Thermoreflectance study of the direct optical gap in epitaxial $Al_xGa_{1-x}Sb$ ($x \leq 0.5$)

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Thermoreflectance spectroscopy was used to precisely determine the direct optical gap E_g^Γ, as a function of composition and temperature of a series of $Al_xGa_{1-x}Sb$ layers ($0.0 \leq x \leq 0.5$) epitaxially grown on GaSb. The experimental line shapes were fitted with a critical-point functional form including excitonic effects, to derive the direct gap and broadening parameter values. The relation between E_g^Γ and x shows a x-dependent bowing, which was compared with previous results and theoretical models, leading to the conclusion that $E_g^\Gamma(x)$ curves in $Al_xGa_{1-x}Sb$ alloys have a cubic polynomial form. [S0163-1829(99)10303-5]

The substitutional semiconducting alloy $Al_xGa_{1-x}Sb$, formed by mixing the zinc-blende constituents GaSb and AlSb, has recently attracted increasing interest for its potential applications in optoelectronic devices:[1] e.g., normal-incidence infrared detectors,[2] modulators,[3] and second-harmonic generators,[4] based on multiple-quantum-well $Al_xGa_{1-x}Sb$/GaSb. The accurate knowledge of the energy gap as a function of Al concentration x and of temperature T is of utmost importance for these devices.

From both the experimental and theoretical point of view the problem is complicated by the fact that GaSb has a direct Γ-Γ gap at $\sim$0.72 eV at RT and an indirect Γ-L gap only 80 meV larger; AlSb has an indirect Γ-X gap. It follows that in $Al_xGa_{1-x}Sb$ the gap is direct E_g^Γ for low x values, becomes indirect E_g^Γ for intermediate x, and then E_g^Γ for high x values. Analogous behavior is shown by $Al_xGa_{1-x}As$, which has been more extensively studied: in particular, an anomalous bowing of E_g^Γ (bowing means nonlinear dependence of the interband critical-point energies on x) has been experimentally observed[5] and theoretically investigated and modeled.[6]

Two relevant and systematic studies on E_g dependence on x were experimentally carried out on $Al_xGa_{1-x}Sb$: the first by using piezo reflectance and electroreflectance spectroscopies at different temperatures;[7] the second, and very recent one, by optical transmittance at very low temperatures.[8] Their results strongly disagree on the values of the bowing parameter and of the x value for which the cross over between E_g^Γ and E_g^L occurs.

For these reasons and with the aim of getting a deeper insight into the x dependence of E_g^Γ, we measured thermoreflectance spectra (TR) at different temperatures on a series of $Al_xGa_{1-x}Sb$ layers (with $x \leq 0.5$), grown by molecular-beam epitaxy (MBE). The growth chamber and the sample characteristics were the same as in Ref. 8, instead the substrate in our case was GaSb and not GaAs, to reduce the effects of the lattice mismatch (less than 0.3% against 7%) and of different temperature coefficients between layer and substrate. The advantages of TR among the modulation spectroscopies are well known.[9,10] With respect to transmittance, TR gives more precise values of the direct gap energy, because it is as a derivative technique and it is insensitive to indirect transitions.[9,10]

The $Al_xGa_{1-x}Sb$ layers were grown by MBE in a Intervac Gen II modular chamber on (100) GaSb substrates, capped by a thick (≥ 1 μm) GaSb buffer layer, with x ranging between 0.0 and 0.5 with step of 0.1. The compositions were measured by reflection high-energy electron diffraction oscillations with an accuracy within $\pm 5\%$. The nominal layer thicknesses were 1 μm for $x = 0.1$, 0.3, and 0.5; and 3 μm for $x = 0.2$ and 0.4. In order to improve the homogeneity and the purity of the material, the sample substrates were heated radiatively. The growth temperature T_g was monitored with an optical pyrometer. T_g and the Sb_4/(Al+Ga) beam equivalent pressure ratios ($\mathcal{B}$) were chosen to optimize the low-temperature photoluminescence properties of $Al_xGa_{1-x}Sb$ and varied in the ranges $500\,^\circ\text{C} \leq T_g \leq 600\,^\circ\text{C}$ and $5 \leq \mathcal{B} \leq 8$. Details on growth and characterization of the samples are reported elsewere.[11,12]

TR measurements at near-normal incidence were performed in the 0.6–0.9 eV range with energy step and spectral resolution of 1 meV. The standard experimental configuration[9,10] included a 100 W halogen lamp as the light source and a thermoelectrically cooled $In_xGa_{1-x}As$ photodiode as detector. The sample was mounted in thermal contact with the cold finger of a microminiature Joule-Thompson refrigerator coupled with a programmable temperature controller (resolution 0.02 K; temperature sweeping rate 0.2 K sec) allowing measurements in the 80–300 K temperature range. Spectra were taken at twenty 20 K temperature steps. A modulation of $\Delta T \sim 2$ K at 0.1 Hz of the cold finger was used to produce the periodic thermal perturbation of the sample. Phase-sensitive detection was used to measure the reflectivity modulation (ΔR). A lock-in amplifier allowed the $\Delta R/R$ signal to be sampled at a rate of 16–128 readings

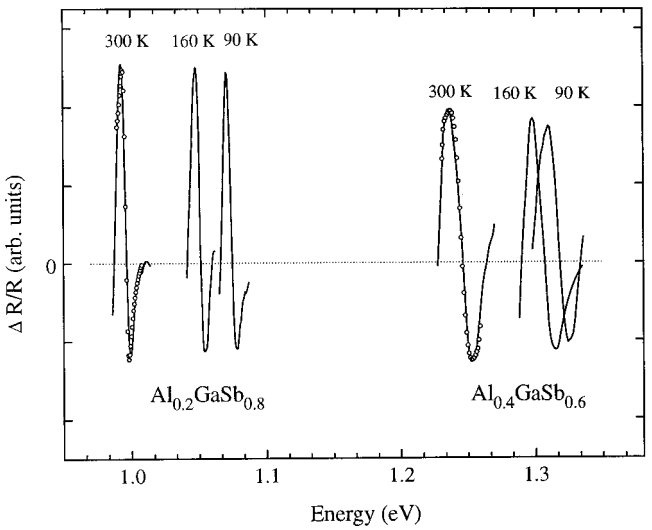

FIG. 1. Thermoreflectance spectra at different temperatures of $Al_{0.2}Ga_{0.8}Sb$ and $Al_{0.4}Ga_{0.6}Sb$ epitaxial layers. The dotted lines are the best fits using the line shapes from Eqs. (1)–(3).

per second for an amount of time (20–60 s) appropriate to obtain a satisfactory signal-to-noise ratio.

In Fig. 1 we report some experimental TR spectra for the $Al_xGa_{1-x}Sb$ films (with $x=0.2$ and 0.4.) around the direct energy gap E_g^Γ at different temperatures, together with a best-fit (dots) performed using the theoretical analysis reported later.

The TR features, corresponding to the M_0 critical point in the joint density of states, are sharp and retain the same shapes for all values of x and all temperatures. They display a strong blueshift in energy position with increasing x, as expected because the gaps of the end members GaSb and AlSb are very different and with decreasing T, which is typical of zinc-blende semiconductors. The linewidth increases with x, due to the growing compositional disorder, and decreases very little with T. To precisely determine the values of the energy gaps and the broadening parameter γ, we analyzed the experimental line shape on the basis of the first-derivative functional forms, including excitonics effects, which are characteristic of TR spectroscopy. This analysis was successfully applied to GaSb MBE layers and described in detail in a previous paper,[13] of which we recall here only the main steps and assumptions.

(a) The relative modulation of R is expressed by[9,10]

$$\frac{\Delta R}{R}=\alpha(\varepsilon_1,\varepsilon_2)\Delta\varepsilon_1+\beta(\varepsilon_1,\varepsilon_2)\Delta\varepsilon_2, \tag{1}$$

where α and β are the Seraphin coefficients,[14] which depend on the real (ε_1) and imaginary (ε_2) part of the complex dielectric function $\tilde{\varepsilon}$; $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are the thermally induced variations.

(b) The small binding energy of the exciton in GaSB (Rydberg energy $\sim 1.5\times10^{-3}$ eV),[13,15] the increase in alloy disorder with x, and the relatively high temperature mean that the excitonic peak may reasonably be thought to be immersed in the fundamental absorption tail. Thus, the complex dielectric function $\tilde{\varepsilon}$ can be expressed by[10]

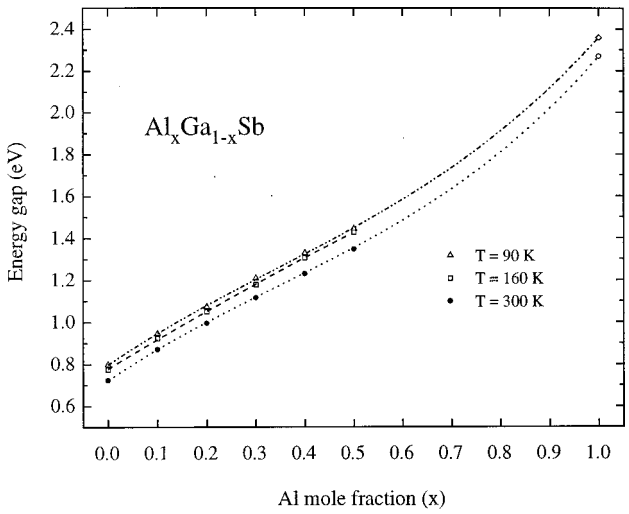

FIG. 2. Energy values of the direct gap E_g^Γ in $Al_xGa_{1-x}Sb$ as a function of Al mole fraction (x) at three different temperatures; the lines represent the fits using a cubic polynomial expression. The values for $x=1$ at 300 and 90 K are from Refs. 18 and 7, respectively.

$$\tilde{\varepsilon}-1\propto\int_{E_g}^{E_g'}\frac{dE}{(E-\eta\omega)-i\gamma}=\int_x^{x'}\frac{dy}{y+i}, \tag{2}$$

where $\eta\omega$, E_g, and γ are the photon energy, the critical-point energy, and the broadening parameter, respectively; $x=(\eta\omega-E_g)/\gamma$, $x'=(\eta\omega-E_g')/\gamma$, and $y=(\eta\omega-E_g)/\gamma$. In this model, E_g' stands for the upper limit of the absorption band, and it is assumed that $E_g'-E_g\gg\gamma$. The functions ε_1 and ε_2 obtained from this simple and physically transparent model (ε_2 is a step function at E_g, broadened by lifetime effects) are in good agreement with those calculated analytically by Tanguy[16] for a direct semiconductor with Wannier excitons, which included the exact contribution of all bound and unbound states.

(c) The coefficient β is negligible with respect to α, in accordance with our previous results[13] on GaSb and with the general behavior of semiconductors in the region of the fundamental gap.[9,10] The experimental spectra of Fig. 1 show that from 80 to 300 K the E_g shift is much greater than the broadening of the line shape, so that the temperature modulation coefficient $d\gamma/dT$ is practically negligible with respect to the gap modulation dE_g/dT, as is generally observed for zinc-blende semiconductors.[9,10] Thus, by differentiating Eq. (2) and by Eq. (1) we find, approximately, near the absorption edge[10]

$$\frac{\Delta R}{R}\cong\alpha\Delta\varepsilon_1\propto\frac{\alpha}{\gamma}\left(\frac{x}{x^2+1}\frac{dE_g}{dT}\right)\Delta T. \tag{3}$$

The best fit of the $\Delta R/R$ spectra with the line shape given by Eq. (3) permitted the precise determination of E_g and γ, with typical uncertainties of 0.2 and 0.1 meV, respectively.

Figure 2 shows the resulting values of E_g^Γ vs x for three temperatures (see symbols). Note that in the compositional range $0.0\leqslant x\leqslant 0.5$ the dependence of E_g^Γ on x is quasilinear or over linear for all temperatures, i.e., the bowing parameter is positive. This behavior agrees with that obtained from transmittance measurements at $T=2$ K on samples with the

same characteristics.[8] Moreover, our E_g^Γ values, extrapolated to $T=2$ K with Varshni formula[17] $E_g(T)=E_g(0)-AT^2/(T+B)$ agree very well with those in Ref. 8, which, however, are systematically 5 meV redshifted, probably due to strain effects arising from differential thermal expansion between layer and substrate.

This result is apparently in contrast not only with that of Ref. 7 but also with the conventional assumption for which, in the III-V zinc-blende alloys, $E_g(x)$ and other critical-point energies can be fitted by a simple quadratic expression:

$$E_g(x)=a+bx+cx(1-x), \tag{4}$$

with the bowing parameter $c<0$. However, it has been experimentally established[5] that in $Al_xGa_{1-x}As$, E_g^Γ is described not by a quadratic but by a cubic polynomial: thus, in Eq. (4) the bowing is not a constant but a function of x, i.e., $c(x)=c_0+c_1x$. The inflection point for $x=0.37$ separates the region $x<0.37$ with very slight positive bowing from that with high-negative bowing values. This dependence of bowing on x is theoretically justified in Ref. 6 on the basis of first-principle band-structure calculations and traced to the fact that the AlAs end member is an indirect gap semiconductor. The same argument can be applied to $Al_xGa_{1-x}Sb$ assuming for AlSb the E_g^Γ values of 2.27 eV at RT (Ref. 18) and 2.36 eV at 90 K,[7] $E_g^\Gamma(x)$ is very well fitted by a cubic polynomial for all temperatures, as is shown in Fig. 2 (lines). The room-temperature values (in eV) of a, b, c_0, and c_1 fit parameters are 0.723, 1.547, 0.044, and -1.22, respectively, and the inflection point is at $x=0.35$. Observe that the bowing appears to be independent of temperature. The energy gap increases by a uniform amount with temperature, independent of alloy composition. In effect, for $T=90$ K the fit values of a, b, c_0, and c_1 are in the order 0.797, 1.562, 0.034, and -1.11.

Concerning the broadening, γ values resulting from the fit of $\Delta R/R$ at room temperature vary quasilinearly from 1.9 to 9.5 meV as x increases from 0 to 0.5. We did not observe for $x>0.2$ the strong increase reported in Ref. 8 and attributed to the occurrence of the E_g^Γ-E_g^L crossover. The same trend is followed by γ values at low temperatures. The broadening modulation $d\gamma/dT$ has an average value of $\sim 7\times10^{-6}$ eV/K for all concentration, which is indeed negligible with respect to $dE_g/dT\cong -4\times10^{-4}$ eV/K.

In conclusion, the combined use of TR technique and a physically simple model accounting for excitonic effects allowed the direct gap and the broadening values of $Al_xGa_{1-x}Sb$ for $x\leqslant 0.5$ to be accurately determined. The low-negative bowing values for $x<0.35$ also quantitatively confirmed the results of transmittance on samples of the same quality, and agreed with the experimental and theoretical evidence of an x-dependent bowing for alloys in which an end member is an indirect gap semiconductor. No evidence was obtained of anomalous broadening growth with x, which might be correlated to direct-indirect gap crossing.

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