Valence-band splitting and shear deformation potential of dilute $GaAs_{1-x}N_x$ alloys

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The valence-band splitting in thin $GaAs_{1-x}N_x$ ($0.011 \leq x \leq 0.033$) epilayers strained coherently by the GaAs substrate is observed in electroreflectance. This study reveals that the valence-band deformation potential does not follow the linear interpolation of those for GaAs and GaN, but shows a rather strong composition dependence with a surprising bowing in a small composition region of the alloy. These results contradict the currently held view that the conduction band is greatly altered but that the valence band is only weakly perturbed by dilute nitrogen doping of GaAs.

Experimental[1–9] and theoretical[10–13] studies during the past few years have shown that the dilute $GaAs_{1-x}N_x$ alloy exhibits many unusual properties when compared to normal semiconductor alloys. For instance, this material exhibits a large band-gap reduction and a strong bowing of $E_g(x)$,[1–13] a nitrogen-induced resonant state in the conduction band,[8] and an unusual composition dependence of the conduction-band effective mass as a result of the formation of a nitrogen-related impurity band.[9] However, both experimental and theoretical investigations of the $GaAs_{1-x}N_x$ alloy seem to indicate that the nitrogen-induced perturbation to the valence band is small in the dilute nitrogen region. The spin-orbit splitting was found to be independent of the nitrogen composition at least up to $x = 2.8\%$.[8] The valence-band offset between GaAs and $GaAs_{1-x}N_x$ was calculated to be fairly small,[13] which has been confirmed experimentally.[9] The underlying physics here is that since the nitrogen atomic level is much higher than that of As, the bonding state of Ga and N is far below the top of the GaAs valence band and the antibonding state is resonant in the conduction band,[14] leaving the topmost valence band of GaAs in the middle of the window between the two states, and hence expected to be less perturbed by nitrogen incorporation.

The electronic and optical properties of thin $GaAs_{1-x}N_x$ epilayers have been studied using various techniques: photoluminescence, absorption, photoluminescence excitation,[1–5,7] and electroreflectance.[6,8,9] Uesugi, Morooka, and Suemune[7] recently showed that the critical thickness (h_c) of the $GaAs_{1-x}N_x$ epilayer was much larger than that predicted by Matthew and Blakeslee's model[15] ($h_c > 0.1 \mu m$ for $x = 4.5\%$ compared to 0.03 μm predicted by the model). Thus, it is reasonable to believe that most of the samples used in the previous studies[1–7] were coherently strained by the GaAs substrate. A direct consequence of the epitaxial strain is the valence-band splitting due to symmetry lowering. Because the $Ga_xAs_{1-x}N$ layer is under biaxial tensile strain (in the growth plane), the topmost valence band is light-hole like (LH) and the lower band is heavy-hole like (HH). However, this splitting has not yet been observed experimentally, presumably due to either the sample quality or the limitation of the experimental techniques.

In this article, we report a surprising finding, which is that the shear deformation potential for the valence band of the $GaAs_{1-x}N_x$ alloy is greatly altered even in the dilute nitrogen region of $x \leq 3.3\%$. Our results are obtained by analyzing the strain induced valence band splitting as a function of nitrogen composition for the thin $GaAs_{1-x}N_x$ epilayers.

A series of $GaAs_{1-x}N_x$ samples, with $x = 0.011$, 0.013, 0.017, 0.023, and 0.033, were grown by gas-source molecular-beam epitaxy on semi-insulating (100) GaAs substrates. All these samples are 1000 Å thick with a 200-Å GaAs cap and a 2500-Å GaAs buffer. Nitrogen compositions were determined by high-resolution x-ray rocking curve measurements, assuming the validity of Vegard's law. Details about the sample growth and the x-ray measurement can be found in a previous publication.[16] Figure 1 shows (400) x-ray rocking curves for all the samples. There are clear Pendelloesung fringes for all the samples, indicating high-crystalline quality and uniformity of the films, and the smooth interfaces between GaAs and $Ga_xN_{1-x}As$. Asymmetric {511} x-ray rocking curves were carried out to check strain relaxation in the epilayers. Calculation from elasticity theory indicates that there is only a negligibly small relax-
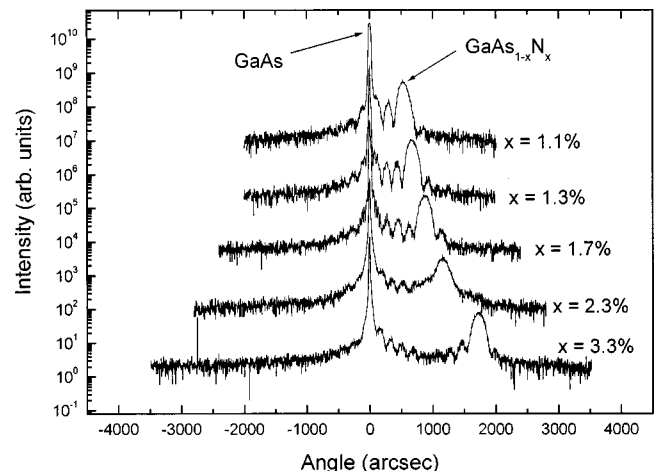

FIG. 1. X-ray θ-2θ curves of $GaAs_{1-x}N_x$ epilayers.
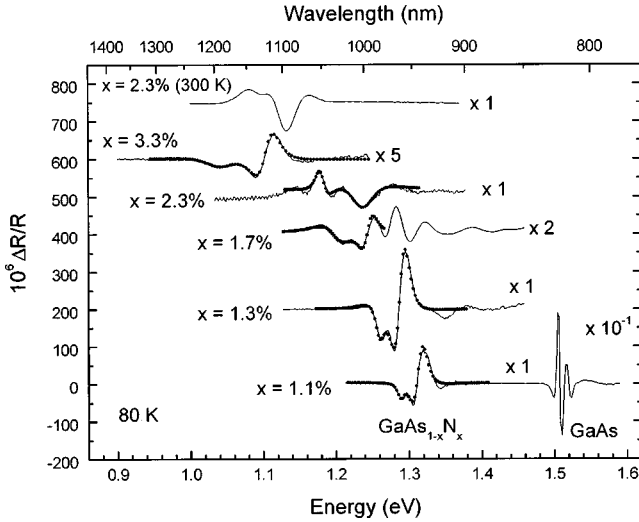
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FIG. 2. Electroreflectance spectra of $GaAs_{1-x}N_x$ epilayers. The solid lines are the experimental data, and the dots are the fitting results.

ation of 3.5% for the $x=3.3\%$ sample. Electroreflectance spectra were measured in a temperature range of 80–300 K, using a contactless electroreflectance technique and the experimental setup described by Perkins et al.[8]

Figure 2 shows electroreflectance spectra for the five samples measured at a temperature of 80 K. The higher energy feature (only shown for the $x=1.1\%$ sample) is related to the GaAs cap and/or substrate. The lower energy feature originates from the $Ga_xAs_{1-x}N$ epilayer.[6,8] It is clearly seen that the $Ga_xAs_{1-x}N$ portion of any one of the spectra has two features. Thus, we fit all the spectra with a lineshape function[17] for two critical points. The splitting is usually less well resolved at room temperature, but values similar to those observed at low temperatures are obtained by lineshape fitting. As an example, the room temperature spectrum for the $x=2.3\%$ sample is included in Fig. 2. Figure 3 shows the valence-band splitting versus the nitrogen composition, where the uncertainty is determined from the fluctuation in the results from multiple measurements. Also shown are the
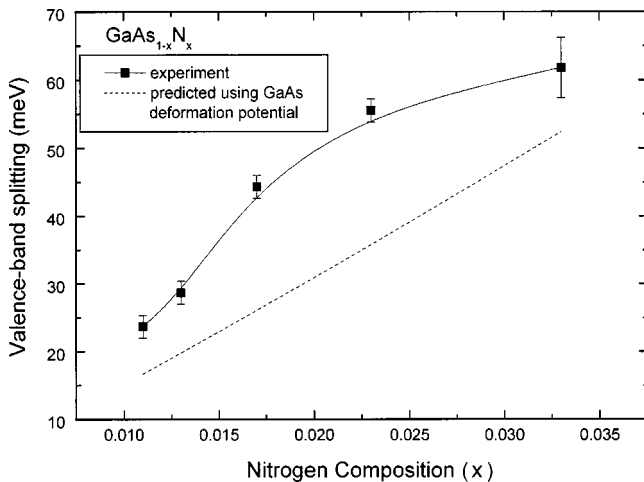

FIG. 3. Valence-band splitting $GaAs_{1-x}N_x$ vs nitrogen composition x.

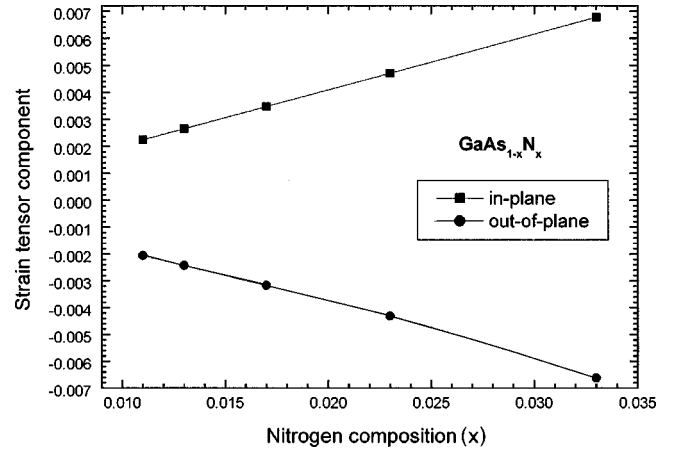FIG. 4. Strain tensor components $\varepsilon_\perp$ (in-plane) and $\varepsilon_\parallel$ (out-of-plane) in $GaAs_{1-x}N_x$ epilayers.

calculated results using a conventional perturbation theory (discussed below) using the deformation potential of GaAs. Such a perturbation calculation predicts a nearly linear composition dependence, whereas the experimental results shows a significant deviation from linear dependence.

The shear deformation potential b can be derived from the valence-band splitting shown in Fig. 3. The in-plane biaxial strain component is given by $\varepsilon_\perp=(a_{GaAs}-a_{GaAsN})/a_{GaAs}$, and the out-of-plane component is $\varepsilon_\parallel=-(2c_{12}/c_{11})\varepsilon_\perp$, where $a_{GaAs}=5.6533$ Å (Ref. 18), and $a_{GaAsN}=(1-x)a_{GaAs}+xa_{GaN}$, $a_{GaN}=4.50$ Å (Ref. 19). The elastic constants c_{11} and c_{12} are taken as linear interpolations of those for GaAs and GaN. For GaAs, $c_{11}=11.88$ and $c_{12}=5.38$ (Ref. 18); for GaN, $c_{11}=29.6$ and $c_{12}=15.4$ (Ref. 20) (all in the units of 10^{11} dyn/cm^2). Figure 4 shows the strain tensor components $\varepsilon_\perp$ and $\varepsilon_\parallel$ for the samples studied here. The energy levels of the HH and LH states can be expressed as follows (apart from a common hydrostatic deformation term) according to the conventional perturbation treatment of the strain-induced valence-band splitting[21]

$$E_{HH}=q, \tag{1}$$

$$E_{LH}=-\frac{1}{2}(q+E_{SO}-\sqrt{E_{SO}^2-2qE_{SO}+9q^2}), \tag{2}$$

where $q=b(\varepsilon_\perp-\varepsilon_\parallel)$, and $E_{SO}(=0.341$ eV) is the spin-orbit splitting, which has been shown independent of the nitrogen composition.[8] The deformation potential b can be obtained by solving the splitting $E_{LH}-E_{HH}$. This splitting approximately equals $-2q$ when $q\ll E_{SO}$. Figure 5 gives the composition dependence of the deformation potential b. A surprising enhancement and a bowing are found over a small composition region, where the enhancement in b near $x=1.7\%$ is greater than 60%, compared to the linearly interpolated value between $b=-1.9$ eV for GaAs (Ref. 22) and -1.6 eV for GaN.[23] It approaches the values for bulk GaAs or GaN, respectively with decreasing or increasing nitrogen
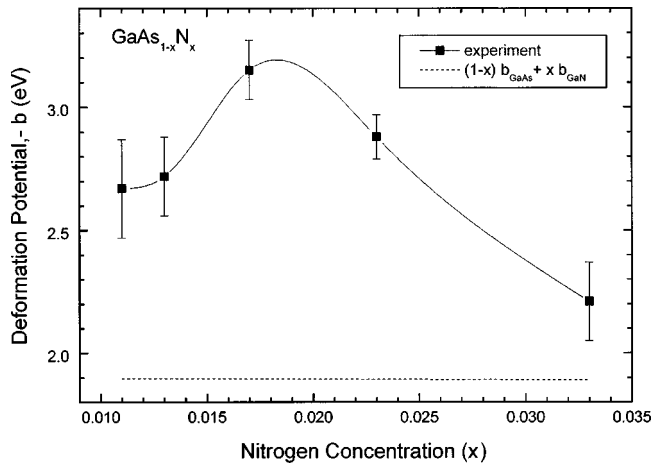
FIG. 5. Valence-band deformation potential of $GaAs_{1-x}N_x$ vs nitrogen composition x.

composition. These results contradict the currently held view that the valence band is only weakly perturbed by nitrogen incorporation.

In principle, what we really have observed is the composition dependence of the quantity $b(1+2c_{12}/c_{11})$. However, we have assumed that the elastic properties of the dilute $Ga_xAs_{1-x}N$ alloy do not exhibit a significant abnormality. The x-ray study of Ref. 7 seems to be supportive of this assumption. In case that the factor $f=(1+2c_{12}/c_{11})$ does exhibit an unusual composition dependence, the sample composition needs to be corrected by the factor of f_0/f, where f_0 is the value of f at $x=0$. Because this same factor f also appears in the valence-band splitting, the possible x dependence of f will not influence the observed bowing shown in Fig. 4 but will modify the absolute values of b and x determined.

Many recent studies[1–13] have showed that the electronic properties of $Ga_xAs_{1-x}N$ tend to show large irregularities in the dilute nitrogen region. This can be better understood by viewing nitrogen atoms as heavily doped isoelectronic impurities in GaAs as contrasted with viewing the $Ga_xAs_{1-x}N$

system as a dilute alloy. It was pointed out by Allen[24] that the lattice relaxation around the nitrogen impurity would give rise to a shear strain. Such a strain is then expected to split the degenerate valence band around the impurity site. Morgan[25] showed that not only the strain field but also an accompanying polarization field would perturb the valence band and modify the deformation potential. In the very dilute situation, the number of the impurity states is relatively small and so the valence band behaves mostly GaAs-like. On increasing the nitrogen doping, the strain fields for the individual nitrogen atoms start interacting with each other, first as pairs then as larger clusters along certain preferred directions. Such a strain field in addition to the substrate induced coherency strain is expected to increase the valence-band splitting. On further increasing the nitrogen composition, the impurity strain tends to average out to zero spatially, so the valence band splitting approaches the bulk value. The band structure calculation of Bellaiche, Wei, and Zunger[13] indicated that the valence-band state is partially localized on nitrogen, and that the average Ga-N bond length obtained by the valence force-field technique showed an abnormal increase in the region $x<6\%$ with increasing x. Thus, in the dilute limit, either the conventional theory[21] is not applicable to states that have a significant impurity character or the application of the conventional theory yields an abnormal composition dependence of the deformation potential.

In summary, we have observed valence band splitting in thin $Ga_xAs_{1-x}N$ alloy epilayers caused by the coherency strain of the GaAs substrate. A strong composition-dependence and bowing of the shear deformation potential is found in a small composition region. The finding adds another abnormality to the unusual properties of dilute GaAs:N.

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