm^{-1}$), an energy shift of $\sim$110 meV. Both absorption edges of the annealed epitaxial layer and GaAs substrate can be clearly seen in the square of the absorption coefficient

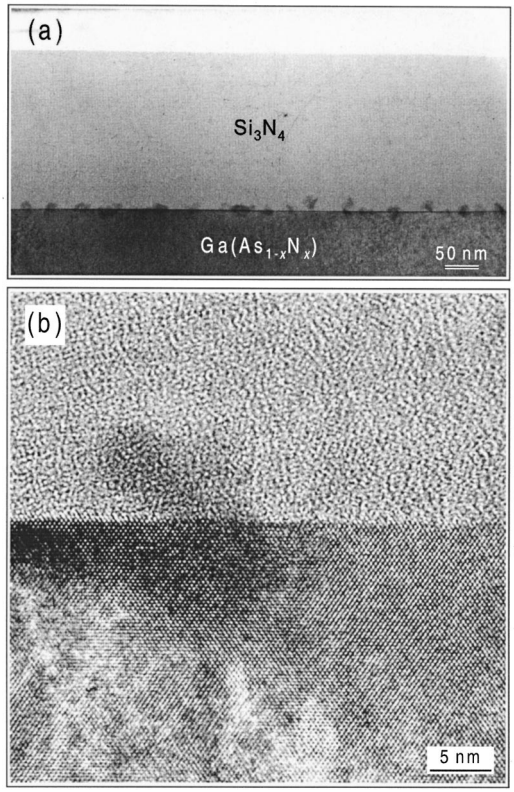


FIG. 2. Cross-sectional TEM micrographs of the annealed $GaAs_{0.99}N_{0.01}$ film with a PECVD-grown amorphous $Si_3N_4$ cap layer. Dark spots at the $GaAsN/Si_3N_4$ interface are N-rich regions.

($\alpha^2$) vs energy plots displayed in Fig. 4 (derived from the transmittance data). The measured absorption coefficients of annealed epitaxial layers obey a square law vs energy, indicating direct band-to-band absorption. The band-gap energy ($E_g$) of the measured samples was obtained by extrapolating the linear part of the square of the absorption coefficient to zero. The decrease of measurement temperature from 300 to 80 K causes a ''blue'' shift of the absorption edge from

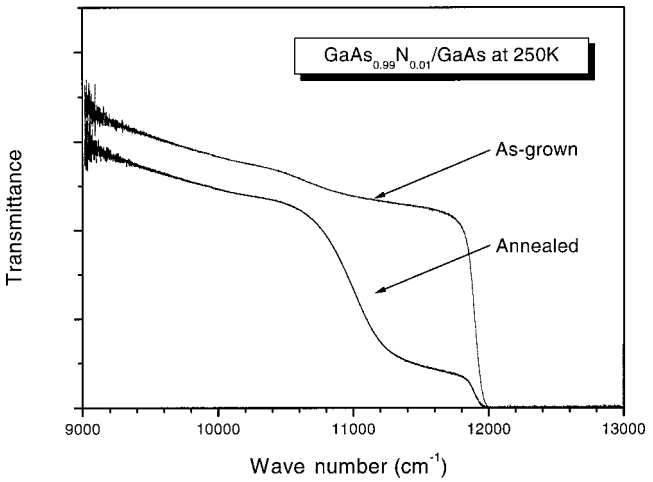


FIG. 3. Infrared transmission spectra of as-grown and annealed $GaAs_{0.99}N_{0.01}$ measured at 250 K.

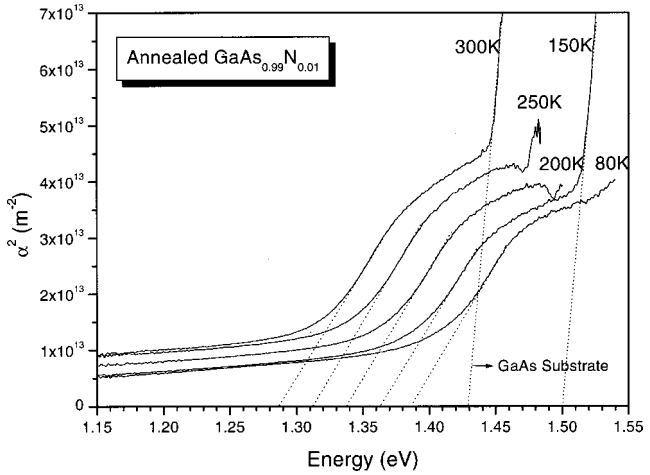


FIG. 4. Plots of the square of the absorption coefficient ($\alpha^2$) of annealed $GaAs_{0.99}N_{0.01}$ film as a function of photon energy at different temperatures, showing direct band-gap absorption. The band-gap energy values are obtained by extrapolating the linear part of $\alpha^2$ to zero. The absorption edges of GaAs substrate can also be seen at higher energies.

~1.29 to ~1.39 eV for GaAsN without a substantial change of the spectrum shape. The measured ''blue'' shift of the substrate is ~70 meV from 300 to 150 K, in good agreement with the standard temperature dependence of the GaAs energy gap derived from Varshni's equation. The temperature-induced energy shift of the band gap of the annealed GaAsN film is of the same magnitude (~10% larger) as GaAs. This is another indication that the observed absorption edge of the annealed GaAsN layer has a very different origin compared to the as-grown GaAsN alloy, which has a reported $dE_g/dT$ value significantly lower (~40%) than that of GaAs.[19,20]

It is interesting to know why homogeneous as-grown samples show low optical quality compared with that of phase-separated annealed samples. First of all, it is clear that the reduction of recombination-trap density cannot be the origin because of significantly poorer structural characteristics exhibited in the annealed samples. Second, hydrogen-related compensation effects typically shown in the CVD or gas-source MBE as-grown nitride samples also cannot be accounted for due to the fact that the growth method by $N_2$-plasma-enhanced MBE is known to be free from this problem. Third, activation of N interstitial atoms is unlikely since SIMS and x-ray measurements indicate most incorporated N atoms are substitutional ($N_{As}$) and the activation of N interstitial atoms would increase lattice mismatch instead of inducing lattice relaxation. Thus the observed improvement in optical properties should result from the N-rich clusters. Long range alloy ordering (such as those in $In_{0.5}Ga_{0.5}P$ and $Al_{0.5}In_{0.5}As$) is unlikely to occur because of the dilute nitrogen concentration (~1%) in our sample. Alloy ordering within the phase-separated and nanocrystallized regions could be an option, but is not observed in our high-resolution cross-section TEM image [Fig. 2(b)]. Furthermore, the band gap reduction effect due to the alloy ordering is typically quite small (a few tens of meV; see, for example, Ref. 21) and not accountable for the observed large band-gap reduction. We believe that the formation of nanocrystallized nitrides increases greatly the oscillator strength of the band-to-band direct transition. And the volume deformation (VD) of N-rich clusters in a dilute GaAsN matrix leads to a large band-gap energy reduction in N-rich nitride clusters. Using the calculated deformation potential parameters and elastic constants, the GaN-like spherical cluster, which has a volume mismatch strain of ~24% embedded in a GaAs matrix, can have a gap energy reduction on the order of ~1.7–2.0 eV (the original gap is 3.2–3.3 eV).[15] In contrast, the VD band-gap reduction in the dilute GaAsN alloy film grown on GaAs is quite negligible due to a small VD.[5]

In conclusion, we have observed a drastic improvement of optical properties of $GaAs_{0.99}N_{0.01}$ dilute alloy upon post-growth annealing. Phase separation due to the formation of N-rich nanocrystals and strongly enhanced direct optical transition were found after annealing of the as-grown dilute alloy film, which shows poor optical properties. Our results indicate that any complete theoretical understanding of this class of material should consider the possible compositional inhomogeneity originated from the short-range nitride clustering.

We would like to acknowledge the Center of Electron Microscopy, National Tsing-Hua University (Professor F.-R. Chen and Professor J.-J. Kai) for the TEM analysis, Dr. S. Miwa for the SIMS measurements, and Professor K. F. Huang of National Chiao-Tung University for the help of sample capping and rapid thermal annealing. This work was supported in part by the National Science Council (NSC 89-2112-M-007-093 and NSC 90-2112-M003-009) and the Program for Promoting Academic Excellence of Universities, the Ministry of Education, Taiwan.

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