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Photoreflectance and photoluminescence study of localization effects in GaAsBi alloys

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ABSTRACT

Photoreflectance (PR) and photoluminescence (PL) spectra of $GaAs_{1-x}Bi_x$ alloys grown by metalorganic vapor phase epitaxy, for x up to 4.8%, were measured at temperatures ranging from 12 to 300 K. The PR signal shifts due to the temperature change decreases with increasing Bi content of GaAsBi alloys. For temperature below 100 K, a dominant peak in PL spectra of GaAsBi was observed. This peak is attributed to carrier localization resulting from Bi-related localized states in GaAsBi. A decrease in PR signal has been also found when the temperature was lowered. This behavior is attributed to a weakening of modulation efficiency, which is induced by carrier localization that has been evidenced in low temperature PL. The localized state emission partly contributes to the decrease in the band gap energy shift. In addition, at high temperatures the small PR signal shift is due to the reduction in the temperature dependence of the band gap energy. The analysis of the band gap energy evolution with temperature using the Bose–Einstein statistical expression shows that the average phonon energy is much larger than that expected from the linear interpolation between GaAs and GaBi. This fact is related to the interaction between electrons and phonons localized at Bi atoms playing an important role in the reduction of the temperature dependence of the band gap energy of GaAsBi alloys.

1. Introduction

Currently there is a considerable interest in III–V–Bi alloys, such as GaAsBi because of their fundamental physical properties and potential device applications [1–3]. The substitution of a few percent of As by Bi atoms, acting as an isoelectronic impurity, in GaAs leads to a large reduction in band gap energy, accompanied with a rapid increase in the spin–orbit-splitting energy [3–7]. This characteristic makes GaAsBi alloys very attractive candidates for high performance infrared emitters and detectors and high-efficiency solar cells [8–10]. Several theoretical and spectroscopic studies show that only the valence band of GaAs is affected by alloying it with Bi [9,11,12]. The Bi incorporation in GaAs is mainly perturbing the valence band and adding a carrier localization effect. Disorder effects, i.e., compositional fluctuations together with the Bi clustering within the GaAsBi alloy structure, lead to an increasing density of localized states [13–15]. However, the photoluminescence (PL) spectra measured at low temperature are dominated by the recombination of localized carriers trapped at local potential minima [15]. The GaAsBi alloy was successfully grown by metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy [16–21]. Epitaxial layers of GaAsBi have demonstrated a reduced temperature dependence of the lasing wavelength, which makes them promising for the manufacture of laser diodes and semiconductor optical amplifiers that do not require Peltier cooling [10]. Recently, a large number of reports on detailed optical characterizations of GaAsBi were published [7,14,22–37]. They include temperature dependence of PL, time-resolved PL, Photomodulated transmittance and photoreflectance (PR). These reports are more or less related to the effect of the alloy disorder characteristic of the bismuth containing alloys, which leads to radiative recombination of the localized carriers at low temperature. In view of these reports, many fundamental optical properties of GaAsBi alloys grown by MOVPE are yet unknown. Thus, detailed studies are necessary in order to clarify the role of Bi amount on the optical properties of GaAsBi.

In this paper, we report a detailed PR study on the Bi content and temperature dependence to the optical transition in GaAsBi and the influence of localized states. The PR behavior change will be discussed together with PL measurements.

2. Experimental details

The samples studied in the present work were grown by atmospheric pressure metalorganic vapor phase epitaxy with varying Bi

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contents up to 4.8%. The Bi content and thickness of the GaAsBi epilayers were determined using high resolution X-ray diffraction by assessing the Bragg angle of the GaAsBi reflections and pendellosung oscillations respectively [5]. The growth parameters are summarized in Table 1.

The PR measurements were carried out employing a standard setup with the 514.5 nm line of an argon laser as the pump light in a variable temperature close-cycle cryostat, and detected by an InGaAs detector. The probe light was obtained from a tungsten-halogen lamp analyzed with a 50 cm focal length monochromator. Further details of the sample preparation and characterization are given elsewhere [5,6,16–18,34].

3. Results and discussion

Fig. 1 shows the PR spectra of GaAsBi layers measured at 300 K. A distinct spectral feature due to GaAsBi was observed in each spectrum. The PR signal shifts to lower energies with increasing Bi content, which corresponding to the reduction of the bandgap energy. For all the layers the spin–orbit (SO) splitting is observed in PR spectra. The bandgap energies (E_g) and the optical transition between the SO splitted valence band and the conduction band ($E_g + \Delta_{SO}$) are indicated with arrows in Fig. 1.

In order to determine the energies of E_g and $E_g + \Delta_{SO}$ transitions a theoretical multilayer model based on the matrix method has been applied [6]. The energies of E_g and $E_g + \Delta_{SO}$ transitions extracted from the fitting curves are shown in Fig. 2(a). Their evolutions decrease significantly with increasing Bi content. By subtracting the band gap energy from the SO energy, the SO splitting Δ_{SO} was extracted and plotted also in Fig. 2(b). The composition dependence of the bandgap and the SO splitting of a semiconductor alloy is usually described by introducing a constant bowing parameter b. For the ternary system $GaAs_{1-x}Bi_x$, the relationships are:

$$E_g^{GaAsBi} = xE_g^{GaBi} + (1-x)E_g^{GaAs} - b_g x(1-x) \quad (1a)$$

$$\Delta_{SO}^{GaAsBi} = x\Delta_{SO}^{GaBi} + (1-x)\Delta_{SO}^{GaAs} - b_{SO} x(1-x) \quad (1b)$$

where x is the bismuth content in GaAsBi alloy. $E_g^{GaBi} = -0.360$ eV (Ref. [27]) and $E_g^{GaAs} = 1.425$ eV are the bandgap energies of GaBi and GaAs, respectively. Also $\Delta_{SO}^{GaBi} = 2.15$ eV [3] and $\Delta_{SO}^{GaAs} = 0.34$ eV are the SO splitting energies of GaBi and GaAs, respectively. For the GaAsBi alloy investigated here, using a constant bowing coefficient would result in a bad fit of experimental data, especially when Bi content increases (see the dashed line in Fig. 2(b)). In order to remedy to this failure, we define a bowing parameter that decreases monotonically with increasing Bi content as follows [27]:

$$b_g(x) = \frac{\alpha_g}{1+\beta_g x} \quad (2a)$$

$$b_{SO}(x) = \frac{\alpha_{SO}}{1+\beta_{SO} x} \quad (2b)$$

By substituting Eq. (2) into Eq. (1), we get good fits as shown by solid lines in Fig. 2(a) and (b). We find $\alpha_g = 6.5$, $\beta_g = 35$, $\alpha_{SO} = 6$ and $\beta_{SO} = 140$. This result indicates that the bowing parameter decreases with increasing Bi content. Similar results are found in GaAsN and InAsN alloys [38,39]. The composition dependence of the bowing parameter are due to the large differences between the sizes of the alloyed As and Bi atoms and between their atomic orbital energies, spatially separated and sharply localized band edge states are formed in the alloy. Our data indicate that the GaAsBi is III–V alloy exhibiting a Bi dependent bowing parameter not only for E_g, but also for Δ_{SO}.

Table 1
Growth parameters of GaAsBi alloys. The Bi content and the thickness are determined by high-resolution X-ray diffraction.

Sample	GaAsBi growth temperature (°C)	GaAs buffer thickness (nm)	GaAsBi layer thickness (nm)	Bi content (%)
A	420	100	210	0.2
B	420	80	160	0.7
C	420	80	50	1.3
D	420	80	125	2
E	420	80	50	3.7
F	420	80	50	4.8

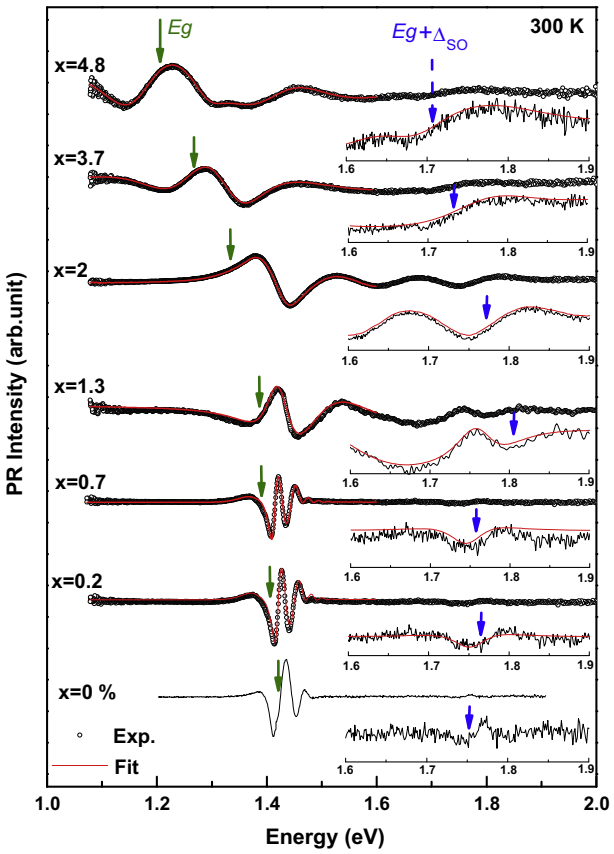

Fig. 1. Room temperature PR intensity spectra of the GaAsBi samples as a function of Bi content. The solid lines represent adjustments by a multilayer model. Arrows designate the position of E_g and $E_g + \Delta_{SO}$ transitions. Parts of PR spectra from 1.6 to 1.9 eV are zoomed.

Fig. 3(a) and (b) shows the temperature dependence of PL and PR spectra of GaAsBi layer with Bi = 4.8%, respectively. The measurements were performed in the temperature range of 12–300 K. At low temperatures (12–100 K), the PL spectra are dominated by only one peak located at 1.34 eV, which shows a significant reduction in the intensity as the temperature increases. As discussed in our previous work [15], this thermal quenching effect is an indicative of the presence of localized states. Such behavior is generally observed for mismatch materials such as GaAsN and GaAsBi [14,36,40]. Various procedures are required to understanding the origin of this phenomenon. The inset of Fig. 3(a) shows low temperature (12 K) PL spectra of GaAsBi sample with Bi = 4.8% measured at three incident light wavelengths of $\lambda = 514$ nm, 442 nm and 325 nm. It can be observed that the peak position exhibits no change or shows small blueshift with decreasing wavelength. Depending on the wavelength, the penetration depth varies. Indeed, the penetration depth increases with increasing wavelength. However, for the lower excitation wavelength of 325 nm, PL intensity of peak located at 1.34 eV is more pronounced than the GaAs peak. On the other hand, at higher wavelength (514 nm) the PL intensity of this peak is less marked