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Effect of nitrogen on the GaAs_{0.9-x}N_xSb_{0.1} dielectric function from the near-infrared to the ultraviolet

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We study the effect of nitrogen on the GaAs_{0.9-x}N_xSb_{0.1} ($x=0.00, 0.65\%, 1.06\%, 1.45\%$, and 1.90%) alloy dielectric function by spectroscopic ellipsometry in the energy range from 0.73 to 4.75 eV. The compositional dependences of the critical points energies for the GaAs_{0.9-x}N_xSb_{0.1} are obtained. In addition to the GaAs intrinsic transitions E_1 , $E_1 + \Delta_1$, and E_0' , the nitrogen-induced Γ -point optical transitions E_0 and E_+ , together with a third transition $E^\#$, are identified. We find that with increasing the N content, the E_0 transition shifts to lower energies while the E_+ and $E^\#$ transitions shift to higher energies. We suggest that the origin of the E_0 , E_+ , and $E^\#$ transitions may be explained by the double band anticrossing (BAC) model, consisting of a conduction BAC model and a valence BAC model. © 2010 American Institute of Physics. [doi:10.1063/1.3518479]

Dilute nitride III-V alloys have sparked considerable research interest due to their unique properties and a wide range of optoelectronic applications.¹ The GaAsSbN quaternary alloy presents a particular case of interest since it can be grown lattice matched to GaAs with a band gap much narrower than GaAs.² GaAsSbN material system presents strategic advantages in terms of a lower strain than the In containing alloys, and good optical quality by introducing a lower nitrogen amount.³ This makes GaAsSbN promising for long wavelength telecommunication lasers on a GaAs substrate and highly efficient hybrid solar cells.

Despite the increasing interest in GaAsSbN material,⁴ the alloy dielectric function and the compositional dependencies of the transition energies still remain largely unknown. So far, very scarce information only about the fundamental band gap of GaAs_{0.87}N_{0.03}Sb_{0.1} and GaAs_{0.91}N_{0.02}Sb_{0.07} has been reported.⁴ In this work, we present spectroscopic ellipsometry (SE) study on GaAs_{0.9-x}N_xSb_{0.1} ($x=0.00\%, 0.65\%, 1.06\%, 1.45\%$, and 1.90%) alloys. We accurately determine the GaAsSbN dielectric functions in the energy range from 0.73 to 4.75 eV. A thorough investigation of the GaAs_{0.9-x}N_xSb_{0.1} optical properties analyzed by the Adachi model dielectric function allows us to establish the effect of nitrogen on the critical point (CP) parameters in the entire energy range studied.

The GaAs_{0.9-x}N_xSb_{0.1} samples were grown on GaAs (001) oriented substrates by molecular beam epitaxy (MBE) with the same Sb concentration (10%) and variable N concentrations from 0% to 1.9%. SE measurements were performed at room temperature in the spectral range of 0.73–4.75 eV, with steps of 5 meV at the incidence angle of 70°.

The complex dielectric function, $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$, of a semiconductor is closely related to its electronic band structure which can be drawn from features called CPs in the optical spectra. SE is a well-known technique for measurement of thin film dielectric function spectra and thicknesses

of layered samples by comparing the measured data with model calculations.^{5,6} SE could be particularly valuable for retrieving information on the CPs in dilute nitrides where the oscillator strengths of the N-induced transitions are relatively small (especially for low-N content samples as in our case) and there is N-induced broadening.⁷⁻⁹

Figure 1 shows experimental (scatters) and best-fit calculated (solid lines) data in the GaAs_{0.9-x}N_xSb_{0.1} pseudodielectric function representation for the different nitrogen compositions. We determine the dielectric function of GaAs_{0.9-x}N_xSb_{0.1} from the experimental ellipsometric data analysis using a five-layer model: GaAs substrate/GaAs_{0.9-x}N_xSb_{0.1} layer/GaAs caplayer/GaAs native oxide/ambient. We employed the Adachi model dielectric function (MDF) for the GaAs_{0.9-x}N_xSb_{0.1} layer parameterization. The MDF includes all electron interband-transitions.¹⁰ Each transition (CP) is represented by the following parameters: en-

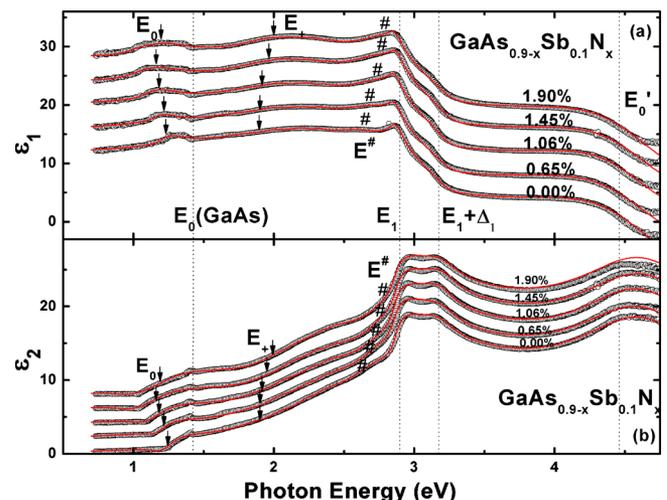


FIG. 1. (Color online) Experimental (scatters) and best-fit calculated (solid lines) data in the GaAs_{0.9-x}N_xSb_{0.1} pseudodielectric function representation; (a) real and (b) imaginary parts. The spectra with $x=0.65\%, 1.06\%, 1.45\%$, and 1.90% are shifted for clarity. The dotted vertical lines represent, respectively, the GaAs absorption edge and intrinsic transitions E_1 , $E_1 + \Delta_1$, and E_0' . The arrows indicate the E_0 and E_+ positions and the # those of $E^\#$.

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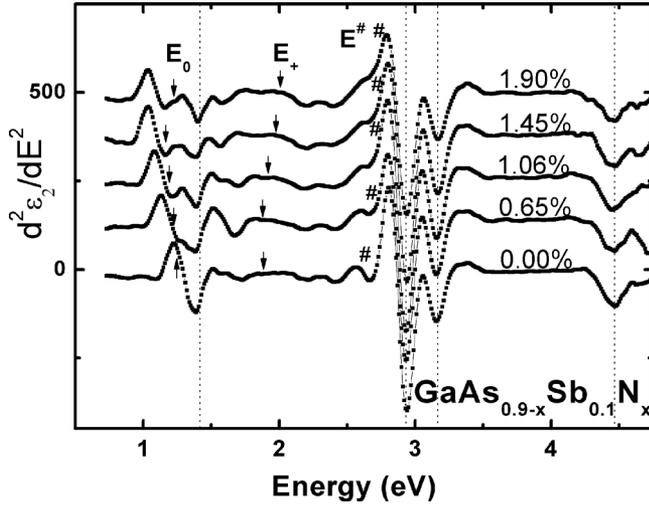


FIG. 2. Imaginary part second derivatives of the experimental pseudodielectric functions of $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ layers ($x=0.00\%$, 0.65% , 1.06% , 1.45% , and 1.90%). The alloy nitrogen containing spectra are shifted for clarity.

ergy E , strength B_1 , damping Γ . B_1^{ex} and G_1 are, respectively, the strength and the binding energy of the excitons with Lorentzian line shape.⁶ We have found that six interband transitions describe best the $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ dielectric function in the entire energy range studied.

We use the same nomenclature for the $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ alloy CPs as for the bulk GaAs.⁵ This is justified by the low compositions of Sb and N, and the great similarity between the $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ and GaAs spectra. The experimentally determined energy positions of the E_0 $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ alloy band gap are indicated by arrows below the GaAs band gap in Figs. 1 and 2 (vertical lines). The E_0 energy position shifts to low energies and broaden linearly by a factor of 2 (from 100 to 180 meV) with increasing nitrogen content. The increase of the broadening versus nitrogen content corresponds to potential fluctuations resulting from random N placement in the alloy. The near band gap energy region reveals well-defined E_0 edges, while the transition $E_0+\Delta_0$ between the conduction band and the spin-orbit valence band is not apparent in all spectra. Another spectral feature, indicated by arrows in Fig. 1 and labeled E_+ , occurs below 2 eV and experiences a blueshift with increasing nitrogen content. The E_+ transition was previously observed for GaAsN and GaInAsN alloys by photoreflectance spectroscopy,¹¹ electroreflectance,¹² and SE.⁸ A sixth critical point very close to the E_1 transition, denoted as $E^\#$ (indicated by # in Figs. 1 and 2), was obtained from the $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ dielectric function analysis. This feature appears around 2.7 eV, shifts to higher energies, and seems to increase in amplitude by increasing nitrogen content. This clearly shows that the ellipsometric measurements are sensitive enough to give qualitative and quantitative results on these below and above-gap transitions. Furthermore, on the high energy side, the E_1 and $E_1+\Delta_1$ transitions around 3 eV, and E_0' around 4.4 eV occur. In Fig. 2, the E_0 , E_+ , and $E^\#$ transitions are well resolved (arrows), and one can see the effect of nitrogen on the relative transition strength in the pseudodielectric function imaginary part second derivatives spectra.

The experimentally determined energy transitions are plotted in Fig. 3(a) as function of nitrogen composition and listed in Table I. It can be clearly seen that the energy positions of E_1 , $E_1+\Delta_1$, and E_0' remain unchanged with increas-

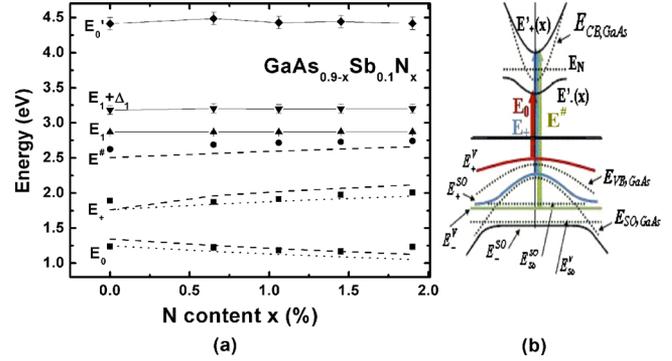


FIG. 3. (Color online) (a) $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ transition energies (symbols) determined by the SE analysis, CBAC model calculation (dotted lines), and a combination of VBAC and CBAC models (dashed lines): E_0 , E_+ , $E^\#$, E_1 , $E_1+\Delta_1$, and E_2 vs N content x . When not visible, the error bars are smaller than the symbol size. (b) Schematic diagram showing the combination of CBAC and VBAC models and the E_0 , E_+ , and $E^\#$ assignments.

ing nitrogen content. On the other hand, the E_0 energy decreases with increasing nitrogen content, while E_+ shifts to higher energies by increasing nitrogen content. The opposite and nearly equal shifts of E_0 and E_+ with increasing nitrogen content suggest that a nitrogen-induced level repulsion contributes to the observed band gap reduction. This effect was observed in other nitrogen containing materials such as GaAsN and GaInAsN, and was explained using band anti-crossing (BAC) model.¹³ Shan *et al.* showed that an anti-crossing interaction of nitrogen localized states with the extended states of the host semiconductor leads to a characteristic splitting of the conduction band into two subbands denoted E' (or E'_0) and E'_+ given by the expression

$$E'_\pm(x) = \frac{1}{2}[(E^M + E^N) \pm \sqrt{(E^M - E^N)^2 + 4V^2x}], \quad (1)$$

where E^M and E^N are the energies of the unperturbed conduction band edge (the one of $\text{GaAs}_{0.9}\text{Sb}_{0.1}$ in our case) and of the nitrogen level with respect to the top of the valence band, respectively. V is the matrix element of the term describing the interaction and hybridization between localized N states and the extended states. The conduction BAC model provides a good fit to our ellipsometric data, for the E_0 and E_+ energy transitions, by using $E^N=1.76$ eV and $V=2.7$ eV [see Fig. 3(a) dotted lines], where no strain contributions are considered. However, the conduction BAC model cannot explain the presence of the $E^\#$ transition. The $E^\#$ transition, not observed until now for GaAsSbN, first led us to assign it to the strong nitrogen-induced intraband Γ - L coupling and a nitrogen-induced splitting of the conduction band L -point GaAs host states into two levels, as for GaAsN established by first principles calculations.¹⁴ However, by comparing the nitrogen dependence linear fit for both E_+ and $E^\#$ transitions, we have found that the increase is the same for each, about 65 meV per %N (Table I). Recently, Alberi *et al.*¹⁵ demonstrated a valence BAC (VBAC) model that is capable of explaining the energy gap of As-rich GaAsSb. Consequently, the addition of a few atomic percent of Sb to GaAs results in an anticrossing interaction leading to a valence band restructuring. The split levels (E_+^V , E_-^V , E_+^{so} , and E_-^{so}) for the three valence bands at $k=0$ (heavy- and light-hole bands and spin orbit splitting band) have the similar form as the BAC two-level model above [Eq. 2].¹⁵ The VBAC model in $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ alloys is illustrated in Fig. 3(b). Until now, the double BAC model has been

TABLE I. GaAs_{0.9-x}N_xSb_{0.1} ($x=0.0\%$, 0.65% , 1.06% , 1.45% , and 1.90%) transition energies: E_0 , E_+ , and $E^\#$ obtained from SE analysis, CBAC model calculations, and CBAC and VBAC model calculations. Errors are given in parentheses.

x (%)	E_0 transition (eV)			E_+ transition (eV)			$E^\#$ transition (eV)	
	SE analysis	BAC calculation	BAC and VBAC calculation	SE analysis	BAC calculation	BAC and VBAC calculation	SE analysis	BAC and VBAC calculation
0.00	1.237(0.043)	1.246	1.345	1.891(0.037)	1.760	1.760	2.624(0.026)	2.504
0.65	1.224(0.042)	1.166	1.252	1.871(0.037)	1.839	1.959	2.688(0.026)	2.563
1.06	1.182(0.041)	1.125	1.205	1.914(0.038)	1.881	2.019	2.714(0.027)	2.596
1.45	1.166(0.040)	1.089	1.167	1.973(0.039)	1.917	2.067	2.727(0.027)	2.626
1.90	1.230(0.043)	1.051	1.126	2.004(0.040)	1.955	2.113	2.741(0.027)	2.658

verified experimentally by absorption measurements for GaAs_{0.97-x}N_{0.3}Sb_x and GaAs_{0.98-x}N_{0.2}Sb_x only in the energy range of 0.70–1.35 eV.¹⁶ In Fig. 3(a), we represent the calculation using the double BAC model (dashed lines) by using the localized levels $E_N=1.76$ eV, the E_{Sb} and hybridization parameters according to Refs. 15 and 16. It is important to notice that the VBAC provides a possible explanation about the origin of the $E^\#$ energy transition. For the nitrogen free sample ($x=0$), we have found that the E_0 and E_+ transitions may originate from the transition between the E_+^V and E_+^{so} levels, respectively, and the conduction band minimum (CBM) [see Fig. 3(b)]. Likewise, the $E^\#$ transition in the same sample may originate from the E_-^V level to CBM transition. Note that in the N-containing samples the E_0 , E_+ , and the $E^\#$ transitions involve different levels as a result of the N-induced splitting of the conduction band [see Eq. (1) and Fig. 3(b)]. In this case, the E_0 , E_+ , and $E^\#$ energy transitions may originate from E_+^V to $E'_-(x)$, E_+^{so} to $E'_+(x)$, and E_-^V to $E'_+(x)$ transitions, respectively [see Fig. 3(b)], according to the double BAC model. Although, a transition around 2.7 eV (labeled E^*) has previously been observed for GaAsN in Refs. 7 and 17, we note that it has a different origin than in our GaAs_{0.9-x}N_xSb_{0.1} alloy. Perkins *et al.* speculated that E^* may originate from the transition between the GaAs VB and the N-induced CB state in the dilute limit, and to a new CB-resonant N impurity level for higher nitrogen content. A good agreement between the E_0 transition energies predicted by the double BAC model and the respective experimental values can be seen [Fig. 3(a)]. On the other hand, the predicted E_+ and $E^\#$ transition energies slightly deviates from the respective experimental energies being somewhat higher (lower) for the $E_+(E^\#)$ [Fig. 3(a)]. A higher amount of Sb in the films could in principle provide a possible explanation for the observed discrepancy. However, the upward (downward) shift per 1% Sb is 16 meV for $E_+^V(E_-^V)$ and 13 meV for $E_+^{so}(E_-^{so})$.¹⁵ Therefore, this would require an underestimation of Sb content in our samples by as much as 7% in order to match our experimental results for E_0 and $E^\#$ with the double VBAC model predictions. Clearly, this exceeds by far the error in the composition, which is 1%. On the other hand, one should keep in mind that the VBAC is strictly valid only for dilute impurity concentrations.¹⁵ Indeed, the experimental value of the spin-orbit splitting in GaAsSb determined by photomodulated reflectance starts to deviate from the VBAC at 10% Sb.¹⁵ Interestingly, this deviation is of the order of 100 meV very similar to the difference we observe between our E_0 and $E^\#$ experimental values and the VBAC model

predictions. Therefore, it may be speculated that the observed difference between our SE results and the double CBAC and VBAC calculations are related to deviations in the value of the spin-orbit splitting in GaAs_{0.9}Sb_{0.1} from the VBAC.

In summary, we have established the effect of nitrogen on the dielectric function of GaAs_{0.9-x}N_xSb_{0.1} ($x=0.00\%$, 0.65% , 1.06% , 1.45% , and 1.90%) alloys in the energy range from 0.73 to 4.75 eV. In addition to the GaAs intrinsic transitions (E_1 , $E_1+\Delta_1$, and E_0'), the nitrogen-induced optical transitions E_0 , E_+ , and $E^\#$ are identified and their compositional dependences determined. Our results suggest that the origin of the E_0 , E_+ , and $E^\#$ transitions may be explained by the double BAC model, consisting of a CBAC model and a VBAC model.

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