Optical properties of GaAs$_{1-x}$N$_x$ on GaAs

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(Received 12 June 2000)

The optical properties of GaAs$_{1-x}$N$_x$ with x up to 2.5% grown by metalorganic chemical vapor deposition on GaAs(001) substrates are reported. Fundamental band gaps are obtained by photoreflectance measurements. Room-temperature pseudodielectric functions obtained by spectroscopic ellipsometry in the range from 2.7 to 5.2 eV are modeled with a three-phase structure that accounts for the GaAs$_{1-x}$N$_x$ layer, native oxide, and ambient. We employ Adachi’s critical-point composite model for the parametrization of GaAs$_{1-x}$N$_x$, and the compositional dependence of critical-point energies is obtained. While the energy of $E_0$ decreases with x, those of $E_1$ and $E_1 + \Delta_1$ increase with x. This fact, somewhat anomalous compared with conventional III-V alloys, indicates that the lowest-lying conduction bands along (111) directions may be perturbed by the incorporated nitrogen.

I. INTRODUCTION

The incorporation of nitrogen atoms into III-V semiconductor hosts leads to a remarkable band-gap reduction, which makes such alloys of technological interest for long-wavelength optoelectronic devices and multijunction high-efficiency solar cells. In particular, a reduction of the band gap more than 0.1 eV per atomic percent of N content was observed in GaAs$_{1-x}$N$_x$ for x < 1.5%. In contrast to conventional III-V semiconductor alloys, a composition-dependent bowing parameter of the order of 10–20 eV has to be introduced to describe the band-gap reduction. It was shown experimentally and theoretically that the repulsing interaction between nitrogen-related state in the conduction band and the conduction-band edge is responsible for the large band-gap reduction. Such a nitrogen-related state was observed in the electroreflectance spectra. More recently, an unusual composition dependence of the conduction-band effective mass as a result of the formation of a nitrogen-related impurity band was also observed. Furthermore, a strong composition dependence and bowing of the shear deformation potential of GaAs$_{1-x}$N$_x$ were found, which implies that not only the conduction-band but also the valence-band edge states are perturbed by the incorporated nitrogen. These research studies indicate that the irregular electronic properties of GaAs$_{1-x}$N$_x$ near the band edge can be better understood by viewing nitrogen atoms as heavily doped isoelectronic impurities in GaAs, as contrasted with viewing GaAs$_{1-x}$N$_x$ as a dilute alloy. Obviously, a more detailed study of the band structure of GaAs$_{1-x}$N$_x$ systems is required.

Due to the difficulty in preparing high-quality GaAs$_{1-x}$N$_x$ samples, optical studies including photoluminescence, electroreflectance, photoreflectance, (PR), photoconductivity, and spectroscopic ellipsometry (SE) measurements on this material were limited to x < 5%, while the optical transmission spectra were measured up to x ~15%. All the studies were limited to the fundamental gap region. On the other hand, the optical response properties of GaAs$_{1-x}$N$_x$ at energies greater than those of the fundamental band gap $E_0$ are of particular interest. This is because the structures in the optical spectra can be assigned to direct electronic transitions at specific regions of the Brillouin zone (BZ) and can therefore be related to the band structure of such systems.

SE is a powerful technique that gives information on dielectric functions and band-structure critical points (CP’s). In the present work, SE measurements of GaAs$_{1-x}$N$_x$ with x up to 2.5% were performed at room temperature. The data were analyzed for photon energies between 2.7 and 5.2 eV and the CP energies were identified by parametrizing the GaAs$_{1-x}$N$_x$ dielectric functions with Adachi’s critical-point composite model. The $E_1$ and $E_1 + \Delta_1$ transition energies show a clear tendency to increase with increasing nitrogen content x, contrary to the case of the fundamental transition $E_0$, which decreases with x. This observation, although it seems to be “anomalous” as compared with the other zinc-blende semiconductor alloys (their $E_1$ and $E_0$ have the same trends with x), is probably consistent with the existence of nitrogen-induced states (or perturbations) above the conduction-band edge.

II. SAMPLE PREPARATION

The GaAs$_{1-x}$N$_x$ epitaxial layers with x = 0.20%, 0.56%, 1.20%, and 2.50% (in atomic percentage) were deposited on unintentionally doped GaAs buffers (~0.1 μm thick) on Si-doped GaAs(001) substrates by metalorganic chemical vapor deposition in a low-pressure (150 Torr) close-spaced vertical reactor. The reagents were triethylgallium, arsine, and dimethylhydrazine. Hydrogen was used as the carrier gas. The growth temperature was 550 °C. Samples were examined with a high-resolution x-ray diffractometer using the Cu Kα$_1$ line. Figure 1 shows the (004) x-ray spectra for two of the samples grown. Nitrogen compositions were determined by assuming the validity of Vegard’s law and no strain relax-
ation. The latter assumption was verified by evaluation of the in-plane lattice constant obtained from the asymmetric $2\theta$ x-ray rocking curves. The lattice constants of GaAs and $c$-GaN used are 5.654 and 4.506 Å, respectively. The Poisson ratios are taken to be 0.310 and 0.366 for GaAs and $c$-GaN, respectively. The clear Pendellösung fringes shown in Fig. 1 indicate high crystalline quality and uniformity of the films and smooth interfaces between GaAs and GaAs$_{1-x}$N$_x$. The thickness of the films ranges from 380 to 480 nm, as determined from the separations of these fringes.

III. PHOTOREFLECTANCE MEASUREMENTS

In order to obtain the energy gap $E_0$, room-temperature PR measurements were performed at near-normal incidence with an energy step of 2 meV. The experimental apparatus operated with a 150-W tungsten-halogen lamp as a probe source. The excitation source was provided by a 5-mW He-Ne laser mechanically chopped at a frequency of 200 Hz. The resulting spectra for all the samples are shown in Fig. 2. The transition energies are determined by fitting the spectra to the Aspnes third-derivative functional form $\Delta R/R = \Re\{Ce^{i\theta}/(E-E_0+i\Gamma)^{5/2}\}$. Figure 3 shows $E_0$ as a function of nitrogen content $x$. As expected, $E_0$ redshifts with increasing $x$. Several data obtained by other authors are also shown for comparison. Our results agree well with those obtained by contactless electroreflectance measurements. The $E_0 + \Delta_0$ feature corresponding to the transition from the split-off valence band was also observed for the sample with $x = 0.56\%$, as is shown in the inset of Fig. 2. The obtained value of $\Delta_0$ is 340 meV. Such a weak transition was not observed for the other samples possibly due to the film quality or the masking by the strong features from the GaAs substrate. Perkins et al. performed electroreflectance measurements on a series of thick (2-μm) GaAs$_{1-x}$N$_x$ films and found that $\Delta_0$ is nearly independent of the nitrogen composition for $x < 2.8\%$.

IV. SPECTROSCOPIC ELLIPSOMETRY MEASUREMENTS

SE measurements on the samples were performed at room temperature using an automatic spectroscopic ellipsometer Sopra GESP5. The system uses a 75-W xenon lamp, a rotat-
ing polarizer, an autotracking analyzer, a double monochromator, and a single-photon-counting photomultiplier detector. Data were collected in the 1.4–5.2-eV photon energy region with the energy interval of 5 meV, at an incident angle of \( \Phi = 75^\circ \).

Ellipsometry determines the complex reflectance ratio \( \rho \) defined in terms of the standard parameters \( \Psi \) and \( \Delta \) via

\[
\rho = \frac{r_p}{r_s} = (\tan \Psi) e^{i \Delta},
\]

where \( r_p \) and \( r_s \) are the reflection coefficients for light polarized parallel (\( p \)) and perpendicular (\( s \)) to the plane of incidence, respectively. The pseudodielectric function \( (\epsilon) \), which is a common representation of the ellipsometric data \( \Psi \) and \( \Delta \), is obtained by treating the sample as a bulk (two-phase model):

\[
(\epsilon) = \sin^2 \Phi + (\sin^2 \Phi)(\tan^2 \Phi) \left( \frac{1 - \rho^2}{1 + \rho^2} \right) = (\epsilon_1) + i(\epsilon_2).
\]

The ellipsometric parameters depend on the photon energy, the sample layer structure, the material dielectric function of each layer, and the incident angle. A model calculation is needed for sample analysis. Instead of the apparent four-phase model (air–native oxide–GaAs\(_{1-x}\)N\(_x\)–GaAs), we limited our analysis to the energy region between 2.7 and 5.2 eV and treated our sample as a three-phase structure (air–native oxide–GaAs\(_{1-x}\)N\(_x\)). This is justified by the fact that the penetration depth (<550 Å) in this region is far less than the film thickness (~4000 Å) and the fact that the CP’s such as \( E_1 \), \( E_1 + \Delta_1 \), \( E_0 \), and \( E_2 \) are well included in this region. We do this for two reasons. First, our measurements did not cover the region below the band gap, where the interference effects (oscillating structures in the spectrum) would allow accurate determination of the film thickness. Second, the errors caused by the correlations between the parameters of the model dielectric function (MDF) and the thickness of GaAs\(_{1-x}\)N\(_x\) layer can be avoided.

We employ Adachi’s critical-point composite model for parametrization of the GaAs\(_{1-x}\)N\(_x\) dielectric functions. Adachi’s MDF is based on the one-electron interband-transition approach and includes terms for the \( E_0 \), \( E_0 + \Delta_0 \), \( E_1 \), \( E_1 + \Delta_1 \) transitions and phenomenological terms that describe contributions from high-lying transitions. In the following, we summarize the MDF for each CP. The detailed descriptions can be found in the literature.\(^{19,20}\)

(A) \( E_0 \) and \( E_0 + \Delta_0 \) transitions occur in the center of the BZ and are of the three-dimensional \( M_0 \) CP’s:

\[
(\epsilon)^{(0)}(E) = \sum_{j=0,s} A_j E_j^{-1.5} \chi_j^{-2} \left[ 2 - (1 + \chi_j)^{0.5} - (1 - \chi_j)^{0.5} \right],
\]

with \( \chi_j = (E + i \Gamma_j)/E_j \) (\( j = 0 \) and \( s \) for \( E_0 \) and \( E_0 + \Delta_0 \), respectively). \( A_j \) and \( \Gamma_j \) are, respectively, the strength and broadening parameter for each CP structure.

(B) The \( E_1 \) and \( E_1 + \Delta_1 \) transitions for the III-V zincblende semiconductors take place along the \{111\} directions of the BZ and are of the two-dimensional \( M_0 \) type:

\[
(\epsilon)^{(1s)}(E) = -\sum_{j=1,s} B_j \chi_j^{-2} \ln(1 - \chi_j^2),
\]

\[ B_j \] and \( \Gamma_j \) are, respectively, the strength and broadening parameter for each CP.

The contribution of the Wannier-type two-dimensional excitons to \( (\epsilon) \) can be written, with Lorentzian line shape, as

\[
(\epsilon)^{(1)}(E) = \sum_{n=1}^{\infty} \frac{1}{(2n-1)^3} \left( \frac{B_{1x}}{E_1 - E - i \Gamma_1} + \frac{B_{2x}}{E_1 + \Delta_1 - E - i \Gamma_{1s}} \right),
\]

FIG. 4. (a) Real and (b) imaginary parts of pseudodielectric function \( (\epsilon) \) for GaAs\(_{1-x}\)N\(_x\). The solid lines correspond to the best fit of the experimental data (represented by circles) to the three-phase model and the MDF parameters described in the text. Graphs are shifted for convenience.
where $B_{1x} \ (B_{2x})$ is the strength parameter of the $E_1 \ (E_1 + \Delta_1)$ exciton.

(C) The pronounced structures in the spectrum in the region higher than $E_1$ are labeled $E_0$ and $E_2 \ [E_2(X) \ and \ E_2(\Sigma), \ etc.]$. They do not correspond to a single, well-defined CP and are characterized by three damped harmonic oscillations with energy $E_j$, strength parameter $C_{E_j}$, and damping constant $\Gamma_{E_j}$:

$$e^{(2)}(E) = \epsilon_{\infty} + \sum_{j=1}^{3} \frac{C_{E_j} E_j^2}{E_j^2 - \epsilon^2 - iE\Gamma_{E_j}},$$

where $\epsilon_{\infty}$ is a constant included to account for the contribution of higher-lying transitions.

The complete model for the dielectric function is then obtained by summing over all these contributions:

$$\epsilon(E) = \epsilon^{(0)}(E) + \epsilon^{(1)}(E) + \epsilon^{(1x)}(E) + \epsilon^{(2)}(E).$$

To determine the unknown parameters (MDF parameters and oxide thickness), the Levenberg-Marquardt regression algorithm was used to minimize the unbiased merit function

$$\chi^2 = \sum_{i=1}^{N} \left[ (\epsilon_i)^{\text{calc}} - (\epsilon_i)^{\text{exp}} \right]^2 + \sum_{i=1}^{N} \left[ (\epsilon_i)^{\text{calc}} - (\epsilon_i)^{\text{exp}} \right]^2,$$

where $i$ indicates data sets $(\epsilon_1, \epsilon_2)$ at photon energy $E_i$, $(\epsilon_i)^{\text{exp}}$ represents the measured pseudodielectric function and $(\epsilon_i)^{\text{calc}}$ represents the calculated pseudodielectric function from the three-phase model and the MDF. The CP energies $E_0$ and $E_0 + \Delta_0$ were not treated as adjustable (unknown) parameters of the fit. The values of $E_0$ were determined from PR measurements, as shown above. The spin-orbit splitting $\Delta_0$ was assumed to be a constant value 0.34 eV, as described in Sec. III. We assumed the optical constants of the GaAs$_{1-x}$N$_x$ native oxide to be the same as those of the GaAs, which can be found in the literature. This is reasonable due to the very small amount of nitrogen content. The oxide thickness obtained for our samples with $x = 0.20\%$, $0.56\%$, $1.20\%$, and $2.50\%$ is 6.7, 4.0, 5.4, and 4.7 nm, respectively.

Figure 4 shows real (a) and imaginary (b) parts of the pseudodielectric function $\epsilon$ obtained from the four samples investigated here. The graphs are shifted for convenience. The symbols refer to the experimental data and the solid lines represent the best-fit calculation in the range 2.7–5.2 eV. It can be seen that the best-fit curves match the experimental data very well.

The extracted GaAs$_{1-x}$N$_x$ dielectric functions are shown in Fig. 5. For clarity we only show the spectra for $x = 0.56\%$ and $2.50\%$. The structures due to the $E_1$ and $E_1 + \Delta_1$ transitions (around $E \sim 3$ eV) shift toward higher-energy side with increasing $x$, but become broader and reduce in strength. It is noticeable, compared to conventional
III-V semiconductor alloys, that such a small amount of incorporated nitrogen can result in so large changes. One can expect that fairly large amounts of defects or compositional disorders may exist in the GaAs$_{1-x}$N$_x$ alloys due to the large difference in atomic size and electronegativity between As and N. Such disorders will cause a finite lifetime of the band states and their energy redistribution. This may partly account for the broadening of the E$_1$ and E$_1+\Delta_1$ structures. However, another possibility exists that the broadening may also be the consequence of some kind of perturbation on the band structure resulting from the N doping, as discussed below. On the other hand, the structures due to the E$_2$ and E$_2$ CP’s do not show a clear trend with x compared with E$_1$ and E$_1+\Delta_1$.

The obtained CP energies as a function of x are plotted in Fig. 6. While the energies of E$_0^0$, E$_2$(1), and E$_2$(2) remain nearly unchanged, the energies of E$_1$ and E$_1+\Delta_1$ increase with increasing N composition, in contrast to the case of E$_0$ and E$_0+\Delta_0$. This behavior is somewhat “anomalous” when compared with other zinc-blende semiconductor alloy systems. One exception is the Cd$_{1-x}$Mn$_x$Te alloys, in which the energies of E$_0$ CP’s increase with x while those of E$_1$ and E$_1+\Delta_1$ decrease slightly. This anomaly may be explained as due to a repulsion of the upper valence bands along (111) directions by the occupied spin-up Mn 3d states. In the case of GaAs$_{1-x}$N$_x$, it is known that a single nitrogen in GaAs induces a resonant state E$_N$ about 0.2 eV above the conduction-band minimum. The repulsion between this resonant N level and the GaAs band-edge state (the two-level model) was proposed to explain the band-gap reduction and the observed N-related E$_+$ level above the conduction-band edge. Since the energy separations between E$_N$ and the conduction-band states along (111) directions that participate in the E$_1$ and E$_1+\Delta_1$ transitions are not large (about 0.5–0.6 eV), it can be expected that the conduction-band states will be repelled to higher energies. Thus E$_1$ and E$_1+\Delta_1$ energies increase as nitrogen atoms are introduced into GaAs. Our result therefore implies the existence of the repulsion between nitrogen-related states and the conduction band in GaAs$_{1-x}$N$_x$. However, detailed theoretical and experimental investigations showed that the simple two-level repulsion model may be inadequate. Instead, the mixing of the I and L conduction-band states, which results from the nitrogen-induced symmetry breaking, has been suggested recently as the origin of the observed E$_+$ level. Such N-induced effects should also modify the band states along (111) directions and thus affect the structures of dielectric function spectra around E$_1$ and E$_1+\Delta_1$ CP’s. Further theoretical investigation is needed to clarify this point, which is beyond the scope of the present work.

Finally, it is worth pointing out that in order to interpret all the experimental results, the simple two-level model has to include the existence of the N pair bound states and how those levels evolve with increasing nitrogen composition.

V. CONCLUSION

In conclusion, we have reported optical studies of the dielectric functions of GaAs$_{1-x}$N$_x$ layers on GaAs for x up to 2.50%. Fundamental band gaps determined from PR measurements show a very large bowing effect. The dielectric functions and the CP energies of the 2.7–5.2-eV region have been determined using room-temperature SE measurements. The E$_1$ and E$_1+\Delta_1$ transitions were found to shift toward higher photon energies with increasing x, while the E$_0$ (and E$_0+\Delta_0$) transition shows the opposite. This observation, which is anomalous compared with conventional alloy systems, may be a result of the N-induced modifications of the GaAs band structure. Our result calls for a further theoretical investigation of the band structure of GaAs$_{1-x}$N$_x$ material.

ACKNOWLEDGMENT

This work was partly supported by the National Science Council of the Republic of China.