Molecular beam epitaxy and properties of GaAsBi/GaAs quantum wells grown by molecular beam epitaxy: effect of thermal annealing

Hajer Makhloufi, Poonyasiri Boonpeng, Simone Mazzucato, Julien Nicolaï, Alexandre Arnoult, Teresa Hungría, Guy Lacoste, Christophe Gatel, Anne Ponchet, Hélène Carrère, et al.

Molecular beam epitaxy and properties of GaAsBi/GaAs quantum wells grown by molecular beam epitaxy – Effect of thermal annealing

[1,2,6] Hajer Makhloufi

Email: hmakhlou@laas.fr

[1,2,6] Poonyasiri Boonpeng

Email: P_boonpeng@hotmail.com

[3,6] Simone Mazzucato

Email: mazzucat@insa-toulouse.fr

[4,6] Julien Nicolai

Email: julien.nicolai@cemes.fr

[1,6] Alexandre Arnoult

Email: aarnoult@laas.fr

[5,6] Teresa Hungria

Email: hungria@insa-toulouse.fr

[1,6] Guy Lacoste

Email: lacoste@laas.fr

[4,6] Christophe Gatel

Email: gatel@cemes.fr

[4,6] Anne Ponchet

Email: anne.ponchet@cemes.fr

[3,6] Hélène Carrere

Email: carrere@insa-toulouse.fr

[3,6] Xavier Marie

Email: xavier.marie@insa-toulouse.fr

[1,6,a] Chantal Fontaine

Email: chantal.fontaine@laas.fr

[1] CNRS, LAAS, 7, avenue du Colonel Roche, F-31400 Toulouse, France

[2] Université Paul Sabatier, 118 route de Narbonne F-31400 Toulouse, France

[3] Université de Toulouse, LPCNO, INSA-UPS-CNRS, 135 avenue de Rangueil, F-31400 Toulouse, France

[4] CNRS-CEMES, 29, rue Jeanne Marvig, F- 31400 Toulouse, France

[5] Service Analyseur ionique, INSA, 135 avenue de Rangueil, F-31400 Toulouse, France

[6] Université de Toulouse, F-31400 Toulouse, France

Keywords

Dilute bismides; molecular beam epitaxy; heteroepitaxy; X-ray diffraction; transmission electron microscopy; photoluminescence

Abstract

We have grown GaAsBi quantum wells by molecular beam epitaxy. We have studied the properties of a 7%Bi GaAsBi quantum well and their variation with thermal annealing. High resolution x-ray diffraction, secondary ion mass spectrometry and transmission electron microscopy have been employed to get some insight into its structural properties. Stationary and time-resolved Photoluminescence show that the quantum well emission, peaking at 1.23µm at room temperature, can be improved by a rapid annealing at 650°C while the use of a higher annealing temperature leads to emission degradation and blue-shifting due to the activation of non-radiative centers and bismuth diffusion from the quantum well.

.

[a]*Corresponding author: email Chantal.fontaine@laas.fr, tel +33/0-561336462*

Background

Dilute bismuth alloys grown on GaAs attract more and more attention because of their peculiar electronic properties. Adding bismuth to GaAs efficiently decreases the gap energy of this semiconductor [**1**] through a change in its valence band properties, and increases the spin-orbit interaction [2]. GaAsBi/GaAs quantum wells (QWs) are of interest with a view to fabricate laser diodes which could benefit from these properties, in particular from the higher spin-orbit splitting expected to lower the non-radiative carrier recombination due to Auger mechanisms [3]. Moreover, their emitting wavelength range could meet the requirements for infra-red GaAs-based laser diodes as an alternative to low temperature GaInAs/GaAs [4] and GaInAsN/GaAs [5] QWs. Besides the properties of these III-V alloys are also very promising for photovoltaics [6]. Up to now, literature on GaAsBi has mainly been devoted to thick layers (see [**7**] and ref. herein), and only a few papers on the growth of quantum well structures have been published [8]. Here, we present the structural and optical properties of a GaAsBi/GaAs QW grown by molecular beam epitaxy (MBE) and discuss their change after rapid thermal annealing (RTA).

Method

GaAsBi quantum well structures were grown using a 32P RIBER molecular beam epitaxy system (MBE). Substrates were pieces of a semi-insulating GaAs substrate soldered with indium on a silicon wafer mounted on the substrate-holder to be loaded in the MBE system. The substrate thermocouple temperature for the molybdenum substrate-holder was first calibrated by using a band-edge thermometry system (BandIT). The control of the growing material was performed by reflection high energy electron diffraction (RHEED). Our MBE system is designed to grow in the RIBER “optimal cell/sample oven” geometry which leads to high thickness uniformity on 2-inch samples even though the 32P Riber MBE system is not normally designed to get high uniformity on these large surface areas. In such a geometry, substrate rotation is required to be used continuously during the growth, since the fluxes are not converging towards the substrate-holder center.

QWs with different Bi contents and widths were grown and the results presented here come from the QW emitting at the longer wavelength. They were grown after careful calibration of the growth conditions, the GaAs growth rate, i.e. the V/III ratio, the substrate temperature and the Bi content, on thick GaAsBi layers. Note that we do not have any flux gauge in our MBE system, so the Bi control was carried out via the cell temperature.

The investigated QW sample consists of a 500nm-thick buffer GaAs layer, the GaAsBi/GaAs QW well and finally a 100nm-thick cap layer. After the growth of the buffer layer at 580°C, the temperature is lowered to 365°C, the value selected for the quantum well growth. The As cell valve opening is reduced in order to yield the As_4 flux corresponding to a V/III atomic ratio close to unity, as needed for GaAsBi growth [9]; the As cell is an Addon VCAS700 cracker one whose nose temperature is set to 650°C, thus mostly ejecting As_4 species. At the same time, the Ga cell temperature is decreased to a value which leads to a low growth rate for GaAs, of the order of 0.25ml/sec. After substrate temperature cooling, care is taken to get temperature stabilization since this parameter plays a major role in Bi incorporation [7]. At this step, the Ga and Bi cell shutters are opened simultaneously. For the first period of growth, bismuth plays the role of a surfactant for the low temperature grown GaAs [9], until a (2x1) reconstruction of a bismuth-rich GaAs surface [10] is observed, the required condition for efficient incorporation of this element into GaAs [11]. Then the bismuth element contributes to the formation of a GaAsBi QW. At the end of the QW growth, the Bi cell shutter is closed first. The Ga shutter is only closed once a 5nm layer of GaAs has been grown; we have observed that the GaAs RHEED pattern deteriorates for a GaAs layer thickness higher than 5-10nm, after the floating bismuth was incorporated in GaAs or desorbed [7]. The growth is then interrupted to heat the structure temperature to 520°C. Finally a 30nm-thick GaAs layer is grown at 0.7ml/s at this temperature and the 100nm thick barrier growth is completed whilst the temperature is raised to 580C.

Once grown, the GaAsBi/GaAs QW structures were analysed by stationary photoluminescence using the 514 nm line of an Argon laser, and a GaInAs photodetector. The quantum well emitting at 300K at the longer wavelength, 1.23µm, was selected. The sample was cleaved into pieces, which were subjected to *ex situ* rapid thermal annealing (RTA) in an AnnealSys AS-One system. RTA was carried out in a nitrogen atmosphere during 30 seconds at annealing temperatures of 650, 700, 750 and 800°C. Samples were covered with a GaAs substrate during these annealings in order to prevent surface degradation by arsenic desorption.

High resolution X-ray diffraction (HR-XRD) was performed on the as-grown sample using a Di8 Discober BRUKER equipment in order to determine its thickness and strain, from which we deduce its bismuth content. It was also used on the annealed samples to get insight into the evolution of their structural properties upon annealing. Secondary ion mass spectrometry (SIMS) with a CAMECA IMS-6f was employed to measure the profile of the bismuth element within the structure for the as grown and annealed samples. Primary Cs+ ions were accelerated at 3kV while the positive secondary ions were collected at 2kV. Transmission electron microscopy (TEM) in conventional and high resolution (HREM) modes was carried out on the as-grown QW sample. A <110>-oriented cross-section sample was thinned by mechanical polishing and ion milling. HREM observations were performed at 200 kV on a TECNAI F-20, equipped with a spherical aberration corrector tuned to avoid the delocalization effect at the interface and to achieve a 0.12nm resolution.

Time-resolved photoluminescence spectroscopy was performed at room temperature on the as grown and annealed samples. Optical excitation was provided by focusing 1.5ps pulses generated by a mode-locked Ti-Sapphire laser with 80MHz repetition frequency. The laser wavelength was set to λ_{exc}=795nm with 20mW incident power, focused to a 50µm diameter spot at the sample surface. The signal was recorded using a S1 photocathode Hamamatsu streak camera with an overall time resolution of 8ps. The signal was recorded in the high energy side (1120-1220 nm) of the PL spectrum.

Results and discussion

As-grown quantum well structure

SIMS analysis was carried out on the as-grown sample in order to image the bismuth profile through the structure. Indeed, it is worth to recall that we opened bismuth with Ga and As for a longer duration compared to the one which should be applied for growth of a 7nm QW. We postulated that the incorporation of the bismuth occurs when the right content of the element saturates the surface, giving rise to the (2x1) surface which promotes its incorporation as explained in [10]. The use of this method allows us to optimize the lower QW interface. We actually observe in Fig.1a for this QW that the bismuth content actually exhibits a step shape within the structure. We only observe a small Bi shoulder close to the lower interface which we associate to a slight incorporation of Bi before the quantum well. Moreover, no bismuth is observed to be incorporated in the subsequent 5nm GaAs grown at low temperature while a As/Ga stoechiometric ratio was still being used. This supports our hypothesis that this element plays the role of a surfactant during the first stage of low temperature GaAs:Bi growth and, once the bismuth cell was closed, during the low temperature GaAs growth . Note that, contrary to the case of thick layers, the bismuth content cannot be directly inferred from the

SIMS profile as the QW is too thin for SIMS to provide a direct correspondence with the absolute Bi content.

In order to determine the Bi content and QW thickness, HR-XRD analysis is used. As it can be observed in Fig.1b, the presence of thickness fringes and a narrow diffraction peak in the resulting 2θ transverse scan indicates that the grown material is of high quality. It allows us to accurately evaluate the thickness, content and strain of the QW. The X-ray diffractogram was simulated. This calculation was done using the software provided by Bruker, with GaAs and GaBi lattice parameters taken equal to 0.56353nm and 0.633nm respectively [12], and with the elastic constants of GaAs (C_{11}=118.81 GPa and C_{12}=53.8 GPa) for a structure under complete elastic tetragonal strain. For a thickness of 7.5nm and a Bi content of 7%, we observe perfect agreement of the experimental rocking curve with the simulated one, further highlighting that the as-grown QW structure exhibits good quality structural properties.

Figure 1 SIMS profiles of the different elements (Ga,As,Bi) within the QW structure (a); (004) X-ray diffraction ω/2θ transverse scans measured (black) **and simulated** (blue) **for the QW structure (b).**

This is also supported by the TEM analysis. The abruptness and flatness of the lower and upper interfaces are confirmed. First conventional TEM experiments reveal the absence of extended defects and insignificant roughness (Fig. 2a). HREM performed on various areas confirms on a more local scale the absence of dislocations (Fig. 2b), indicating a full accommodation of the lattice misfit by elastic deformation. The strain related to a reference zone chosen in the GaAs buffer was determined with a spatial resolution better than 1 nm, by the means of geometrical phase analysis of the HREM images [13,14]. As shown by the profile along the growth direction (Fig. 2b-insert), the out-of-plane strain ε can be considered as homogeneous in the quantum well. Following the linear elasticity and taking into account the fact that ε is measured related to a GaAs reference zone, ε is related to the misfit f through:

$$\varepsilon = (1+2C_{12}/C_{11})f$$

The average strain measured from HREM is 0.016 but this value has to be corrected for surface relaxation effects: the strain before thinning is numerically estimated to be 10 to 20% larger [14].

Figure 2 TEM observation of a cross-section of the QW structure by conventional (a) and high resolution modes (insert: strain profile measured along the growth direction**) (b).**

Thus after this correction, the estimated misfit is in the range 0.0095 to 0.0105. Applying the Vegard's law, this corresponds to a Bi amount of 7.8 to 8.8 %, close to the content provided by HR-XRD. Different analyzed zones have given comparable values of strain. In addition, the measured QW thickness in Fig.2b is measured to be 7 nm, again close to the value estimated through HR-XRD.

Taking into account the values measured by HR-XRD and TEM, the assumption of late incorporation of the bismuth is valid. The thickness of the QW is thinner than the one which would have been obtained had the Bi atoms been directly incorporated as soon as the Bi cell was opened.

Annealed QW samples

Fig. 3a shows that the RTA of the QW structure leads to a drastic change in its X-ray 2θ transverse scan. The diffractogram is similar to the as-grown one except for the 650°C annealing temperature. At 700°C, a slight difference is observed, while for two highest annealing temperatures, the background is observed to drastically evolve, which can be accounted for by a modification of the bismuth profile within the structure. Fig. 3b shows how the SIMS Bi signal broadens with annealing. This analysis confirms that the Bi profile has become more distributed within the structure, as a result of its diffusion into the GaAs surrounding barriers for the two higher annealing temperatures. This Bi diffusion at high temperature is certainly supported by strain for this QW with a high Bi content. Indeed, Mohmad et al [15] have shown that the optimal annealing temperature is affected by the local strain supported by the GaAsBi alloys due to the high atomic size of the Bi atom.

Figure 3 (004) X-ray diffraction ω/2θ transverse scans (a) and Bi SIMS profiles for the differently annealed samples (b).

As a consequence, the QW optical properties are greatly affected by the RTA treatment. Fig. 4a shows the evolution of the 20K PL spectra for different annealing temperature conditions. The QW emission wavelength is unchanged for the 650°C and 700°C RTA, but it strongly blue-shifts at higher RTA temperatures, due to the Bi diffusion out of the annealed QW.

Moreover, only the 650°C RTA improves the emission intensity compared to the as-grown sample. For higher temperatures, a rapid reduction of the PL intensity is found. Additionally, at room temperature the PL emission of the 650°C RTA QW is found to be better than the one of the as-grown QW, while no PL emission is visible for the annealed samples at the 750°C and 800°C. RTA is known to improve structural properties of materials. In the case of GaAsBi thin layers, a decrease of the density of localized defects, due to bismuth aggregates or alloy disorder, has been claimed to occur during annealing by Mohmad et al [15] and Mazzucato et al [16].

Figure 4 20K photoluminescence spectra of the as-grown and annealed QW samples (a); room temperature time-resolved luminescence for the as-grown sample and those annealed at 650 and 700°C (b).

The increase of the carrier decay-time in the time-resolved luminescence analysis measured for the 650C annealed sample, in Fig.4b, also supports its better crystallinity, in agreement with the improved emission recorded under CW photoluminescence analysis. On the contrary, for annealing treatment at temperatures higher than 700C, the room-temperature carrier decay-time like the other properties of this annealed QW degrades with respect to the as-grown QW, showing again that a too high annealing temperature leads to the activation of additional non-radiative centers.

Conclusions

We have shown that a 7%Bi GaAsBi quantum well grown by molecular beam epitaxy, emitting at 1.23µm at room temperature, is completely elastically strained and exhibits good structural properties, with a uniform thickness, sharp interfaces, and the absence of extended defects. Annealing this QW leads to bismuth out-diffusion as soon as the applied annealing temperature is higher than 650°C. At the latter annealing temperature the photoluminescence emission, and decay time at room temperature are all improved.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

H. M. and C.F. grew and annealed the samples. P. B. studied their PL properties. A. A. took in charge the X-Ray diffraction analyses. S. M. and H. C. carried out the TRPL experiments. G. L. settled the MBE system for bismide growth. T. H. performed the SIMS analyses. J. N., C. G. and A. P. carried out the TEM analyses. All authors interact on the results, on their analysis, read and approved the final manuscript.

Authors' information

Hajer Makhloufi is a PhD student at LAAS
Poonyasiri Boonpeng is a TECHNO Tempus Erasmus Post-doctorate at LAAS
Simone Mazzucato is a visitor researcher at LPCNO
Hélène Carrère holds an Assistant Professor position at INSA and is a researcher at LPCNO
Julien Nicolai is a CNRS post-doctorant at CEMES
Alexandre Arnoult and Guy Lacoste are CNRS engineers at LAAS
Teresa Hungria is an engineer at INSA
Christophe Gatel (Assistant Professor at Université Paul Sabatier) and Anne Ponchet (Research Director at CNRS) are researchers at CEMES
Xavier Marie is a Professor at INSA and is a researcher at LPCNO
Chantal Fontaine (Research Director at CNRS) is a CNRS researcher at LAAS

Acknowledgements

This work was supported by the Paul Sabatier University (AO1 programme), the LAAS-CNRS technology platform (RENATECH), and the LPCNO laboratory. We acknowledge the TECHNO Erasmus Mundus Programme for its support through the Post-doctoral grant of Poonyasiri Boonpeng. Part of this work has been supported by the NAIADE project (ANR-11-BS10-017). We would also like to thank the cooperation with COST Action MP0805 and Stephane Calvez for fruitful discussions.

References

1. Francoeur S, Seong MJ, Mascarenhas A, Tixier S, Adamcyk M, Tiedje T: **Band gap of $GaAs_{1-x}Bi_x$, 0<x<3.6%.** Appl Phys Lett 2003, **82**: 3874 (1-3)

2. Broderick CA, Usman M, Sweeney SJ, O'Reilly EP: **Band engineering in dilute nitride and bismide semiconductor lasers.** Semicond. Sci. Technol. 2012, **27**: 094011 (1-14)

3. Batool Z, Hild K, Hosea TJC, Lu X, Tiedje T and Sweeney SJ : **The electronic band structure of GaBiAs/GaAs layers: Influence of strain and band anti-crossing**. J Appl Phys 2012, 111: 113108 (1-7)

4. Mogg S, Chitica N, Schatz R, Hammar M: **Properties of highly strained InGaAs/GaAs quantum wells for 1.2-µm laser diodes**. Appl Phys Lett 2002 **81**: 2334 (1-3)

5. Shan W, Walukiewicz W, Ager III JW, Haller EE, Geisz JF, Friedman DJ, Olson JM, Kurtz SR, Phys Rev Lett 1999, **82**: 1221 (1-4)

6. Ptak AJ, France R, Jiang CS, Reedy RC: **Effects of bismuth on wide-depletion-width GaInNAs solar cells.** J Vac Sci Technol B 2008, **26**: 1053 (1-5)

7. Lewis RB, Masnadi-Shirazi M, Tiedje T: Growth of high Bi concentration $GaAs_{1-x}Bi_x$ by molecular beam epitaxy. Appl Phys Lett 2012, 101: 082112 (1-4)

8. Tominaga Y, Kinoshita Y, Oe K, Yoshimoto M: **Structural investigation of $GaAs_{1-x}Bi_x$ / GaAs multiquantum wells.** Appl Phys Lett 2008, **93**: 131915 (1-3)

9. Ye H, Song X, Gu Y, Wang S: **Light emission from InGaAs :Bi/GaAs quantum wells at 1.3µm.** AIP advances 2012, **2**: 042158 (1-5)

10. Laukkanen P, Punkkinen MPJ, Kosma HP, Ahola-Tuomi M, Kokko K, Kuzumin M, Adell J., Sadowski J, Perälä RE, Ropo M, Rantala TT, Väyrynen IJ, Pessa M, Vitos L, Kollár J., Mirbt S, Johansson B: **Anomalous bismuth-stabilized (2×1) reconstructions on GaAs(100) and InP(100) surfaces.** Phys Rev Lett 2008, **100**: 086101 (1-4)

11. Masnadi-Shirazi M, Beton DA, Lewis RB, Lu X, Tiedje T : **Surface reconstructions during growth of $GaAs_{1-x}Bi_x$ alloys by molecular beam epitaxy.** J Cryst Growth 2012, **338**: 80 (1-5)

12. Tixier S, Adamcyk M, Tiedje T, Francoeur S, Mascarenhas A, Wei P, Schiettekatte F : **Molecular beam epitaxy growth of $GaAs_{1-x}Bi_x$,** Appl Phys Lett 2003, **82**: 2245 (1-3)

13. Hytch MJ, Snoeck E, Kilaas R : **Quantitative measurement of displacement and strain fields from HREM micrographs**. Ultramicroscopy 1998, **74**: 131 (1-16)

14. Gatel C, Tang H, Crestou C, Ponchet A, Bertru N, Doré F, Folliot H : **Analysis by high-resolution electron microscopy of elastic strain in thick InAs layers embedded in $Ga_{0.47}In_{0.53}As$ buffers on InP(0 0 1) substrate.** Acta Materialia 2010, **58**: 3238 (1-9)

15. Mohmad AR, Bastiman F, Hunter CJ, Richards R, Sweeney SJ, Ng JS, David JPR: **Effects of rapid thermal annealing on $GaAs_{1-x}Bi_x$ alloys**. Appl Phys Lett 2012, 101: 012106 (1-3)

16. Mazzucato S, Boonpeng P, Carrère H, Lagarde D, Arnoult A, Lacoste G, Zhang T, Balocchi A, Amand T, Marie X, Fontaine C: **Reduction of defect density by rapid thermal annealing in GaAsBi studied by time-resolved photoluminescence.** Semicond Sci Technol 2013, **28**: 022001 (1-5)

Figures

a) b)

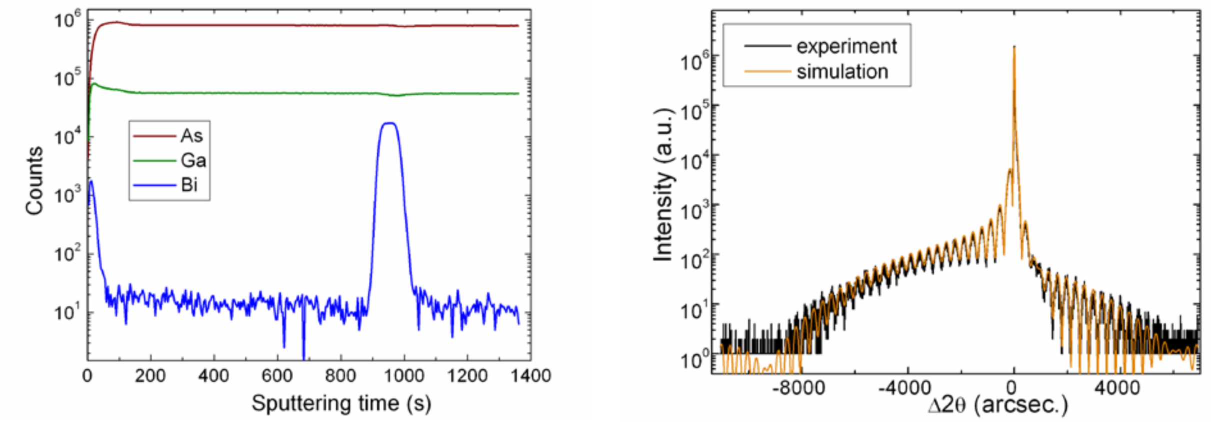

Figure 1

a) b)

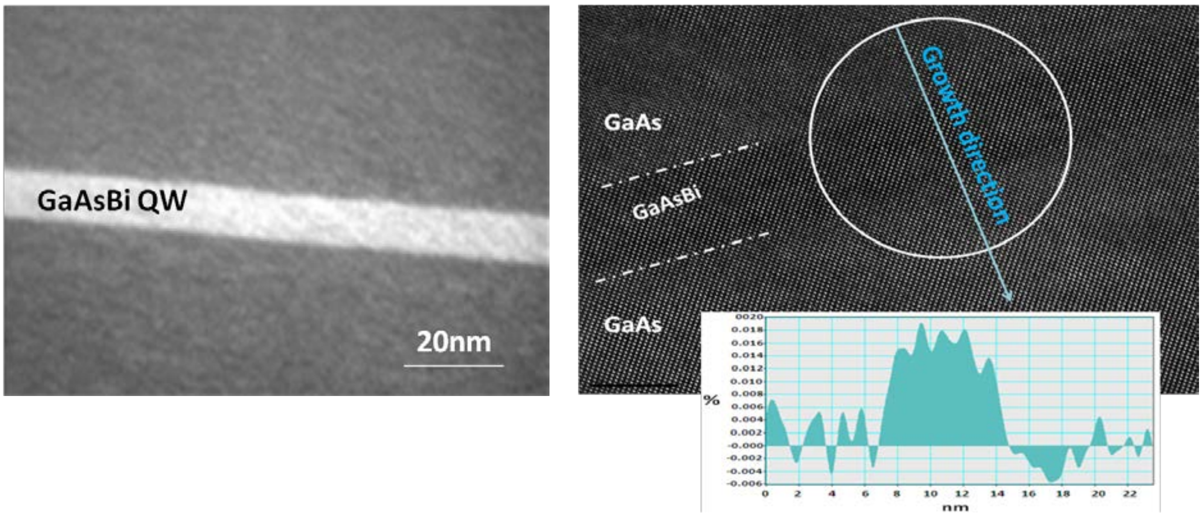

Figure 2

a) b)

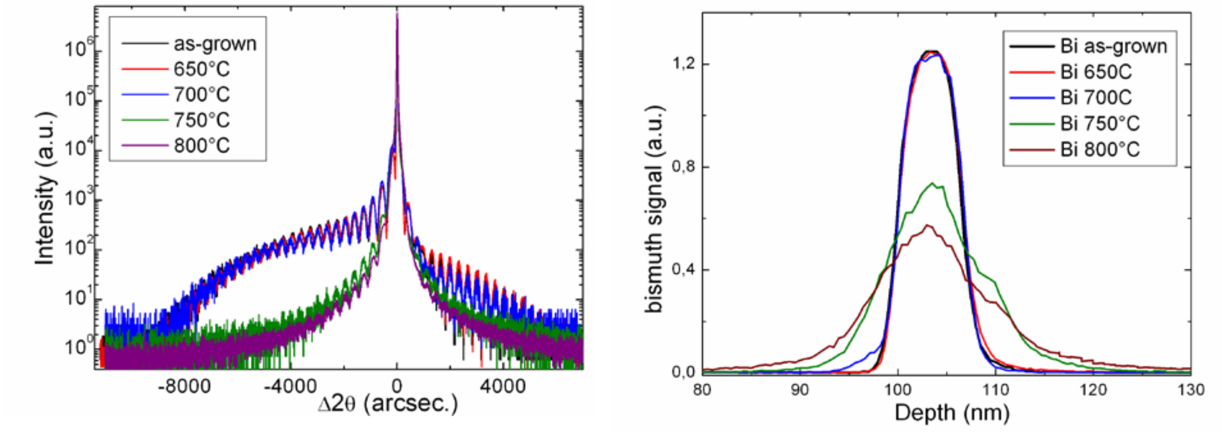

Figure 3

a) b)

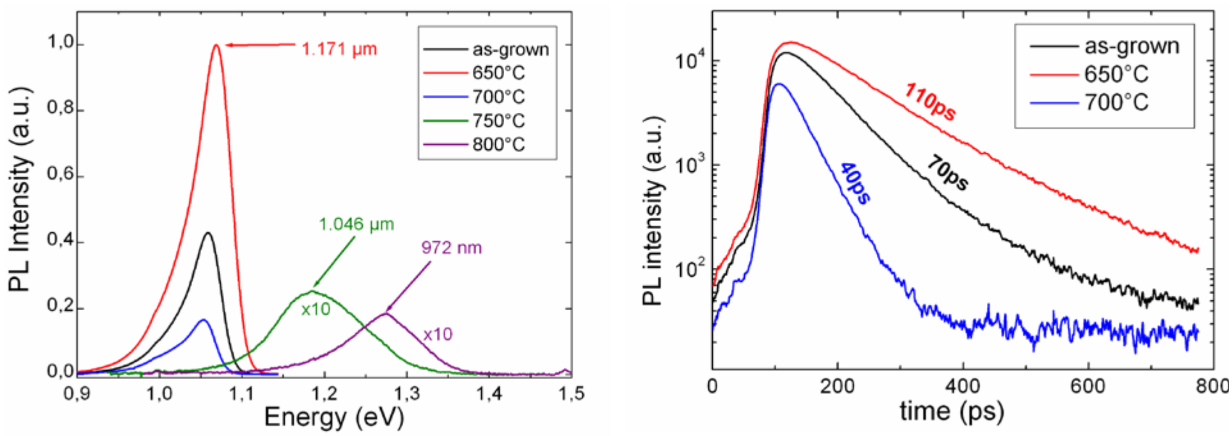

Figure 4