Theoretical and experimental studies of electronic band structure for $GaSb_{1-x}Bi_x$ in the dilute Bi regime

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Photoreflectance (PR) spectroscopy was applied to study the band gap in $GaSb_{1-x}Bi_x$ alloys with Bi<5%. Obtained results have been interpreted in the context of *ab-initio* electronic band structure calculations in which the supercell based calculations (SC) are joined with the alchemical mixing (AM) approximation applied to a single atom in the cell. This approach, which we call SC-AM, allows on the one hand, to study alloys with a very small Bi content, and on the other hand, to avoid limitations characteristic of pure AM approximation. It has been shown that the pure AM does not reproduce the $GaSb_{1-x}Bi_x$ band gap determined from PR while the agreement between experimental data and the *ab initio* calculations of the band gap obtained

within the SC-AM approach is excellent. These calculations show that the incorporation of Bi atoms into GaSb host modifies both the conduction and valence band. The shift rates found in this work are respectively -26.0meV per % Bi for conduction band and 9.6meV per % Bi for valence band what in consequence leads to a reduction of band gap by 35.6meV per % Bi. The found shifts of conduction and valence band give ~27% (73%) valence (conduction) band offset between $GaSb_{1-x}Bi_x$ and GaSb. The rate of Bi-related shift for split-off band is -7.0meV per % Bi and respective increase in the spin-orbit split-off is 16.6meV per % Bi.

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I. INTRODUCTION

Dilute bismides (i.e., III-V alloys with a few percent of Bi atoms) have attracted a lot of interest in recent years due to their unusual electronic band structure properties such as giant band-gap bowing [1-3], spin-orbit bowing [4], and their potential application in optoelectronic devices [5, 6]. So far, the band structure of dilute bismides have been studied quite intensively using various theoretical and experimental methods for GaAsBi and InGaAsBi alloys [1-4, 7-14]. Moreover GaAsBi has been used to form the active region in light-emitting structures such as optically-pumped lasers [15], light emitting diodes [16], and p-i-n diodes [17].

Much less attention has been devoted to GaPBi, GaSbBi, InPBi, or InSbBi alloys. There is a general agreement that the empirical virtual crystal approximation (VCA) does not provide a good description of the band gap variation with composition for dilute bismides and other highly mismatched alloys (HMAs), i.e., a class of semiconductors in which one or more of the component elements are replaced with elements of significantly different size and/or electronegativity [10, 18-22]. The electronic band structure of such alloys is usually calculated within the *ab-initio* approach [23-25] and the sp^3s^* tight-binding method [26-28], or can be described within the band anticrossing (BAC) model, i.e., in terms of an anticrossing interaction between the extended band states of the host material and localized states introduced by the minority component of the alloy [18-22]. In the original formulation the BAC model was applied to calculate the effects of interaction between extended conduction band states of GaAs and localized N-states in GaNAs alloys with small N content [18]. It was later generalized to consider the cases in which localized states of the minority elements affect the valence band structure, for example the case of Bi in GaAs host [10]. According to BAC model the whole Bi-related reduction of the band gap in GaAsBi comes from the interaction between Bi-related levels with the valence band (VB) states of GaAs host and should appear in the valence band. However, it has been recently reported that the incorporation of Bi atoms into GaAs host

influences the conduction band as well [13]. It suggests that the application of the BAC model to describe the band structure of GaAsBi is limited or should be modified. It can be done by taking into account the offset between conduction band (CB) of GaAs and GaBi [29]. However, here is still unclear if the BAC model can be applied to describe the whole band gap reduction in dilute bismides or only the deviation from the VCA. In this context it is very interesting to study the band structure for other dilute bismides such as GaSbBi since the difference between Sb and Bi electronegativities and sizes is much smaller than the respective differences in remaining dilute bismides i.e., GaPBi or GaAsBi. The validity of application of the virtual crystal approximation to describe the electronic band structure of $GaSb_{1-x}Bi_x$ is an open question similarly to the application of BAC model to this alloy.

So far, the theoretical studies of $GaSb_{1-x}Bi_x$ band structure were rather limited. In this work we extend the *ab initio* theoretical studies of $GaSb_{1-x}Bi_x$. Similarly, the band structure and optical properties of $GaSb_{1-x}Bi_x$ have not been explored experimentally very intensively since such materials were not available. Recently, is has been shown that good quality $GaSb_{1-x}Bi_x$ layers can be grown by molecular beam epitaxy (MBE) [30]. In this work we applied photoreflectance (PR) spectroscopy to study the band gap in $GaSb_{1-x}Bi_x$ alloys with Bi<5%. PR spectroscopy, due to its high sensitivity to critical point transitions in the band structure, is an excellent technique to study optical transitions in HMAs [10, 18-20, 31]. Obtained results are interpreted in the context of *ab-initio* electronic band structure calculations, which have been applied many times to study the band structure of HMAs [23-25] and are known to be a very powerful tool in solid state physics. In this work the Hartwigsen-Goedecker-Hutter (HGH) type [32] pseudopotentials have been used together with the Tran and Blaha modified Becke-Johnson functional (MBJLDA) [33] which has been proven to correctly reproduce the band-gap [34]. The use of pseudopotentials grants us the possibility to apply the alchemical mixing (AM) approximation, however, in this work we propose an approach in which the supercell

(SC) based calculations are joined with the AM applied to one atom only, which we call the SC-AM. This new approach offers an opportunity to study alloys with a very small Bi content and, at the same time, to avoid errors characteristic of pure AM (applied to atoms in a primitive cell). The results of *ab-initio* calculations are compared with experimental data. It is shown that the pure AM does not match the $GaSb_{1-x}Bi_x$ band gap determined from PR while the agreement between experimental data and theoretical calculations of the band gap obtained within the SC-AM is excellent. These calculations also show that the incorporation of Bi atoms into GaSb host modifies both the conduction and valence bands that is not expected and observed within the BAC model. It means that using the BAC model to describe the band structure of $GaSb_{1-x}Bi_x$ is insufficient. This conclusion is consistent with the BAC model assumptions regarding the difference between electronegativities of minority and host atoms, i.e., the difference between Sb and Bi atoms is much smaller than the difference between As (or P) and Bi atoms and hence the BAC effect in $GaSb_{1-x}Bi_x$ is weaker than in other dilute bismides.

The remainder of the paper is organized as follows. Experimental details are given in Sec. II. Theoretical model is described in Sec. III. The main results and their discussion are presented in Sec. IV. The overall conclusions of our work are summarized in Sec. V.

II. EXPERIMENTAL DETAILS

The $GaSb_{1-x}Bi_x$ samples of various Bi concentrations were grown by solid source MBE on GaSb (001) undoped substrates as broadly described in Ref. 27. The Bi concentration in the $GaSb_{1-x}Bi_x$ layers has been determined by high-resolution X-ray diffraction and Rutherford backscattering spectrometry measurements [30].

For PR measurements, the samples were mounted on a cold finger in a helium closed cycle refrigerator coupled with a programmable temperature controller, allowing the measurements in the 10-300 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 the 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. Other relevant details of PR measurements can be found in Ref. [35].

III. *AB INITIO* CALCULATIONS

The electronic properties of $GaSb_{1-x}Bi_x$ alloy have been studied from first principles within the density functional theory (DFT) with the use of ABINIT code [36, 37]. The Projector Augmented Waves (PAW) atomic datasets [38-40] have been used for structure relaxation, and the Hartwigsen, Goedecker and Hutter (HGH) relativistic dual-space Gaussian pseudopotentials [32] with the Tran and Blaha Modified Becke Jonson Local Density Approximation (MBJLDA) functional for the exchange energy [33] combined with the Perdew-Wang [41] Local Density Approximation (LDA) correlation part have been used for the electronic structure calculations. The choice of the HGH pseudopotentials was made to enable the calculations including the spin-orbit effects, which play a significant role in the studied alloy and need to be taken into account, and to provide a possibility to apply the alchemical mixing approximation. To simulate an alloy, two approaches have been employed: a pure AM approximation [39, 40] within an elementary zinc-blende (ZB) cell, and a combinations of 16-atom SC with the AM, i.e. a supercell containing one “alchemical” Sb/Bi atom (SC-AM). The alchemical mixing approach implemented in the ABINIT package uses the following construction: the local potentials are mixed in the proportion given by mixing coefficients, the

form factors of the non-local projectors are all preserved, and all considered to generate the alchemical potential, the scalar coefficients of the non-local projectors are multiplied by the proportion of the corresponding type of atom, the characteristic radius of the core charge is a linear combination of the characteristic radii of the core charges, the core charge function f(r/rc) is a linear combination of the core charge functions. In all the linear combinations the mixing coefficients reflecting the proportion at which particular atoms enter the alloy are used. In this approximation, norm conserving pseudopotentials of the same valence electron configuration have to be used, like e.g. Sb and Bi. In the SC-AM approach only one atom in 16-atom supercell is "alchemical" which allows to study the structural and electronic properties of $GaSb_{1-x}Bi_x$ alloy with a small content of Bi ($0<x<12.5\%$), and at the same time significantly reduced the errors characteristic of pure AM, i.e. the deviation of the lattice constant and the band-gap from the pure SC values, which is mainly due to the lack of the local atomic position relaxation, as discussed in Ref. [43]. The computational procedure was then as follows. First, the zinc-blende structural degrees of freedom were relaxed (for elementary, 16-atom SC, and 16-atom SC with one Bi atom) with the use of PAW datasets (with spin-orbit coupling included) which are known to give structural parameters in a very good agreement with the results of the full potential DFT methods, e.g. Full-potential Linearized Augmented Plane Waves (FLAPW). The lattice constants at compositions varying between 0 and 12.5% have been found by a linear interpolation between the GaSb value and that of 16-atom supercell containing one Bi atom. Thus, the full relaxation of the lattice containing one Bi atom (at Sb position) was performed (i.e. also the local distortion of the lattice due to the presence Bi atom has been taken into account). Second, the HGH pseudopotentials combined with the MBJLDA functional has been used to evaluate the band structure, band positions, the band-gap and densities of states. It has been found that the structure relaxation with HGH potentials and LDA exchange-correlation functional leads to a slightly smaller lattice constant (by about 1.5%) and in consequence to a

higher (by about 15%) band-gap, when used with MBJLDA. However, the use of the structural parameters obtained by the PAW calculations in HGH/MBJLDA approach reproduced the experimental band-gap values for GaSb with excellent agreement and no adjustment of MBJLDA parameters was needed. A cutoff energy for the plane-wave basis of 30Ha and an 4x4x4 Monkhorst-Pack grid [44] have been found to be sufficient, and were used in the calculations. In all the calculations the total energy has been converged down to 10^{-8} Ha.

IV. RESULTS AND DISCUSSION

Figure 1 shows PR spectra measured at 15 K for $GaSb_{1-x}Bi_x$ samples with various Bi concentrations. A clear PR resonance is observed for these samples below the energy gap of GaSb. This resonance shifts to red with the increase in Bi concentration. We attribute this resonance to the energy-gap transition (E_0) in $GaSb_{1-x}Bi_x$. In order to determine the energy of E_0 transition, PR spectra are fitted using Aspnes's formula [45]

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

where $\frac{\Delta R}{R}(E)$ is the energy dependence of 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 is assumed to be 2.5 that corresponds to a band-to-band transition. Fitting curves are shown thick grey lines in Fig. 1 together with the moduli of PR resonances which are shown as dashed black lines. The moduli of PR resonance are obtained according to Eq.(2) with parameters taken from the fit.

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

The band gap determined from PR measurements performed for $GaSb_{1-x}Bi_x$ layers of various Bi concentrations is plotted in Fig. 2.

In order to compare experimental data with theoretical predictions for $GaSb_{1-x}Bi_x$ alloys with various Bi concentrations first the electronic band structure was calculated for GaSb and GaBi binaries and compared with the literature. The band plot for GaSb is shown by grey dashed curves in Fig. 3. Such parameters as the band gap, the spin-orbit split off, the energy of the E_1 transition, etc. have been studied experimentally and are very well known [43]. The experimental values are: band gap 0.813eV and the spin-orbit split off 0.76eV and our calculations reproduce these parameters very well: 0.818eV and 0.71eV respectively. It means that we have a strong starting point for studies of the electronic band structure of $GaSb_{1-x}Bi_x$ alloys and our further predictions should be correct. Regarding the electronic properties of GaBi, no experimental data is available since such material has not been synthesized so far. However, some theoretical predictions of the band structure for this material can be found in the literature. We have found that the band gap of GaBi is -1.73 eV while -1.45, 2.14 and -2.91 eV band gaps have been reported by Janotti et al. [47], Rajpalke et al. [30] and Ferhat and Zaoui [48], respectively. There is a significant discrepancy between previously reported theoretical values, and our result fits well among the others.

To calculate the electronic properties of $GaSb_{1-x}Bi_x$ alloys we applied the SC-AM approach (described above). For comparison, a composition dependence of the band-gap was also calculated using the pure AM. An example of the electronic band structure of $GaSb_{0.9}Bi_{0.1}$ obtained within SC-AM is shown by thick curves in Fig. 3. The 10% of Bi content has been chosen to make the band offsets distinct and to show the ability of SC-AM approximation to

produce results for an arbitrary composition. It is clearly visible that the incorporation of Bi atoms into GaSb host significantly modifies the band structure of GaSb. Bi-related changes are more distinct in Fig. 4 where the bands are plotted in the vicinity of the Γ point of the Brillouin zone. This figure clearly shows that the band gap of GaSbBi narrows upon the incorporation of Bi atoms while the spin-orbit split off significantly increases. The narrowing of the band gap of 35.6 meV per % Bi is observed (starting from E_g = 0.82 eV in pure GaSb), which is due to the conduction band downward shift (of -26.0 meV per % Bi) valence band upward shift (of 9.6 meV per % Bi), thus the band alignment in a hypothetical quantum well would be a type I. This change in the band structure is also strongly manifested in the density of states (DOS) plotted in Fig. 5. Moreover, angular-momentum projected local DOS inside a sphere centered on chosen atoms have been evaluated and are shown in Fig. 6. It is worth noting that no shift of CB is expected within the valence BAC (VBAC) model since the resonant level related to Bi *p* states does not interact with the CB. Our calculations show that the Bi related changes in the CB at the Γ point are larger than in the VB. Similar changes in the electronic band structure have been obtained within pure AM, but the agreement with experimental value of the band gap is much worse in this case, as seen in Fig. 2. It is worth noting that theoretical calculations correspond to the lattice temperature of 0 K while experimental data are obtained at 15 K. However the expected variation of band gap in 0-15 K temperature range can be neglected in this case, since it should be much smaller than the size of experimental points in Fig. 2. Considering the fact that the SC-AM calculations were done for the relaxed bulk lattice the experimental values have been corrected for the presence of stress and the results (corresponding to the relaxed bulk lattice) shown by solid diamonds in Fig.2.

The significant deviation of pure AM from SC-AM (and the experimental data) is caused mainly by the lack of the local relaxation in AM, as discussed in Ref. [43]. The use of 16-atom supercell with a single "alchemical" atom significantly improves the band gap vs. Bi

concentration behavior, i.e. the band-gap exhibits larger bowing than that predicted by pure AM and reproduces the experimental values much better. An interesting conclusion can be drawn from Fig. 6. It can be seen that the downward shift of the CB is mainly due to the 6s states of Bi. The upward shift of the top of VB is also distinct, and a significantly dominant contribution comes here from the 6p states of Bi.

As mentioned earlier, within the VBAC model the whole band gap reduction is expected to be due to the interaction between Bi-related levels with the VB states of GaAs host and should appear in the valence band. However, this model assumes that the difference in the electronegativity of minority and host atoms is large and hence the influence of the minority atoms on the second band can be neglected. Such an assumption works very well for N atoms in GaP, GaAs, and InP hosts [18, 19, 22], where the influence of N atoms on the VB is negligible. For GaAsBi alloys the influence of Bi atoms on CB becomes significant, as reported in Refs. [14]. It means that the differences between electronegativities of Bi and As atoms (2.02 vs. 2.18 according to Pauling scale) are not large enough to omit the influence of Bi atoms on CB in this alloy. This difference is even smaller between Bi and Sb atoms (2.02 vs. 2.05) and hence Bi atoms have a significant effect on the CB and, the application of the valence BAC model to explain the whole band gap reduction is rather limited. In this case the energy gap of $GaSb_{1-x}Bi_x$ can be given by the following formula

$$E_g^{GaSb_{1-x}Bi_x} = (1-x)E_g^{GaSb} + xE_g^{GaBi} - \Delta E_g \quad (3)$$

where ΔE_g describes the deviation from the VCA. Usually this deviation is defined by a bowing parameter (b): $\Delta E_g = b(1-x)x$. For $GaSb_{1-x}Bi_x$ samples studied in this paper a good agreement of PR results with the theoretical values is obtained for the bowing parameter b = -1.0±0.1 eV,

see the dashed blue line. This bowing parameter is larger than bowing parameters which are typical of regular III-V alloys [46]. On the other hand this value is smaller than values of bowing parameters estimated for HMAs (for example b = -18 eV for GaNAs [50]). It is worth noting that for HMAs the ΔE_g deviation can be also obtained within the BAC model with the proper BAC parameters.

In the context of application of $GaSb_{1-x}Bi_x$ in optoelectronic devices it is crucial to determine the band offset between $GaSb_{1-x}Bi_x$ and GaSb alloys. Theoretical predictions of the band offset in this material system can be obtained from calculations within the SC-AM approach.. Figure 7 shows Bi-induced shifts of CB, VB, and split-off band found in this work. The variation rates are respectively -26.0meV per % Bi for CB and 9.6meV per % Bi for VB what in consequence leads to a reduction of the band gap by 35.6meV per % Bi. The relative contributions of the VB and CB shifts to the band gap reduction are 27% and 73% respectively. The rate of Bi-related shift for split-off band is 7.0meV per % Bi which results in 16.6meV per % Bi of the increase in the spin-orbit split off value.

V. SUMMARY

The band gap of $GaSb_{1-x}Bi_x$ alloy with x<0.05 has been studied experimentally by PR spectroscopy and theoretically using the *ab-initio* approach. It has been shown that the pure AM does not reproduce the $GaSb_{1-x}Bi_x$ band gap determined from PR while the agreement between experimental data and theoretical calculations of the band gap obtained within the SC-AM approach is excellent. The calculations show that the incorporation of Bi atoms into GaSb host modifies both the conduction and valence bands. The variation rates are respectively -26.0meV per % Bi for CB and 9.6meV per % Bi for VB what in consequence leads to a reduction of band gap by 35.6meV per % Bi. The relative contributions of said shifts to the band gap reduction are 73% for the CB and 27% for the VB. The rate of Bi-induced shift for

split-off band is 7.0meV per % Bi and the resulting increase in the value of the spin-orbit split off is 16.6meV per % Bi.

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Figure Captions:

FIG. 1. Photoreflectance spectra of $GaSb_{1-x}Bi_x$ layers with various Bi concentrations obtained at 15K together with the fitting curves (thick grey lines) in the vicinity of energy gap transition, and the moduli of photoreflectance resonance (dashed lines).

FIG. 2. Energy gap of $GaSb_{1-x}Bi_x$ extracted from photoreflectance measurements at 15 K (open squares), and corrected for the presence of stress (solid diamonds), i.e. representing relaxed bulk lattice values; theoretical predictions of energy gap at 0 K obtained within pure AM (dashed line) and SC-AM (solid line) approach as well as the theoretical formula given by Eq. (3) with the bowing parameter b = 1 eV (short dashed line).

FIG. 3. Electronic band structure of $GaSb_{0.9}Bi_{0.1}$ (thick solid lines) calculated within the SC-AM together with the electronic band structure of GaSb host (grey dashed lines) at 0 K. L-Γ-X(-U)- Γ’ (Γ point from a neighbouring BZ) progression is presented.

FIG. 4. Electronic band structure of $GaSb_{0.9}Bi_{0.1}$ (thick solid lines) and GaSb host (grey dashed lines) in the vicinity of the center of the Brillouin zone at 0 K.

FIG. 5. Density of states for $GaSb_{0.9}Bi_{0.1}$ (thick solid lines) and GaSb host (grey dashed lines) in the vicinity of the VB and CB edge at 0 K.

FIG. 6. The density of states projected on chosen orbitals: 6s, 6p of Bi, 5s, 6p of Sb, and 4s, 4p of Ga of an alloy with 10% Bi content at 0 K. The downward shift of the CB is due to 6s states

of Bi. The upward shift of the top of the VB originates mainly from the 6p states of Bi. The total DOS of GaSb scaled down to match other lines is plotted for comparison purposes.

FIG. 7. Bi-related shifts of CB, VB, and SO band in $GaSb_{1-x}Bi_x$ at 0K.

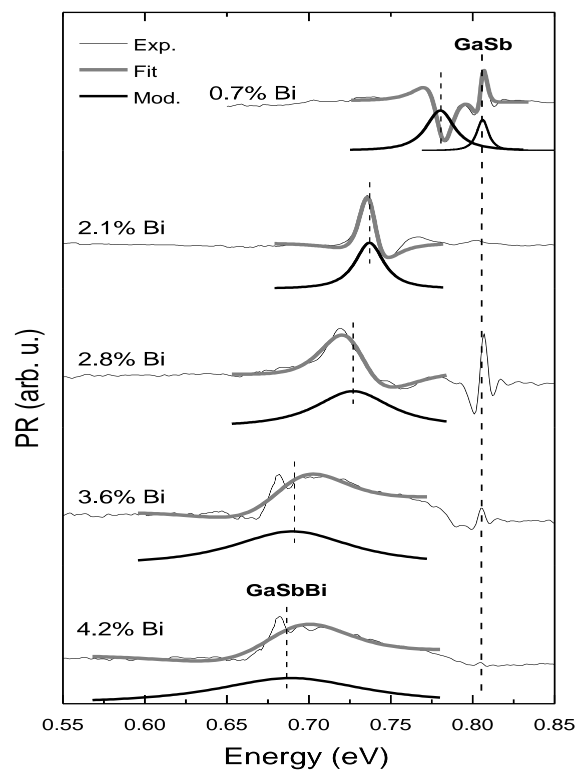

FIG. 1.

(M. Polak et al.)

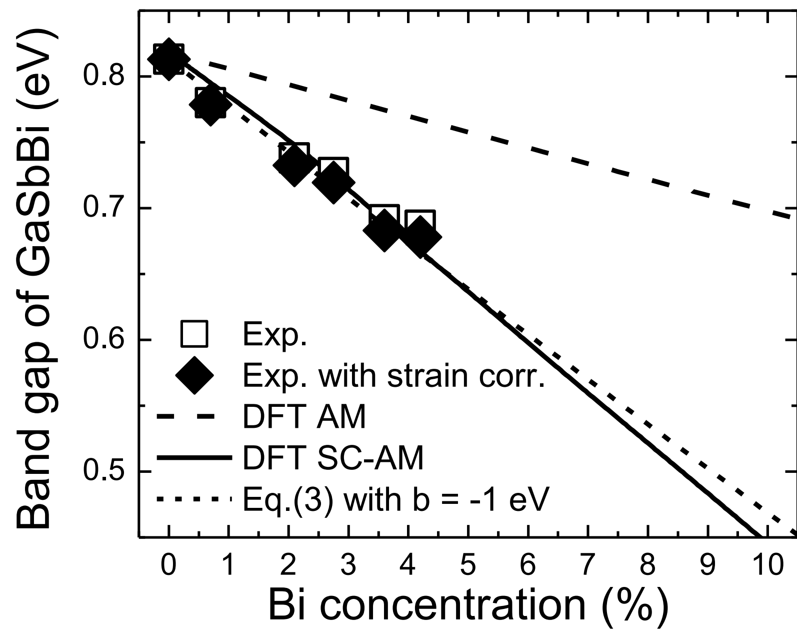

FIG. 2.

(M. Polak et al.)

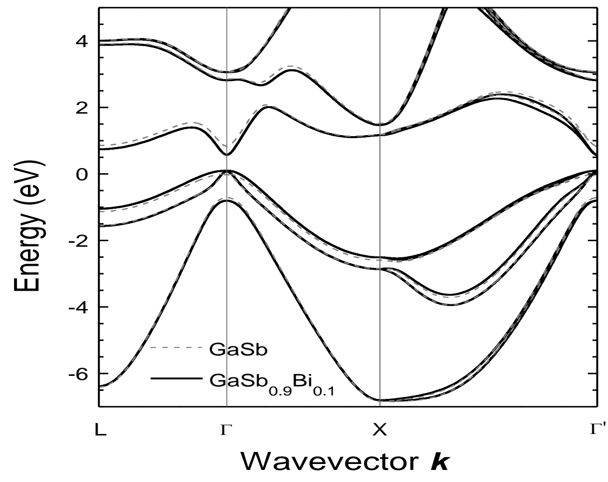

FIG. 3.

(M. Polak et al.)

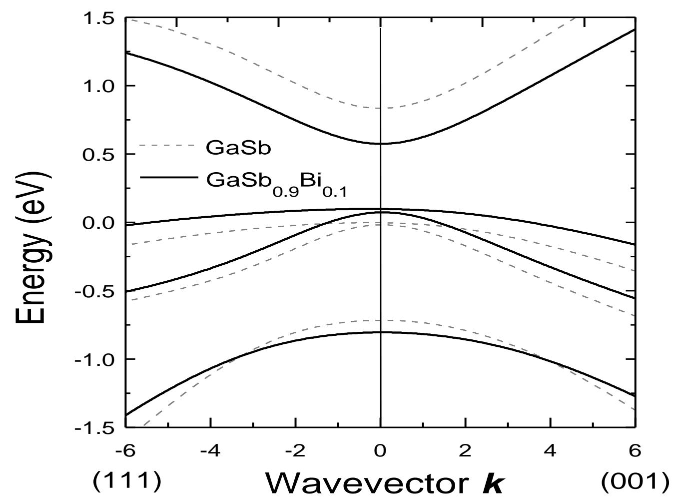

FIG. 4.

(M. Polak et al.)

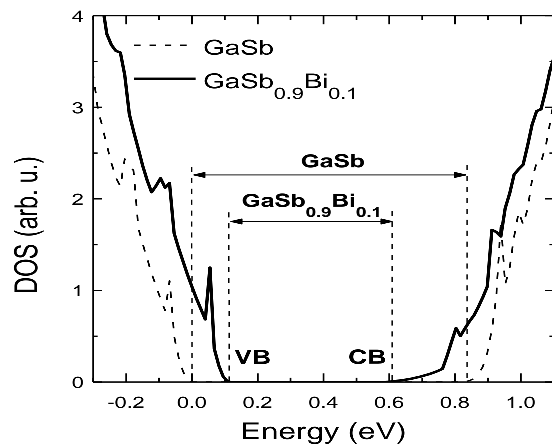

FIG. 5.

(M. Polak et al.)

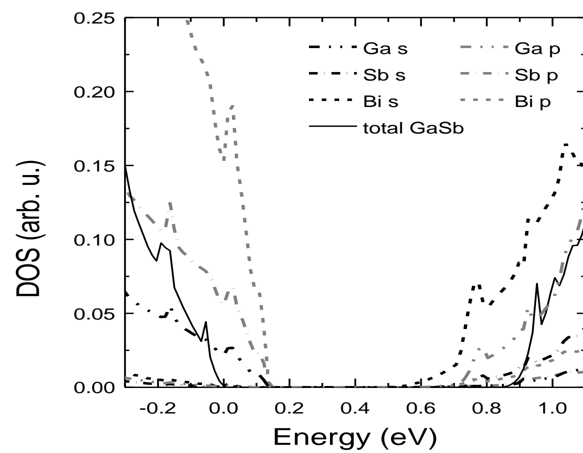

FIG. 6.

(M. Polak et al.)

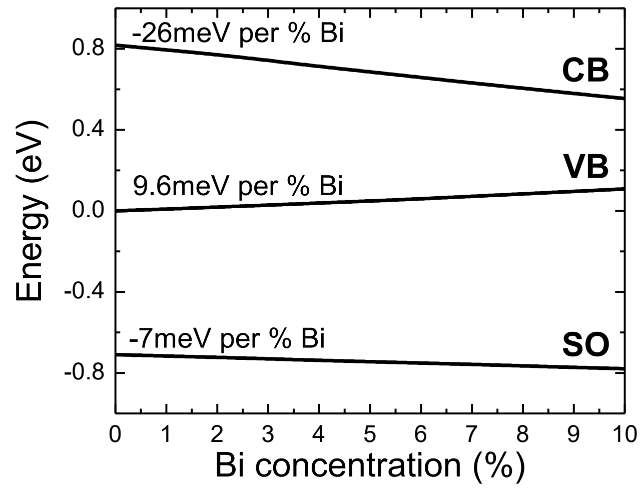

FIG. 7.

(M. Polak et al.)