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Full Length Article

# Local variation in Bi crystal sites of epitaxial GaAsBi studied by photoelectron spectroscopy and first-principles calculations

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ABSTRACT

Epitaxial Bi-containing III–V crystals (III-$V_{1-x}Bi_x$) have attracted increasing interest due to their potential in infrared applications. Atomic-scale characterization and engineering of bulk-like III-$V_{1-x}Bi_x$ properties (e.g., Bi incorporation and defect formation) are challenging but relevant to develop applications. Toward that target, we report here that the traditional surface-science measurement of photoelectron spectroscopy (PES) is a potential, non-destructive method to be combined in the studies of bulk-like properties, when surface effects are properly removed. We have investigated epitaxial $GaAs_{1-x}Bi_x$ films, capped by epitaxial AlAs layers, with high-resolution photoelectron spectroscopy. The Bi5d core-level spectra of $GaAs_{1-x}Bi_x$ together with ab-initio calculations give direct evidence of variation of Bi bonding environment in the lattice sites. The result agrees with photoluminescence (PL) measurement which shows that the studied $GaAs_{1-x}Bi_x$ films include local areas with higher Bi content, which contribute to PL but do not readily appear in x-ray diffraction (XRD). The measured and calculated Bi core-level shifts show also that Ga vacancies and Bi clusters are dominant defects.



## 1. Introduction

The growth and properties of Bi-containing III–V compound-semiconductor crystals, III-$V_{1-x}Bi_x$ bismides, have been intensely investigated during the recent years [1–33]. Integrating device-grade III-$V_{1-x}Bi_x$ materials (e.g., epitaxial films and nanocrystals) on the established semiconductor templates (e.g., Si, GaAs) would enable, for example, the development of infrared photonics components. Incorporation of Bi into the crystal decreases the energy band gap by about 0.08 eV with every percentage of alloyed Bi [1].

For large-scale use, it is essential to synthesize uniform III-$V_{1-x}Bi_x$ crystals with low defect densities. However, the incorporation of Bi into the crystal (into group-V sites) is not straightforward because the phase separation of Bi is an energetically favored process [26,27]. Thus, a kinetically limited growth process at low temperatures (typically below 400 °C) is often utilized to synthesize III-$V_{1-x}Bi_x$ crystals. Significant progress has been made during the last 10 years in the epitaxial growth of III-$V_{1-x}Bi_x$ films. Thus, the atomic-scale understanding and processing of the material properties become more and more relevant to the further development of nanometer-scale bismide films and crystals for devices.

Photoluminescence (PL) spectra of III-$V_{1-x}Bi_x$ films are commonly broad, as compared to PL from the traditional III-V's, and often include two or more emission peaks [1,6,11,23]. This is true even for films showing well-defined x-ray diffraction (XRD) curves, indicative of high crystal quality. However, the XRD signal is largely averaged and is not sensitive to a local variation in the crystal structure. Thus, the PL results indicate local fluctuations (changes) in the electronic structure around the band gap [4,8,9,17,23], suggesting variation of the Bi content and/or defect-state mediated emission. Furthermore, transmission electron microscopy (TEM) measurements have revealed lateral composition modulation for GaAsBi films grown at particular low temperature [32]. Concern-

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ing possible crystal defects, experiments support the presence of As antisites ($As_{Ga}$) [20], while calculations have shown interplay between Ga-vacancy defects and Bi clustering [26].

There is an obvious need to develop the metrology to characterize these materials on atomic scale in a non-destructive manner, in order to tailor III-$V_{1-x}Bi_x$ crystals for large-scale use. In this paper, we address the question of whether the traditional surface-science measurement of photoelectron spectroscopy (PES) can be utilized to clarify the $GaAs_{1-x}Bi_x$ issues. PES is a potential method because it is non-destructive and element sensitive (e.g., via Bi5d core level photoelectrons). Furthermore, different emission components of a core level spectrum (e.g., in Bi5d spectrum) directly reflect changes in the electronic potential at the atomic sites of the element probed. These changes arise from variations in the valence-band electron distribution induced by atomic bonding environment. Previously, it has been shown that PES, in combination with simulated core-level shifts based on ab initio calculated atomic models, is helpful to understand the atomic structures of various Bi-containing III–V surface layers [34–37]. PES is indeed a surface-sensitive method, but nowadays state-of-the-art synchrotron-radiation facilities allow also probing depths close to 50 nm with hard x-ray photons (i.e., photoelectrons with high kinetic energies) [38]. Still, it is crucial to remove various surface effects such as air-induced contamination and reconstruction from the PES signal in controlled way, in order to probe the bulk-like structures.

Toward that target, we have studied the $GaAs_{1-x}Bi_x$ films, capped by epitaxial AlAs layers, by means of synchrotron-radiation based PES. The results reveal variations in Bi bonding environments, including Ga-vacancy related clusters, which lead to energy band gap fluctuations, consistent with photoluminescence (PL) measurements. The presented approach can be generalized to study various crystals.

## 2. Methods

Stacks of epitaxial $GaAs_{1-x}Bi_x$ (210 nm) and AlAs cap (3.5 nm nominally) layers were grown by molecular-beam epitaxy (MBE) on GaAs(100) substrates. Two different growth temperatures, 220 °C and 320 °C, were used for the $GaAs_{1-x}Bi_x$ and AlAs growth. The growth rate was 0.4 μm/h and 0.5 μm/h for the GaAsBi and AlAs layers, respectively. The atomic As/Ga flux ratio was measured with an ion gauge, and set to slightly above the stoichiometric condition for the GaAsBi layer (i.e., the As/Ga ratio below which Ga droplets are observed, which we define as the stoichiometric condition with As/Ga = 1) as required for efficient Bi incorporation [12]. After the AlAs growth, an amorphous As cap was deposited to protect the AlAs layer against oxidation during the sample transfer to PES measurements which were performed at the MAX-lab synchrotron center in Lund on the beamline I311. In addition, a separate 230 nm thick GaAsBi layer was grown for PL characterization at 320 °C without any capping layers.

The PES spectra were taken at room temperature (RT) with 50-eV pass energy and 0.02 eV energy step. The photon energies (550 and 800 eV) were chosen to optimize a signal-to-noise ratio of the core-level spectra measured through the AlAs film, and simultaneously to vary their interface sensitivities. The experimental broadening was estimated to be 0.25 eV or smaller on the basis of Ga3d peak width. This broadening is contributed by the instrumental resolution and thermal broadening at RT, leading to the Gaussian width of the symmetric Voigt-profile peaks used in the spectral fittings. Lorentzian width of the Voigt-profile peaks arised from a finite lifetime of a core hole. Spectra were measured after removing the As cap layer in situ by heating the samples in ultrahigh vacuum to around 350 °C, which is also a high enough temperature to remove possible Bi adsorbates or surfactant atoms remaining on the growth front after the $GaAs_{1-x}Bi_x$ deposition [35–37]. Our previous XRD measurements [18] do not show structural changes after post-growth heating up to 800 °C for films grown at around 320 °C, but we cannot exclude some changes in the film grown at 220 °C after heating at 350 °C. Low-energy electron diffraction showed (1 × 1) after removing the As cap, but no clear reconstruction pattern was observed for the AlAs surface. A separate PES instrument (Perkin Elmer PHI at University of Turku) with monochromatized Al Kα (1486.6 eV) was used with 17.9-eV pass energy to investigate changes induced by heating in the AlAs/GaAsBi structure. Focus was put on analysing the Ga and Bi photoelectron signals because the As signal includes also emissions from AlAs and its topmost surface rearrangements. The photoluminescence measurements were performed using a continuous wave laser with 690 nm excitation and 30 mW power. The signal was detected with a cooled InGaAs detector. The sample temperature was cooled to 20 K.

Theoretical Bi core-level shifts were calculated using the Vienna ab initio simulation package (VASP) [39–42] with the local density approximation [43,44] for various Bi concentrations. The $GaAs_{1-x}Bi_x$ alloys were constructed as random alloys using an efficient stochastic algorithm [45] to generate special quasi-random structures [46,47] for unit cells (the largest ones contain 512 atoms). The optimization of the atomic structure as well as volume was performed using the conjugate-gradient minimization of the total energy. Atom positions were relaxed until the remaining forces were less than 20 meV/Å. The plane wave cutoff energy was set to 350 eV. Ga3d electrons were treated as core electrons. The *k* point sampling was carried out using the Monkhorst-Pack scheme by a 2 × 2 × 2 mesh with the origin shifted to the Γ point. To simulate large, pure Bi clusters, an interface system combining bulk Ga(As,Bi) and Bi was formed using the (111) interface. The rhombohedral Bi cluster was simulated using the face-centred cubic (fcc) initial structure. The total energy of the fcc Bi is only 0.1 eV per atom larger than that of the rhombohedral Bi. After relaxation the Bi atoms have six nearest neighbors as in the rhombohedral structure. There are six Bi layers and six double layers of the GaAs within the unit cell and eight atoms per layer. One of the As atoms in the middle of the Ga(As,Bi) part was substituted by a Bi atom. The interface area of the bulk GaAs was adopted while the distances between the layers were allowed to relax. The *k* mesh was 3 × 2 × 1. The initial state core-level shifts were determined by the average electrostatic potential at the core of the Bi atoms. The complete screening shifts were determined by two ways. The core hole was introduced both in the interface system [either in the middle of the Ga(As,Bi) part or the Bi part] and within the bulk Ga(As,Bi) and Bi systems. In the latter case [Ga(As,Bi) and Bi bulk systems] total energy difference between the calculations with and without the core hole gives the screening energy specific to system [48]. In this case the initial state shift given above is added to the screening energy to get the complete screening shift [48]. The resulting complete screening shifts agree with each other within 0.02 eV.

## 3. Results and discussion

### 3.1. XRD and PL characterization

Average Bi contents (x) were determined by fitting high-resolution X-ray diffraction (XRD) omega-2theta scans over the (004) reflection with dynamical simulation using a lattice constant of 6.33 Å [2]. Fig. 1a shows the measured and simulated XRD curves for the samples grown at 320 °C and 220 °C. These simulations indicate that the Bi contents are 1.5% and 1.6% for the samples grown at 320 °C and 220 °C, respectively.

Fig. 1b presents photoluminescence (PL) from for a $GaAs_{1-x}Bi_x$ film grown at the same conditions, 320 °C but without the As cap-

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