Temperature dependence of the band gap of $GaSb_{1-x}Bi_x$ alloys with $0<x\leq0.042$ determined by photoreflectance

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$GaSb_{1-x}Bi_x$ layers with $0<x\leq0.042$ have been studied by photoreflectance in 15-290K temperature range. We found that due to the incorporation of Bi atoms into the GaSb host, the E_0 band gap-related transition redshifts (~30meV per 1% Bi) and significantly broadens. The shift of the E_0 transition in the temperature range 10-270K has been found to be ~70meV, very similar to the energy shift in GaSb over the same temperature range. We analyzed the energy and broadening of the E_0 transition using the Varshni and Bose-Einstein formulas and found that the Varshni and Bose-Einstein parameters of $GaSb_{1-x}Bi_x$ are similar to those of GaSb. Moreover we concluded that the inhomogeneities in $GaSb_{1-x}Bi_x$ alloys is less important than in dilute bismide arseindes since Bi atoms are more similar to Sb atoms (in electronegativities and ionic sizes).

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Dilute bismides, i.e., III-V alloys with a few percent of Bi atoms, have attracted attention because of their interesting fundamental properties [1-12] as well as potential applications in optoelectronic devices operating in the infrared and mid-infrared spectral region. Regarding the application of dilute bismides in the mid-infrared spectral region, besides $In_{0.53}Ga_{0.47}Bi_xAs_{1-x}$ grown on InP substrate [10, 13-15], $GaSb_{1-x}Bi_x$ grown on GaSb seems to be very promising. The band structure and optical properties of $GaSb_{1-x}Bi_x$ alloys have not previously been explored by photoreflectance (PR) or indeed many other techniques because such materials were not available. Recently it has been shown that good quality $GaSb_{1-x}Bi_x$ layers can be grown by molecular beam epitaxy (MBE) [16]. In this Letter, we apply PR to study the Bi-related reduction of band gap for $GaSb_{1-x}Bi_x$ and the temperature dependence of band gap for this alloy.

Previous studies of dilute bismides claimed that the temperature dependence of the band gap in GaAsBi is strongly reduced upon Bi incorporation [1]. However, this conclusion was mainly based on photoluminescence (PL) measurements, which may be inappropriate for the investigation of the band gap at low temperature due to the emission like character of the PL technique and hence its high sensitivity to localized states [17, 18]. In order to determine the temperature dependence of the band gap, absorption-like techniques are more appropriate since they probe optical transitions between delocalized states. Using PR and modulated transmittance it has been shown that the temperature dependence of the band gap of GaAsBi and $In_{0.53}Ga_{0.47}Bi_xAs_{1-x}$ is similar to that observed in narrow gap semiconductors [10, 14]. In this context, it is very interesting to apply PR spectroscopy to study the temperature dependence of the band gap energy in $GaSb_{1-x}Bi_x$ alloys with various Bi concentrations.

The GaSbBi films with thickness of 330 nm were grown by solid source MBE pseudomorphically on GaSb (001) undoped substrates as described in Ref. 16. The Bi content in the films were controlled by varying both the substrate temperature and the growth rate.

Specifically, in this work the sample with 0.7% Bi was grown at 350°C and 0.4 μmh^{-1}, and samples with 2.1% and 4.2% Bi were grown at 275°C and 0.6 and 0.8 μmh^{-1}, respectively. The Bi concentration in the $GaSb_{1-x}Bi_x$ layers was determined by high-resolution X-ray diffraction and Rutherford backscattering spectrometry measurements as described in Ref. [16]. For temperature dependent PR measurements, samples were mounted on a cold finger in a helium closed cycle refrigerator coupled with a programmable temperature controller, allowing measurements in the 15-300 K temperature range. A single grating 0.55 meter focal-length monochromator and a thermoelectrically-cooled InGaAs *pin* photodiode were used to disperse and detect the reflected light from the samples. A 150W tungsten-halogen bulb was used as the probe, and a semiconductor laser (660nm line) was used as the pump source. The probe and pump beams were focused onto the sample to a diameter of ~3 mm and the power of laser beam was reduced to 20 mW using a neutral density filter. The pump beam was modulated by a mechanical chopper at a frequency of 280 Hz. Phase sensitive detection of the PR signal was accomplished using a lock-in amplifier.

Figure 1 shows PR spectra measured at 15 and 270K for $GaSb_{1-x}Bi_x$ samples with 0.7, 2.1, and 4.2% of bismuth. A clear PR resonance is observed for the three samples below the band gap energy of GaSb. This resonance redshifts with increasing Bi concentration. We attribute this resonance to the energy-gap transition (E_0) in $GaSb_{1-x}Bi_x$ layers. For the $GaSb_{1-x}Bi_x$ sample with the lowest Bi concentration a sharp PR resonance related to absorption by the GaSb buffer layer is visible besides the GaSbBi-related transition. Such a resonance is not visible for samples with larger Bi concentration probably due to the lack of (or very weak) band bending modulation in the GaSb buffer layer in these samples.

Figure 2 shows the temperature dependencies of PR spectra measured for the three $GaSb_{1-x}Bi_x$ samples at the same conditions of band bending modulation. It is clearly visible that the E_0 transition in the $GaSb_{1-x}Bi_x$ layers redshifts and broadens with increasing

temperature. In order to determine the energy of the E_0 transition and its broadening, the PR spectra were fitted using the Aspnes formula [19]

$$\frac{\Delta R}{R}(E) = \mathrm{Re}\left[Ce^{i\vartheta}\left(E - E_0 + i\Gamma\right)^{-m}\right], \tag{1}$$

where $\frac{\Delta R}{R}(E)$ is the energy dependence of the PR signal, C and ϑ are the amplitude and phase of the line, and E_0 and Γ are the energy and the broadening parameter of the optical transition, respectively. The term m depends on the type of optical transition and in this case this parameter is assumed to be 2.5 that corresponds to a band-to-band transition.

Examples of experimental data fitted by the Aspnes formula are shown in Fig. 1 together with the moduli of the PR resonances which are shown as dashed black lines. The moduli of the PR resonances were obtained according to Eq.(2) with parameters taken from the fit.

$$\Delta\rho(E) = \frac{|C|}{\left[\left(E - E_j\right)^2 + \Gamma^2\right]^{\frac{m}{2}}} \tag{2}$$

Note that the character of the E_0 transition in $GaSb_{1-x}Bi_x$ layers can be excitonic at low temperatures and changes to band-to-band as the temperature increases [18]. However the excitonic and band-to-band contributions are difficult to resolve in PR spectra due to alloy inhomogeneities which lead to a significant broadening of PR resonances. Moreover the compressive strain in $GaSb_{1-x}Bi_x$ layers should lead to a splitting of heavy- and light-hole bands and hence the E_0 transition can be composed of two PR resonances: one related to the heavy-hole transition and second related to the light-hole transition. This issue is more important for $GaSb_{1-x}Bi_x$ samples with larger Bi concentration. In our case the valence band

splitting is neglected for all three samples since the two resonances are not well resolved probably due to their large broadening and weak intensity of the light-hole related transition. Therefore the PR spectra for the three samples over the whole temperature range are fitted by one resonance which is attributed to the band-to-band transition between the heavy-hole band and the conduction band at the center of Brillouin zone.

Figure 3 shows the temperature dependence of the energy of the E_0 transition extracted from the fitting procedure for the three $GaSb_{1-x}Bi_x$ samples of various Bi concentrations. In addition, the temperature dependence of the band gap in GaSb is plotted in this figure. It is clearly visible that the temperature induced narrowing of band gap in $GaSb_{1-x}Bi_x$ alloy is quite significant (~70meV meV in the range of 10-290K) and comparable with that observed for GaSb and other narrow gap dilute bismides [14].

The temperature dependence of the E_0 transition has been fitted using both the Varshni [20] and Bose-Einstein (B-E) [21, 22] expressions. The Varshni formula is given by Eq.(3)

$$E_0(T) = E_0(0) - \frac{\alpha T^2}{\beta + T}, \tag{3}$$

where $E_0(0)$ is the band gap energy at $T=0\ K$ while α and β are the so-called Varshni coefficients. The B-E expression, which involves electron coupling to an average phonon, is given by Eq. (4)

$$E_0(T) = E_0(0) - \frac{2a_B}{\exp\left(\frac{\Theta_B}{T}\right) - 1}, \tag{4}$$

where a_B is the strength of the electron-average phonon interaction and Θ_B is the average phonon temperature.

The dashed and solid lines in Fig. 3 correspond to curves fitting the experimental points using Eqs. (3) and (4), respectively. The fit-determined parameters, $E_0(0)$, α, β, a_B, and Θ_B for E_0 transition are listed in Table I. In addition, literature data for GaSb [23], $In_{0.53}Ga_{0.47}As$ [24], and other narrow gap dilute bismides [14] are also given in Table I.

Comparing the Varshni and Bose-Einstein parameters determined for E_0 transition for the three GaSbBi samples with the literature parameters for GaSb [23] and other dilute bismides studied by PR [14], it can be concluded that they are very similar and consistent. Moreover a small evolution of Varshni and B-E parameters can be recognized for this set of samples. Since B-E parameters have a deeper physical interpretation it is interesting to note that the a_B and Θ_B increase with the rise of Bi concentration. It suggests that the Bi incorporation into GaSb enhances the strength of the electron-average phonon interaction and the average phonon temperature.

Figure 4 shows the temperature dependence of the broadening of the E_0 transition, i.e., the Γ parameter extracted from the fitting of the PR spectra by the Aspnes formula. The broadening of the PR resonance (~12meV) at low temperature is associated with alloy inhomogeneities which are typical for all alloys. The increased broadening of the PR resonance with increasing temperature is due to interactions with phonons and can be described by the Bose-Einstein formula

$$\Gamma_0(T) = \Gamma_0(0) + \frac{\Gamma_{LO}}{\exp\left(\frac{\Theta_{LO}}{T}\right) - 1}, \tag{5}$$

where Γ_{LO} is the electron-longitudinal optical (LO) phonon coupling constant, and Θ_{LO} is the LO phonon temperature. Our experimental data have been fitted by Eq. (5) and the fitting curves are shown by solid lines in Fig. 4. The determined B-E parameters are given in Table II.

It is worth noting that $\Gamma_0(0)$ in Eq. (5) is the broadening which results from the intrinsic lifetime and other phenomena like alloy scattering. As previously mentioned, alloy scattering effects are principally responsible for the broadening of the PR transition at low temperatures for GaSbBi samples studied in this paper. On the other hand much larger broadening of the PR resonance was observed for other dilute bismide arsenides [14, 25] due to high alloy inhomogeneity related to the relatively large size and electronegativity mismatch between As and Bi. Results obtained in this work clearly show that the inhomogeneities in $GaSb_{1-x}Bi_x$ alloys is less important than in dilute bismide arseindes since Bi atoms are more similar to Sb atoms (in electronegativities and ionic sizes). This also suggests that better quality alloys can be obtained by alloying GaBi with GaSb than alloying GaBi with GaAs. In addition to being related to the extent of alloy inhomogeneity, the degree of anion size and electronegativity mismatch in dilute bismides also correlates with the amount of band gap reduction upon Bi incorporation. The band gap reduction in the GaSbBi samples studied here is about 30 meV/%Bi. This is about one third of the value for GaAsBi (84-90 meV/%Bi) [2, 3, 6, 25] and almost half that of $In_{0.53}Ga_{0.47}As_{1-x}Bi_x$ (50 meV/%Bi) [10, 14]. Similar trends have been observed for dilute nitrides with, for example, the band gap reduction upon incorporation of 1% N in GaSb being twice that for N in GaAs, reflecting the greater mismatch between N and Sb than between N and As [26].

In conclusion, $GaSb_{1-x}Bi_x$ layers with Bi concentration $0<x\leq0.042$ have been studied by PR spectroscopy in the temperature range of 15-290K. A strong PR signal related to the band gap absorption in $GaSb_{1-x}Bi_x$ (i.e., the E_0 transition) was observed in PR spectra below the

band gap of GaSb. This E_0 transition shifts to lower energy with increasing Bi concentration (~30meV per % of Bi) and broadens significantly compared to the broadening of the GaSb-related transition. The temperature induced shift of the E_0 transition between 15 and 290 K has been found to be ~70 meV which is very close to the shift of the band gap in the GaSb host material over the same temperature range. The energy and broadening of the E_0 transition were determined using the Aspnes lineshape and fitted by the Varshni and Bose-Einstein formulas. The Varshni and Bose-Einstein parameters were found to be close to the parameters of GaSb and other narrow gap dilute bismides.

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Figure Captions:

FIG. 1. Photoreflectance spectra of 330 nm thick $GaSb_{1-x}Bi_x$ layers with 0.7 (a), 2.1 (b), and 4.2% (c) of bismuth obtained at 15 and 270K together with the fitting curves (thick grey lines) in the vicinity of the band gap transition and the moduli of photoreflectance resonance (dashed lines).

FIG. 2. Temperature dependence of photoreflectance spectra of 330 nm thick $GaSb_{1-x}Bi_x$ layers with 0.7 (a), 2.1 (b), and 4.2% (c) in the vicinity of the E_0 transition.

FIG. 3. Temperature dependence of the E_0 transition energy for $GaSb_{1-x}Bi_x$ layers with 0.7, 2.1, and 4.2% Bi together with fits by the Varshni (solid lines) and Bose-Einstein (dashed lines) formulas, Eqs. (3) and (4).

FIG. 4. Temperature dependence of the broadening of the E_0 transition for $GaSb_{1-x}Bi_x$ layers with 0.7, 2.1, and 4.2% Bi together with fits by the Bose-Einstein formula (solid lines), Eq.(5).

TABLE I Varshni and Bose-Einstein parameters extracted from fitting of the E_0 transition shown in Fig. 3 by Eqs. (3) and (4).

Sample	$E_0(0)$ (eV)	α (10^{-4} eV/K)	β (K)	$E_0(0)$ (eV)	a_B (meV)	Θ_B (K)
GaSb[(a)]	0.813	3.78	94	0.811	22	127
$In_{0.53}Ga_{0.47}As$[(b)]	0.803	4.0	226	-	-	-
$In_{0.53}Ga_{0.47}Bi_{0.012}As_{0.988}$[(c)]	0.757±0.001	4.2±0.3	295±80	0.755±0.001	34±2	228±10
$In_{0.53}Ga_{0.47}Bi_{0.044}As_{0.956}$[(c)]	0.585±0.001	3.3±0.3	280±50	0.583±0.001	27±2	219±10
GaSb[(d)]	0.813±0.001	3.7±0.5	90±20	0.811±0.001	20±5	118±20
$GaSb_{0.993}Bi_{0.007}$[(d)]	0.785±0.001	3.9±0.5	120±50	0.781±0.001	35±5	190±50
$GaSb_{0.979}Bi_{0.021}$[(d)]	0.740±0.001	3.7±0.5	110±50	0.738±0.001	46±5	220±50
$GaSb_{0.958}Bi_{0.042}$[(d)]	0.685±0.001	3.2±0.5	160±50	0.683±0.001	42±5	230±50

[(a)] – Ref. [23]

[(b)] – Ref. [24]

[(c)] – Ref. [14]

[(d)] – this work

TABLE 1

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TABLE II Bose-Einstein parameters extracted from fitting of the broadening of the E_0 transition shown in Fig. 4 by Eq. (5).

Sample	E_0		
	Γ_0 (meV)	Γ_{LO} (meV)	Θ_{LO} (K)
$In_{0.53}Ga_{0.47}Bi_{0.012}As_{0.988}$ [(a)]	52±1	33±5	265
$In_{0.53}Ga_{0.47}Bi_{0.044}As_{0.956}$ [(a)]	169±1	17±5	265
$GaSb_{0.993}Bi_{0.007}$ [(b)]	12±1	30±10	330±50
$GaSb_{0.979}Bi_{0.021}$ [(b)]	12±1	24±2	320±50
$GaSb_{0.958}Bi_{0.042}$ [(b)]	11±1	20±5	290±50

(a) – Ref. [14]

(b) – This work

TABLE 2

(J. Kopaczek et al.)

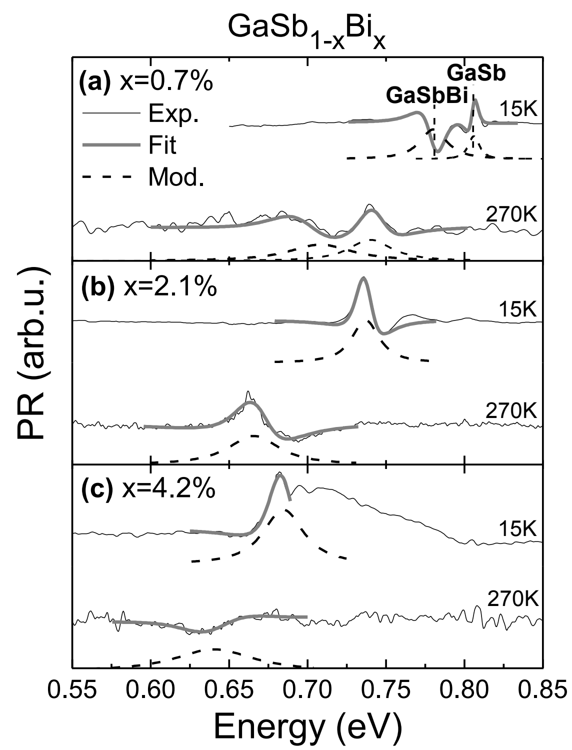

FIG. 1.

(J. Kopaczek et al.)

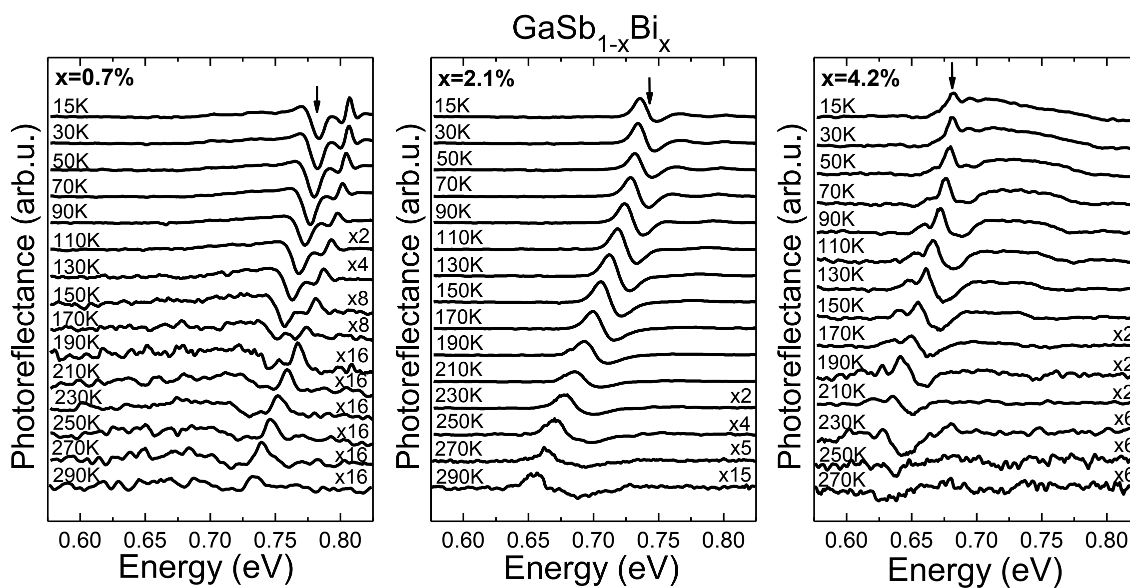

FIG. 2.

(J. Kopaczek et al.)

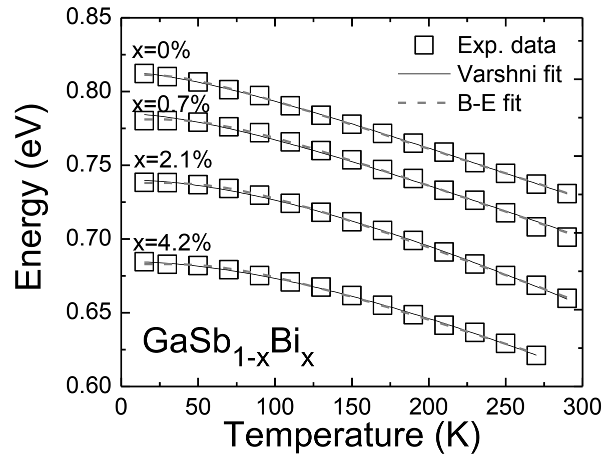

FIG. 3.

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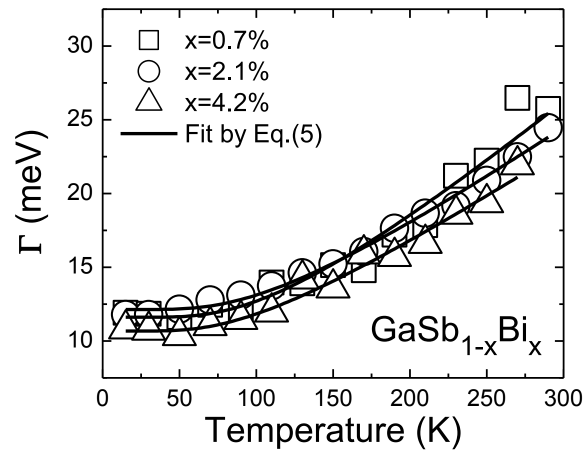
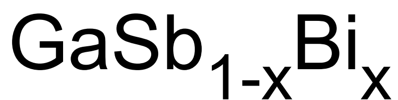
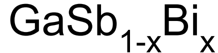


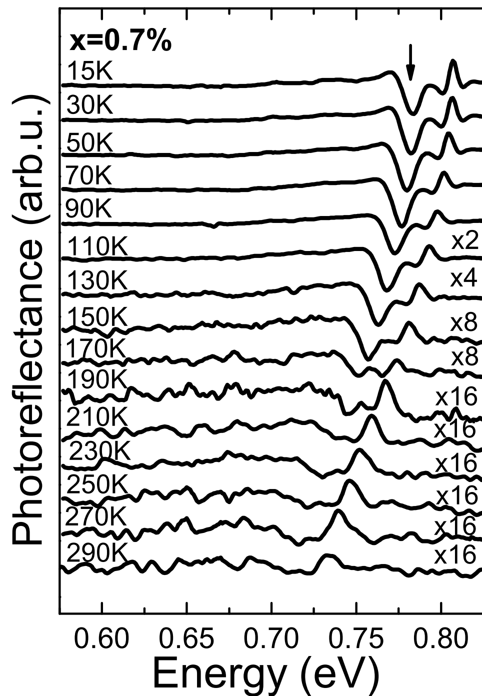
FIG. 4.

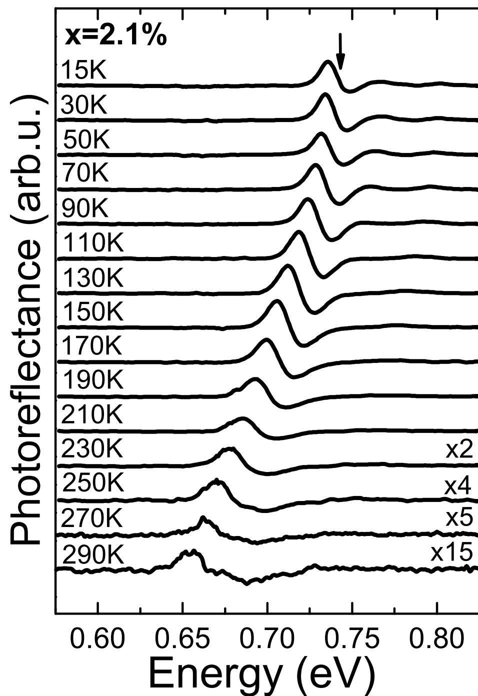
(J. Kopaczek et al.)

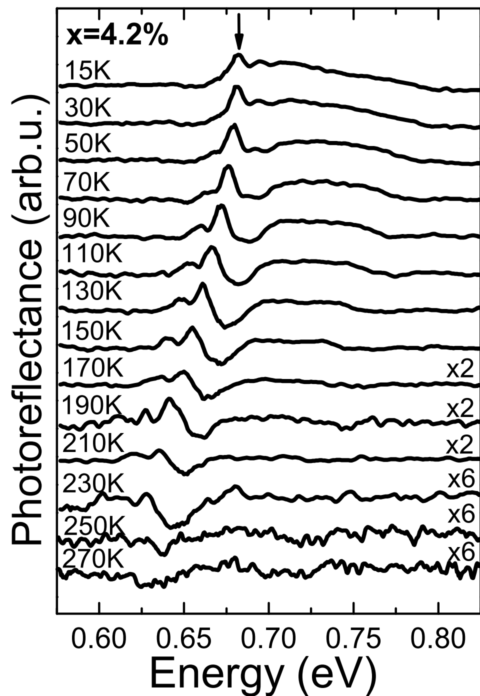


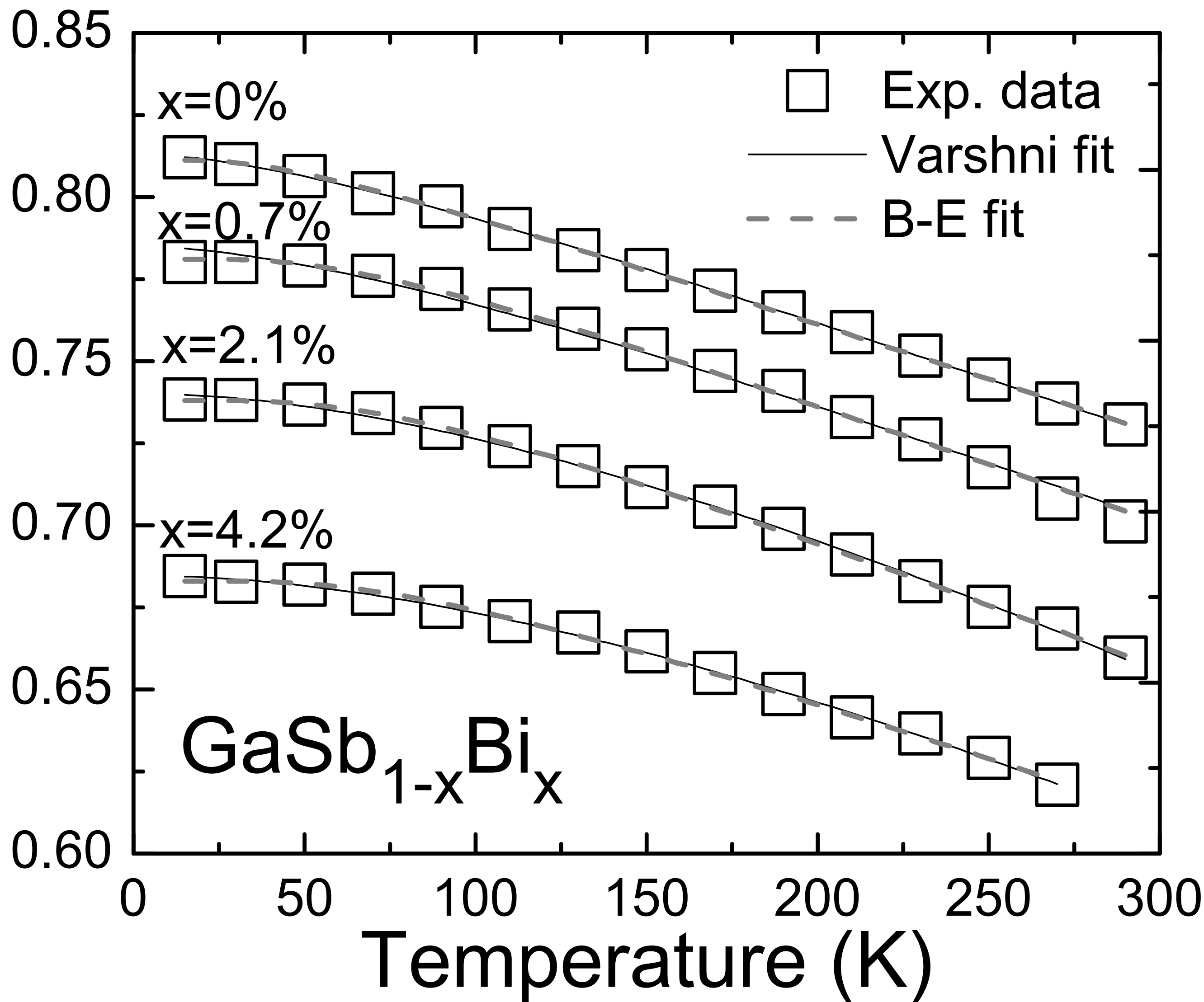
$GaSb_{1-x}Bi_x$
(a) x=0.7%
Exp.
Fit
Mod.
GaSb
GaSbBi
15K
270K
(b) x=2.1%
15K
270K
(c) x=4.2%
15K
270K
PR (arb.u.)
0.55
0.60
0.65
0.70
0.75
0.80
0.85
Energy (eV)


GaSb1-xBix

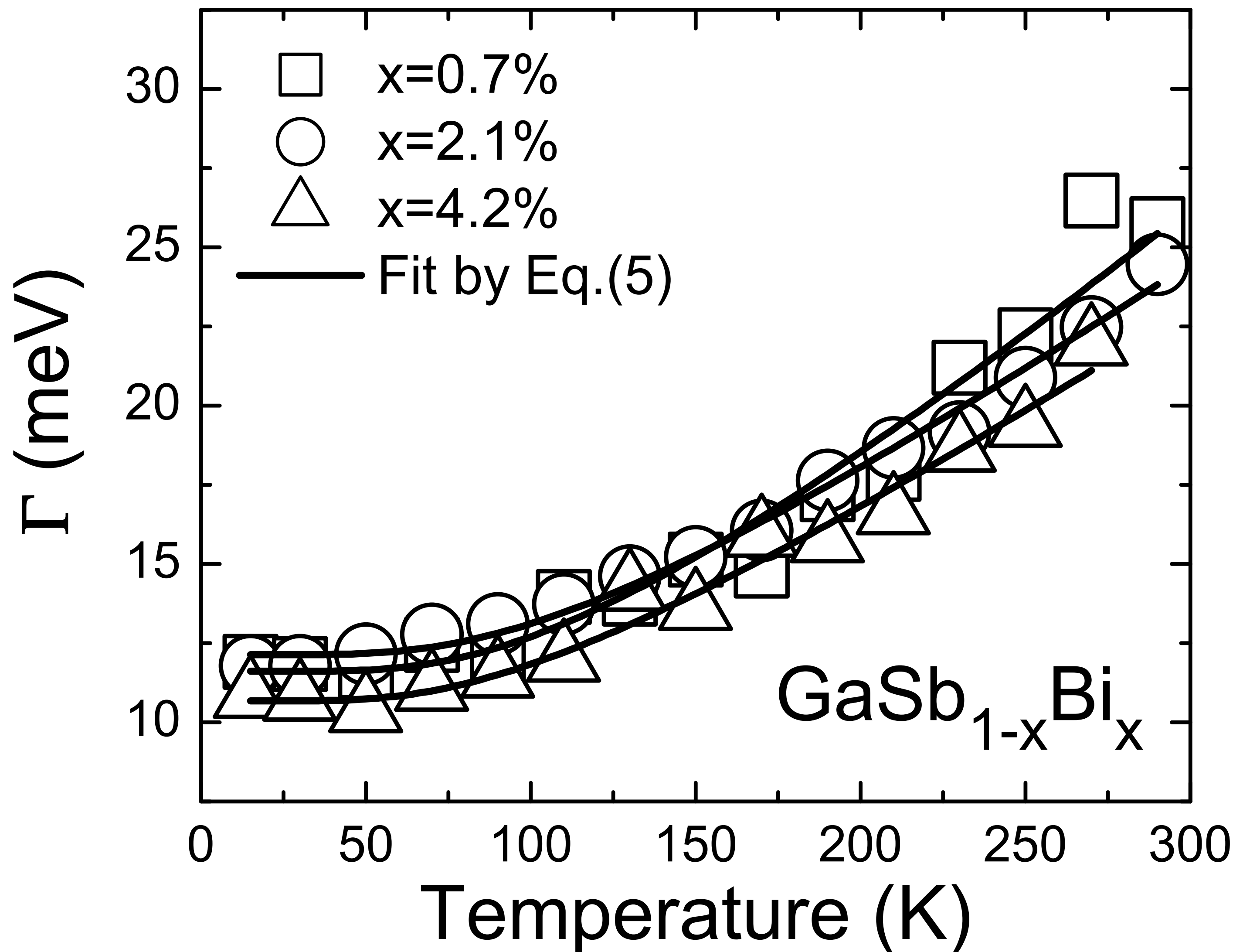

x=0.7%
15K
30K
50K
70K
90K
110K
130K
150K
170K
190K
210K
230K
250K
270K
290K
x2
x4
x8
x8
x16
x16
x16
x16
x16
x16
Photoreflectance (arb.u.)
0.60
0.65
0.70
0.75
0.80
Energy (eV)


x=2.1%
15K
30K
50K
70K
90K
110K
130K
150K
170K
190K
210K
230K
250K
270K
290K
x2
x4
x5
x15
Photoreflectance (arb.u.)
0.60
0.65
0.70
0.75
0.80
Energy (eV)


x=4.2%
15K
30K
50K
70K
90K
110K
130K
150K
170K
190K
210K
230K
250K
270K
x2
x2
x2
x6
x6
x6
Photoreflectance (arb.u.)
0.60
0.65
0.70
0.75
0.80
Energy (eV)



0.85
0.80
0.75
0.70
0.65
0.60
Energy (eV)
0
50
100
150
200
250
300
Temperature (K)
x=0%
x=0.7%
x=2.1%
x=4.2%
Exp. data
Varshni fit
B-E fit
GaSb1-xBix


x=0.7%
x=2.1%
x=4.2%
Fit by Eq.(5)
GaSb1-xBix
Γ (meV)
Temperature (K)
10
15
20
25
30
0
50
100
150
200
250
300