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How much room for BiGa heteroantisites in GaAs$_{1-x}$Bi$_x$?

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We addressed the issue of bismuth heteroantisite defects (BiGa) in GaAs$_{1-x}$Bi$_x$/GaAs epilayers by coupling x-ray absorption spectroscopy at the bismuth edge with density functional theory calculations of the defect structure. Predictions of a large relaxation of the Bi-As interatomic distances when Bi atoms substitute Ga, however we found no experimental evidence of it. Quantitative analysis of the x-ray absorption spectra allows us to establish a maximum concentration limit for BiGa, which corresponds to about 5% of the total Bi atoms. BiGa do not account for the modifications in the spectra previously attributed to short range ordering.

Dilute bismuthides such as GaAs$_{1-x}$Bi$_x$ and GaAs$_{1-x-y}$Bi$_x$N$_y$ ($x < 0.1$ and $y < 0.02$) are an innovative class of semiconductor alloys with enormous potential applications in different fields of technology. Alloying GaAs with Bi produces a giant reduction of the optical band gap, which makes these materials interesting for the manufacture of lasers and solar cell components in the infrared region. Moreover, since the incorporation of Bi on the anion site, at odds with N, perturbs only the valence band of GaAs, electron transport properties in GaAs$_{1-x}$Bi$_x$ are less affected than in GaAs$_{1-x-y}$N$_y$. Finally, a strong enhancement of spin-orbit splitting makes GaAs$_{1-x}$Bi$_x$ promising for the design of spintronic devices.

On the other hand, the electronic structure of dilute bismuthides is not well understood yet. It has been recently shown that the exciton reduced mass has a surprising compositional dependence: it anomalously increases for $x < 5\%$, while for $x > 5\%$ it decreases and follows a conventional behavior. More recently, far-infrared absorption measurements have revealed the presence of acceptor states related to Bi, exclusively in the low-concentration “anomalous” region, the physical origin of these acceptors remains still an open question.

The anomalous optical and electronic properties of GaAs$_{1-x}$Bi$_x$ cannot be accounted for assuming a virtual crystal in which Bi atoms simply substitute the isovalent As ones (Bi$_x$As), and possible deviations from such an ideal situation have been examined by different experimental techniques. Extended x-ray absorption fine structure (EXAFS) spectroscopy allowed us to give evidence of short range ordering (SRO) of Bi atoms for $x < 2.5\%$, while Norman et al. have detected CuPt$_2$-type ordering and coarser phase separation for different concentration ranges via transmission electron microscopy. Sales et al. performing Z-contrast images, have also shown that the distribution of Bi atoms in GaAs$_{1-x}$Bi$_x$ differs from a random spatial pattern.

A still rather unaddressed point, instead, is whether Bi atoms can possess valence different from five and/or occupy Ga lattice sites (heteroantisite defects, BiGa). As a matter of fact, because of the large energy separation between 6s and 6p orbitals related to the large relativistic effects in heavy atoms, valence three is a priori possible for Bi and, at the same time, BiGa have been already observed at the Bi dilute limit by electron spin resonance (ESR). BiGa have been also invoked as possible acceptor compensators to explain the reduction in the effective hole concentration observed upon Bi incorporation. The possibility of Bi multivalency and multisite occupancy would enable four different impurity configurations: isovalent impurity and double acceptor for Bi$_x$As and isovalent impurity and double donor for Bi$_x$Ga. Finally, the presence of a non-negligible fraction of BiGa defects could affect the determination of SRO done by EXAFS. Hence, there are several important reasons for understanding if BiGa defects actually exist in the Bi concentration range of interest for technological applications and for determining their atomic fraction.

In this work, EXAFS at the Bi L2-edge and density functional theory (DFT) calculations are coupled to study quantitatively the lattice location of Bi in GaAs$_{1-x}$Bi$_x$, in particular addressing the structure of BiGa defects. DFT calculations predict a large relaxation of the Bi-As interatomic distances in the case of BiGa, which is not observed experimentally. In fact, the introduction of BiGa in the EXAFS fitting model does not improve the agreement with the experimental data. We establish the maximum concentration limit for BiGa to be $\approx5\%$ of the total Bi atoms in the alloy: this value is smaller than that determined previously at the Bi dilute limit. We also clarify that BiGa cannot reproduce the variations in EXAFS spectra observed with increasing Bi concentration and previously attributed to SRO.

We investigated the same three molecular beam epitaxy-grown Ga$_{1-x}$Bi$_x$ epilayers addressed in our previous paper. We refer to this work and to references therein for details on the sample growth, the optical/structural characterization and the EXAFS setup. Sample characteristics are summarized in Table I. DFT calculations of relaxed geometries of substitutional Bi both on the As and Ga site have been performed within the projector augmented wave method and the Heyd-Scuseria-Ernzerhof (HSE) hybrid

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BiGa distances (2.78 Å) in the BiGa configuration are sensibly larger than NN Bi-Ga ones (2.63 Å) for Bi substituting the As site. NN distances have to be compared in both cases to the calculated Ga-As bulk bond length of 2.46 Å. 2nd shell distances are instead similar in the two structures. We calculate a larger formation energy for BiGa configuration with respect to BiAs, the difference being some eV for any reasonable choice of the chemical potentials. Our calculations describe Bi as isovalent anion when substituting As, ruling out the double acceptor behavior. On the other hand, Bi as a cation on the Ga site is a double-donor impurity, inducing a doubly occupied gap-state roughly located 0.2 eV above the valence band top. BiGa, 5+ oxidation state leaves around two excess electrons that, acting as an excess charge on the Bi site, induce large repulsive interactions with NN As atoms. This explains the larger Bi-NN relaxations occurring in the BiGa configuration with respect to BiAs, as well as its higher formation energy. We point out here that, owing to the small differences in atomic number between Ga and As, there is no chance to discriminate a Bi-Ga EXAFS contribution from a Bi-As one if Ga and As are located at the same distance from Bi. Hence, DFT calculations, predicting Bi-Ga from Bi-As distances to be different by 0.15 Å play a fundamental role in this study.

Fig. 2 shows the Fourier transformed Bi L2-edge EXAFS spectrum (modulus and imaginary part) for a relatively low concentration sample (x = 1.2%), which is the most suitable for the present analysis since no short range ordering of Bi atoms is supposed to exist here according to our previous work. The experimental spectrum (continuous line) is very well reproduced by the simulation for the BiAs configuration (circles). On the other hand, the simulation for the BiGa (dashed line) gives strong disagreement with the data, in particular on the 1st shell peak where the predicted 1st-neighbors distance is sensibly longer than the measured one. We point out that in these simulations all interatomic distances were fixed to the values determined by DFT calculations, while Debye-Waller factors (DWs) and the edge energy shift (ΔE) were fixed to the values determined previously via an independent analysis method, the amplitude factor S0 of the overall EXAFS signal was determined by the fit of a Bi foil. In other words, we used no variable when performing these fits employing the Artemis code. If variable DWs are allowed while fitting with the BiGa model, extremely high (and not realistic) values for the 1st shell Bi-As DWs are obtained, which causes a complete disappearance of the 1st shell peak in the simulated spectrum (not shown). This result gives already a clear indication that Bi heteroantisites, if existing, represent a minority configuration compared to BiAs.

In order to determine how much room is available for BiGa, we performed fits of the experimental spectra by combining the BiAs and BiGa configurations. The only variable used in these fits is the relative percentage of the two structures, being all the other parameters fixed as in the

<table>
<thead>
<tr>
<th>Bi concentration (%)</th>
<th>Thickness (nm)</th>
<th>BiGa fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>270 ± 15</td>
<td>0.2 ± 5.0</td>
</tr>
<tr>
<td>1.9</td>
<td>210 ± 10</td>
<td>1.4 ± 4.5</td>
</tr>
<tr>
<td>2.4</td>
<td>210 ± 10</td>
<td>2.9 ± 6.0</td>
</tr>
</tbody>
</table>

FIG. 1. (Color online) Sketch of BiAs and BiGa configurations.

FIG. 2. (Color online) FT of the Bi L2-edge EXAFS spectrum for the x = 1.2% sample (continuous line) along with simulations performed for the BiAs (circles) and BiGa (dashed line) configurations. FT modulus is vertically shifted with respect to the FT imaginary part for better visualization. Δk interval for the FT was [3.2–12.4 Å⁻¹], ΔΔE = 3.71 eV. Inset: background subtracted k*φ(k) spectrum.
from the figure and the table that introducing a fraction of small (if existing) fraction of BiGa agrees with the larger DFT formation energy calculated for this configuration with Table I together with that of the $x$ in Fig. 3 (lowest spectrum). The best fit is obtained for a percentage of BiGa to understand if the presence of a larger concentration of where SRO of Bi atoms was previously detected, in order two others samples with concentrations $x$ in the concentration range 1.2% to 2.4% and we estimate that the maximum allowed concentration for these defects corresponds to about 5% of the total Bi atoms. Our results are in agreement with those of a recent Z-contrast microscopy experiment, which has suggested that antisite bonding is inexcist in similar samples. Bi multivallency or multisite occupancy are not at the origin of the anomalous electronic properties of these materials, which might be explained by some type of short range ordering or other defects.

We acknowledge the European Synchrotron Radiation Facility for funding through Project Nos. MA237 and MA436. We are grateful to A. Polimeni for useful discussion.

FIG. 3. (Color online) Magnitude of FT of the Bi L2-edge EXAFS spectra for the three samples (continuous line) along with best fits (open circles) obtained combining the Bi$_{As}$ and Bi$_{Ga}$ configurations. $\Delta k = [3.2–12.4 \text{Å}^{-1}]$, $\Delta E = 3.71$ eV. Inset: imaginary part of the FT (data and fits).

\[ \text{Bi}_{As} + \text{Bi}_{Ga} \] model does not describe well the distribution of atoms in the lattice for these two samples, and the low fraction of Bi heteroantisite defects possibly present cannot affect the determination of SRO reported previously.

In conclusion, based on DFT calculations and quantitative analysis of Bi L2-edge EXAFS data, we find no evidence of the presence of Bi heteroantisites in GaAs$_{1-x}$Bi$_{x}$ in the concentration range 1.2% to 2.4% and we estimate that the maximum allowed concentration for these defects corresponds to about 5% of the total Bi atoms. Our results are in agreement with those of a recent Z-contrast microscopy experiment, which has suggested that antisite bonding is inexcist in similar samples. Bi multivallency or multisite occupancy are not at the origin of the anomalous electronic properties of these materials, which might be explained by some type of short range ordering or other defects.

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