EUROPEAN SYNCHROTRON RADIATION FACILITY

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# Experiment Report Form

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*https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

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Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| | Experiment title: A comparative study of crystalline phase and strain relaxation and the early stage of InAs nanowire selective area growth and non-patterned island growth on Si (111) | Experiment number: MA-2645 |
|---|---|---|
| **Beamline**: BM25B | **Date of experiment**: from: 7-Oct-2015 to: 14-Oct-2015 | **Date of report**: 11-Feb-2016 |
| **Shifts:** 21 | **Local contact(s)**: Maria Vila Santos, Juan Rubio | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):


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**Report:**


**Abstract**

The scenario of InAs grown on Si and InAs (111) substrate is studied in terms of crystalline phase transformation, strain state and impurity incorporation. It is demonstrated that the all InAs layers are fully relaxed within the studied range. The crystalline phase of InAs islands is first determined by growth condition. However, after the coalescence, the crystal structure turns out to be zinc-blende again with isolated twin defects. Moreover, the presence of Gallium is identified from both shift of diffraction spots and X-ray photoelectron analysis.


**1. Purpose and methods**

Vertical InAs nanowire (NW) grown on Si (111) substrate is a promising candidate for next generation logic devices. To fabricate the NW, a patterned oxide mask is first prepared on Si (111) substrate, and selective area growth (SAG) using metal-organic vapor phase epitaxy (MOVPE) is applied. However, the high density {111} planar defect (PD) widely observed in grown III-V NWs casts shadows on their application. Meanwhile, the engineering of PDs also provides an opportunity to build polytypism quantum well within the same material. In this study, we focus on the initial stage of InAs growth on Si (111) substrate. To reveal the mechanism of PD formation, InAs (111) homoepitaxy using both MOVEP and molecular beam epitaxy (MBE) were also studied.

To explore the crystalline phase of InAs NW/islands, crystal truncation rod (CTR) in grazing incident diffraction (GID) geometry is used. CTRs of Si (0.89 0 *l*), which is equivalent to

InAs (1 0 *l*'), were measured. Zinc-blende (ZB) and wurtzite (WZ) crystal structures, together with isolated twin defect, have different structure factors and thus different diffraction patterns. For ZB, (1 0 1), (1 0 4) and (1 0 7) are visible, while for WZ (1 0 1.5) (1 0 3) (1 0 4.5) (1 0 6) are visible and twin (1 0 2) and (1 0 5). Therefore using these distinctive patterns, in a CTR *l*-scan the crystalline phase can be determined. In addition, reciprocal space mapping (RSM) around Si (1 0 4) and InAs (1 0 4) were conducted on some of the samples. Details of samples and experiment methods used can be viewed in Table 1. It should be noted that because of the (111) substrate orientation and epitaxial relationship, the Miller index here are in hexagonal system.

Another important issue of InAs NW growth is how to achieve high yield vertical wires controllablely. Based on our previous study, Gallium is suspected to be an important factor at the beginning to facilitate NW nucleation. In this context, hard X-ray photoelectron spectrum (HAXPES) is applied to analyze the buried interface element.

## 2. Sample description

Table 1. Sample summary

| | SAMPLE ID | SAMPLE DESCRIPTION | EXPERIMENT |
|---|---|---|---|
| InAs/blanket Si 111 | A | 467C 28/1 15s | (10*l*), (104) rsm |
| | B | 467C 28/1 60s | (10*l*), (104) rsm |
| | C | 467 28/1 1800s | (10*l*), (104) rsm |
| InAs NW SAE | D | 520C 1020/1 60s | (10*l*), (104) rsm |
| | E | 520C 57/1 20s | (10*l*), (104) rsm, HAXPES |
| InAs/InAs | F | MBE, "WZ-like" condition | (10*l*) |
| | G | MBE, "ZB-like" condition | (10*l*) |
| | H | MOVPE, "WZ-like" condition | (10*l*) |

## 3. Grazing incident XRD and CTR

### a. InAs heteroepitaxy on Si (111) substrate

Sample A, B and C consists of a series of InAs island grown on Si (111) substrate with different growth time. As shown in Fig 1 (a-c), InAs is first in hexagonal island shape, then both the island density and size increase, and finally irregular large blocks form.

InAs (1 0 *l*) CTR scans are plotted in Fig 2. It shows the evolution of crystalline phase with growth time. After 15 sec growth, both ZB and WZ diffraction pattern appear. InAs (1 0 1) diffraction has higher intensity compared with (1 0 2), meaning relatively large proportion of ZB composition. It should be noted that the nominal InAs (1 0 4.5) peak is not fully from InAs but from Si (1 0 4). As shown in Figure 1(d), because very large slit size were used because of the small amount of InAs, Si (1 0 4) diffraction has a very wide elongation along h direction, which falls in InAs (1 0 4.5) diffraction position when h equals to 0.89. Therefore its high intensity at $l$ = 4.5 should not be taken in consideration. When the growth time increases to 60 sec, the WZ phase increases significantly, as indicated by the appearance of InAs (1 0 3) and (1 0 4.5), together with the intensity surpass of InAs (1 0 2) compared with (1 0 1). Further increase of growth time to 1800 sees the appearance of diffraction from twins at (1 0 2) and (1 0 5). Also, a significant change takes place making the crystalline phase largely to ZB, although WZ signal at (1 0 1.5) and (1 0 4.5) still remains as small shoulder peaks.

An important information revealed by RSM is that at 15 sec growth, InAs (1 0 4) spot shifts a little from its ideal position as shown in Fig 1(d). It could related to Gallium atom contamination at the early stage of InAs NW growth. For analysis GaAs (1 0 4) ideal diffraction position is indicated in black. In Fig 1(f), InAs (1 0 4) diffraction elongates into ellipse shape possibly due to crystal quality degradation.

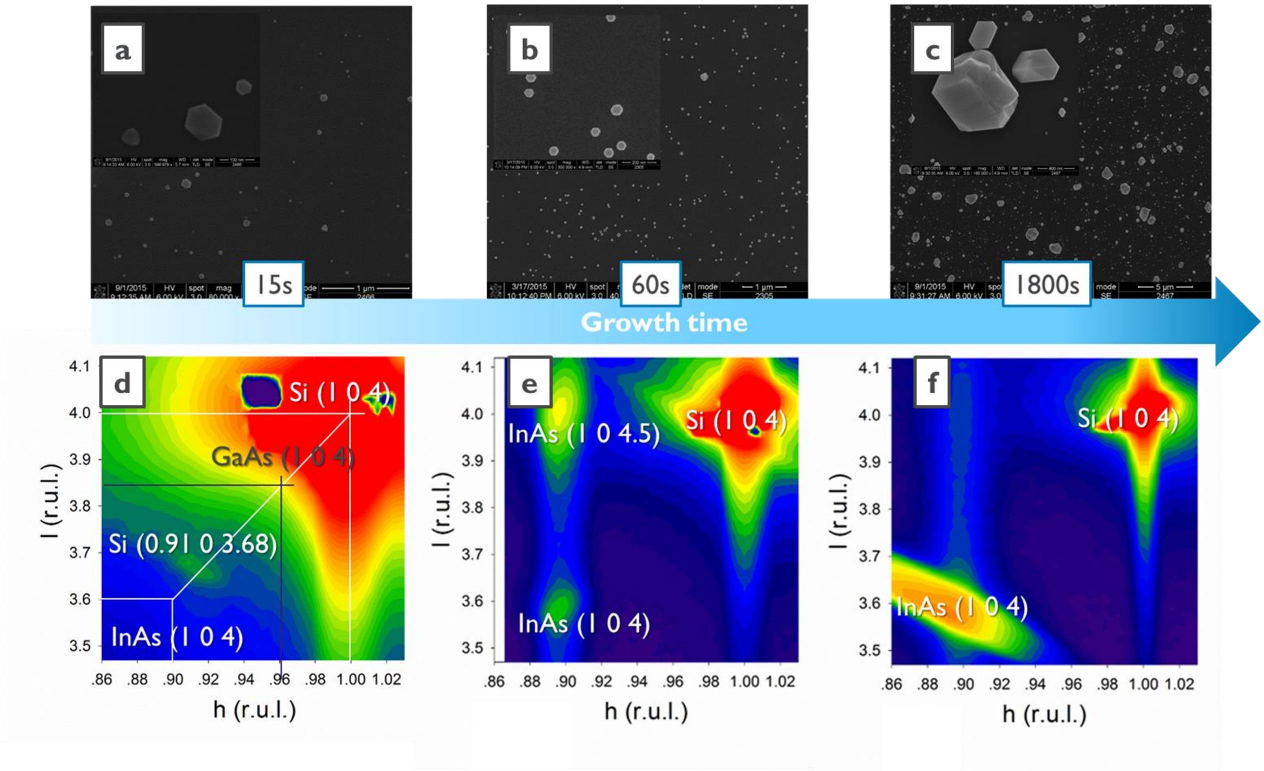


**Figure 1. (a-c) SEM pictures of sample A, B and C, respectively; higher resolution pictures are shown as insets. (d-f) RSM of corresponding samples, To highlight the InAs diffraction, the color scales are varied within these contour plots. Diffraction points are demonstrated in white text, GaAs (1 0 4) are also shown in (d) as a reference for analysis. Reciprocal unit vectors are in Si substrate lattice.**

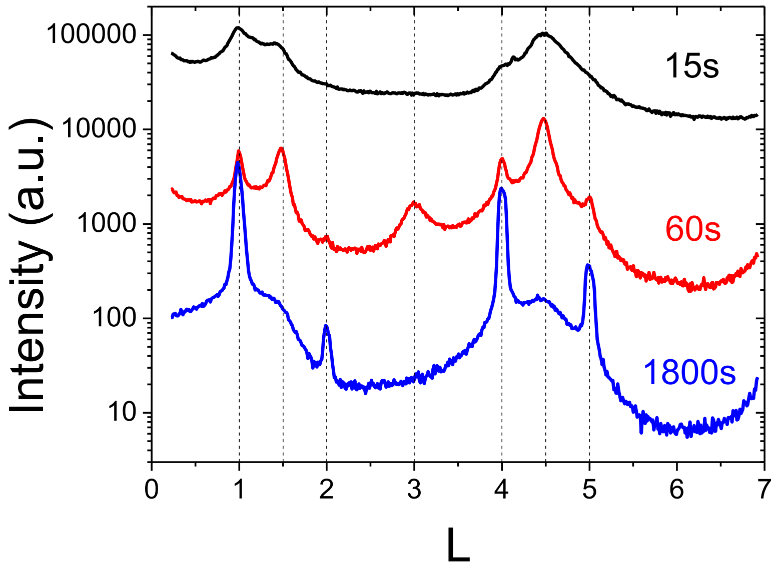


**Figure 2. InAs (1 0 *l*) CTR scan of sample A, B and C, plotted in black, red and blue, respectively. *l* is taken under InAs lattice.**

### b. Study of initial stage of InAs NW selective-area growth on Si (111) substrate

InAs NWs were grown on patterned Si (111) substrates under two different conditions (sample D and E, Table 1). Varied InAs island morpholoy was produced, as shown in Fig 3 (a) and (b). To make the island height small enough for InAs/Si interfacial analysis, very short growth time were used.

InAs (1 0 *l*) CTR scans are plotted in Fig 4. As expected, low V/III ratio produces more hexagonal InAs islands, while high V/III ratio more cubic. RSM mapping in Fig (c) and (d) shows the InAs islands are relaxed at this stage, which is due to the very high lattice mismatch between InAs and Si.

An interesting observation in RSM is the additional diffraction point near Si (1 0 4) in sample D (red dashed circle in Fig 3 (d)). Analysis shows this diffraction point locates near the ideal GaAs (1 0 4) position. This is possible because as mentioned, Ga is predicted present at InAs/Si interface and plays a great roll in InAs NW nucleation. However, it is still not clear why its intensity is larger than InAs (1 0 4). This sample was then sent for HAXPES for further confirmation the presence of Ga.

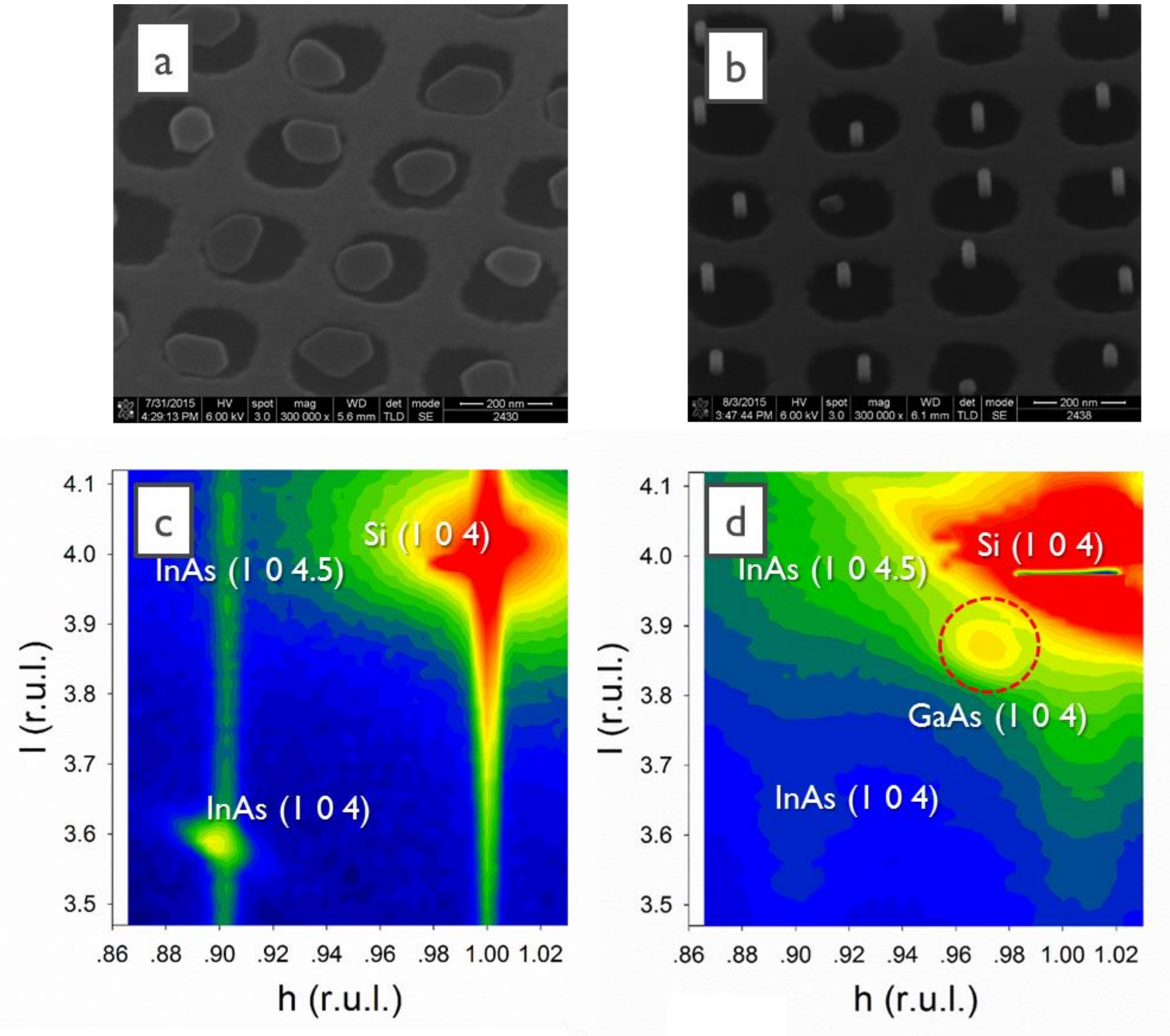


**Figure 3. (a) and (b), SEM pictures of sample D and E, respectively. (c) and (d), RSM of corresponding samples. To highlight the InAs diffraction, the color scales are varied within these contour plots. Diffraction points are demonstrated in white text, reciprocal unit vectors are in Si substrate lattice.**

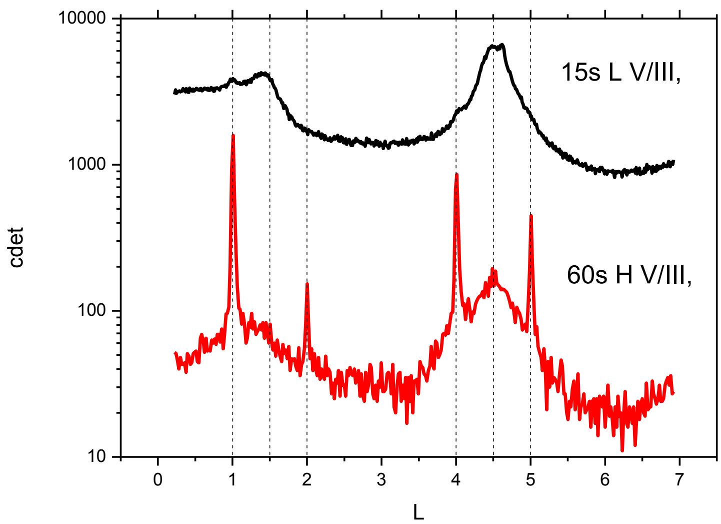


**Figure 4. InAs (1 0 *l*) CTR scan of sample D and E, plotted in black, red and blue, respectively. *l* is taken under InAs lattice.**

## c. InAs homoepitaxy on (111) substrate

(111) InAs homoepitaxy was conducted using both MBE and MOVPE. In MBE, the advantage is to see surface reconstruction in-situ using reflection high-energy electron diffraction. The growth conditions mimic what is used in WZ and ZB InAs NW growth in MOVPE, respectively (Sample F and G, Table 1). For comparison, InAs homoepitaxy was also conducted in MOVPE under the condition of typical WZ phase InAs NW growth (sample H, Table 1)

InAs (1 0 *l*) *l* scans are plotted in Fig 5. The experiment was first conducted under incident angle of 0.3 degree. *l* scan from sample F, G and H are plotted in black, red and blue curves, respectively. In all samples, the dominant peaks are from ZB phase and twins. It is partly because the substrate is ZB InAs. Moreover, the InAs epitaxy island coalescence brings the crystal structure back to ZB, irrespective of their original crystalline phase, also producing isolated twin defects. Meanwhile, it should be noted that in sample H, which was grown by MOVPE following the typical WZ NW condition, (1 0 1.5) and (1 0 4.5) is visible, though in a small intensity. This possibly indicates that as determined by growth condition, the crystalline phase of initial InAs islands is largely in WZ phase, which is burried underneath the ZB layer after coalescence.

(1 0 1) peak is omitted in sample F measurement due to mis-alignment problem. Anyhow, comparing F with G, it is hardly to find any significant difference. However, when increasing the incident angle to 0.5 degree (increased X-ray probing depth), (1 0 1.5) and (1 0 4.5) diffraction are also visible in sample F, similar as what is observed in sample H. It should be noticed that both F and H are intentionally grown using typical WZ InAs NW growth condition. This could suggest that the crystal buried initial island contain WZ phase, and the twinning ZB layer thickness in MBE is larger than that from MOVPE.

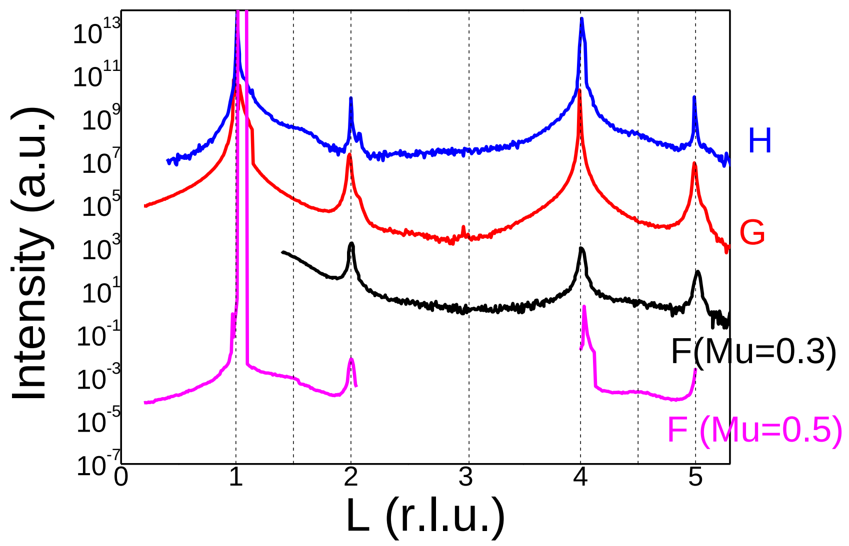


**Figure 5. InAs (1 0 *l*) CTR scan of sample F, G and H, plotted in black, red and blue, respectively.All are conducted in incident angle of 0.3° . F is also measured using incident angle of 0.5° , which is plotted in purple. *l* is taken under InAs lattice.**

**In black curve, (1 0 1) peak is omitted due to extremely high intensity, caused by mis-alignment.**

## 4. HAXPES

As shown in Fig 3 (d), diffraction correlated with lattice similar to that of GaAs was observed. To further analysis this phenomenon, HAXPES was conducted on this sample (E). First attempt was done using X-ray photon energy of 8990 eV, under which condition In 2p peak is quite obvious but there was no hint of Ga 2p peak. Then the Ga 1s peak was considered, whose binding energy is around 10367 eV. To get access to this energy, photon energy was increased to 14972 eV.
Because of the low signal intensity, totally 270 iteration were done to obtain the spectrum shown in Fig 6. The peak locates around 10374 eV, with 7 eV shift compared with the ideal value. This error could be from the calibration step. Thus the presence of Ga is identified. However, the reason why the GaAs-like (1 0 4) diffraction intensity in Fig 3 (d) is relatively high is still unclear.

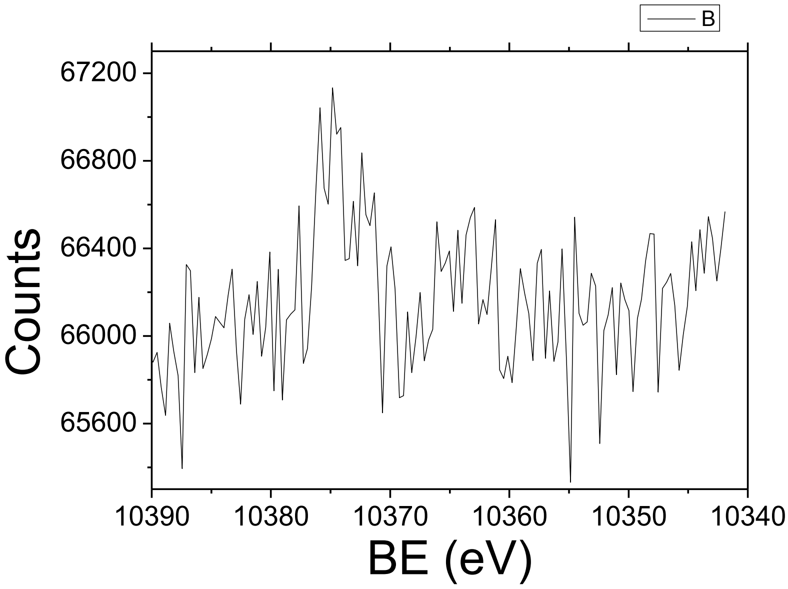


**Figure 6. Ga 1s XPS spectrum using photon energy of 14972 eV.**

## Conclusion

The evolution of strain state and crystalline phase of InAs NW/island was studied. The CTR measurement shows the original island follows the crystal structure determined by growth condition. However once the islands coalescent, the crystalline phase changes to the thermodynamic stable ZB phase, with the formation of isolated twins. The strain is fully relaxed at the very beginning of the growth. In addition, the presence of Gallium is identified using both the diffraction and photoelectron methods. Further analysis about its impact is undergoing using other characterization methods.