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In-situ X-ray Characterization of the crystal growth dynamics of Au-catalyzed InAs Nanowires

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Summary

We report on in-situ x-ray characterization of non-steady state growth dynamics of Au-assisted InAs nanowire growth on InAs (111)B substrates, by molecular beam epitaxy (MBE). By using abrupt changes in the growth conditions we show that we can promote solid phase Wurtzite (WZ)-Zinc Blende (ZB) reconstruction transitions which can lead to sharp and well defined junctions between WZ and ZB. The detailed characterization of the small phase changes is evaluated from crystal truncation rod (CTR) intensities along the out of plane Bragg conditions, from which we see the clear evidence of WZ - ZB solid phase transitions when opening and closing for the In supply. The in-situ results are correlated with the TEM analysis, which suggest that the transition takes place at the liquid-solid growth interface region of the NWs. Based on the obtained in-situ x-ray data combined with an extensive transmission electron microscopy (TEM) post growth analysis, we are able to distinguish between the substrate growth dynamics and NW crystal growth dynamics, by analyzing the respective contributions to the evolution in the Bragg peak intensities of the WZ/ZB polytypic phase formation. Moreover, we can follow the evolution of the overall crystal morphology at the substrate between the NWs, where we observe formation of ZB layers with large amount of the twinning faults. From reciprocal space mapping combined with the dynamical characterization we can conclude that during the NW growth, the substrate growth evolves from 2D structures to pyramid-like structures dominated by {111} facets.

key words:

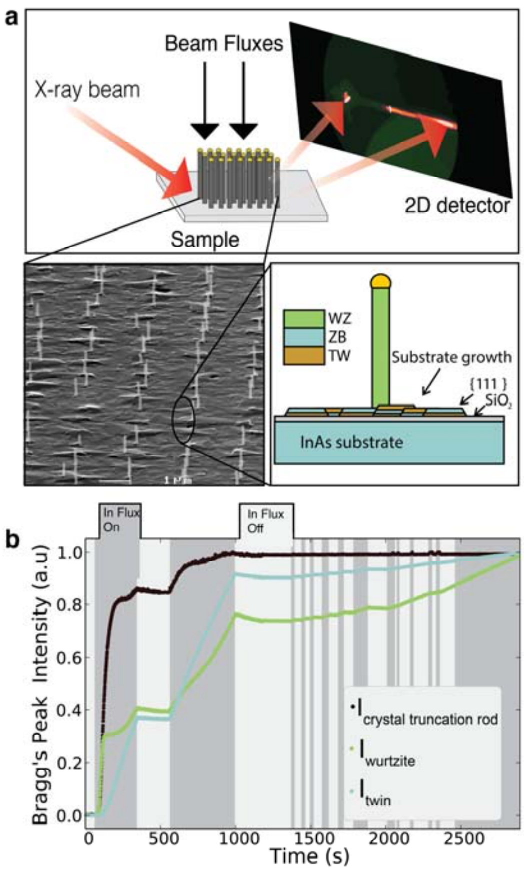
In-situ x-ray characterization, nanowire growth, Molecular beam epitaxy, growth dynamics, band-gap engineering, nanowires

1. Objectives

The growth mechanisms of nanowires still raise many fundamental questions and are still purely understood on a detailed level, mainly because of the experimental challenges associated with characterization of nanowires while they grow. The purpose of this experiment is to analyze the growth dynamics and the mechanisms governing the crystal structure formation during Au-catalyzed InAs nanowire growth by MBE. To our knowledge, no in-situ study on Au-catalyzed InAs nanowire growth has been reported so far. By studying the dynamics of the growth is it possible to understand many details such as the structural and morphological evolution of both the nanowires and the substrates. Therefore we believe, that the MBE/x-ray setup at the Spring8-beamline BL11XU, can help us gain a deeper understanding of the growth mechanism. This is of utmost importance, not only because InAs nanowires are one of the best candidates for the future of nano-opto-electronic devices, but also it can help us understand the fundamental mechanisms of vapor liquid solid growth of III-V nanowires better.

2. Methods

In-situ MBE growth chamber at the synchrotron beamline gives unique possibility to perform characterization of the structural evolution during the nanowire growth. The MBE setup at the BL11XU beamline at Spring8 is mounted on a versatile surface diffractometer equipped with an area detector which allows reaching asymmetric Bragg peaks. Asymmetric Bragg reflections allow separate analysis of the different crystal structures present in the nanowires and the substrate, mainly WZ, ZB and twinned ZB (TW). The sample was aligned in the beam and put in the Bragg condition for the WZ $(10\bar{1}1.5)$ peak (indices given in the ZB surface coordinate system). The Ewald sphere going through the WZ $(10\bar{1}1.5)$ peak comes close enough to the ZB $(11\bar{1}2)$ and TW $(11\bar{1}1)$ peaks, resulting in strong peaks from all three structures present simultaneously on the area detector.



The substrates for the nanowire growth were prepared beforehand in the following way. First 20 nm of SiO_2 were deposited onto the InAs <111>B 20x20 mm^2 wafers with electron gun evaporation, then square arrays of openings were patterned using e-beam lithography and lastly 5nm of gold were deposited into the holes. The nanowires were grown under the flux of As and In, varying the V/III ratio.

An overview of the experimental set up is reported in figure 1a.

No rotation of the substrate was possible in order to keep it in the Bragg condition. Two types of measurements were performed. First are time dependent measurements at a constant sample position during the nanowire growth, intended to study the growth kinetics and structural evolution.

Second, reciprocal space mapping (RSM) was performed during the steady state periods when the In shutter was closed to halt the growth. RSMs give an insight on morphology and amount of different structures in the sample. During the steady state growth pure WZ nanowires were grown. Growth interruption by shutting off the In flux was used in order to study dynamic effects that lead to formation of ZB or TW slabs (see fig 1b).

Figure 1. a) Schematic representation of the experiment set-up. Lower left inset: post growth SEM picture of a representative array of NWs. Lower right inset: schematic representation of the post-growth samples morphology. b) Normalized intensity of the different crystal structures Bragg's peaks for one full growth; the In beam flux is open in darker shaded regions and closed in the light regions.

3. Results and Discussion

From post growth scanning electron microscopy (SEM) and TEM imaging we can conclude that the NWs obtained from a given growth experiment has the same overall morphology, similar faceting and crystal structure distribution. High-resolution TEM and scanning transmission electron microscopy (STEM) studies show that the NWs have a 100% pure WZ structure separated with thin slabs of ZB at the same locations relative to the NW length(see an example in fig. 2). We can correlate these structural changes to the growth interruptions made during growth, where the In shutter was opened and closed, as seen in fig. 2b and c.

During steady state growth conditions we can see that the NWs form a 100% pure WZ phase, while the measured dynamics in the non-steady state growth regime, which is induced by opening and closing for the In flux, allows abrupt changes in the crystal structure. In fact, there exists a certain growth regime that promotes WZ to ZB reconstruction transitions. This regime seems to require a certain stage in growth, as only the reconstruction transitions are measured in certain periods. This behavior indicates that the growth interface morphology plays a crucial role in the resulting crystal structure during growth, as suggested by previously [2,3]. We also found that the length of the growth interruption influence the height of the slabs.

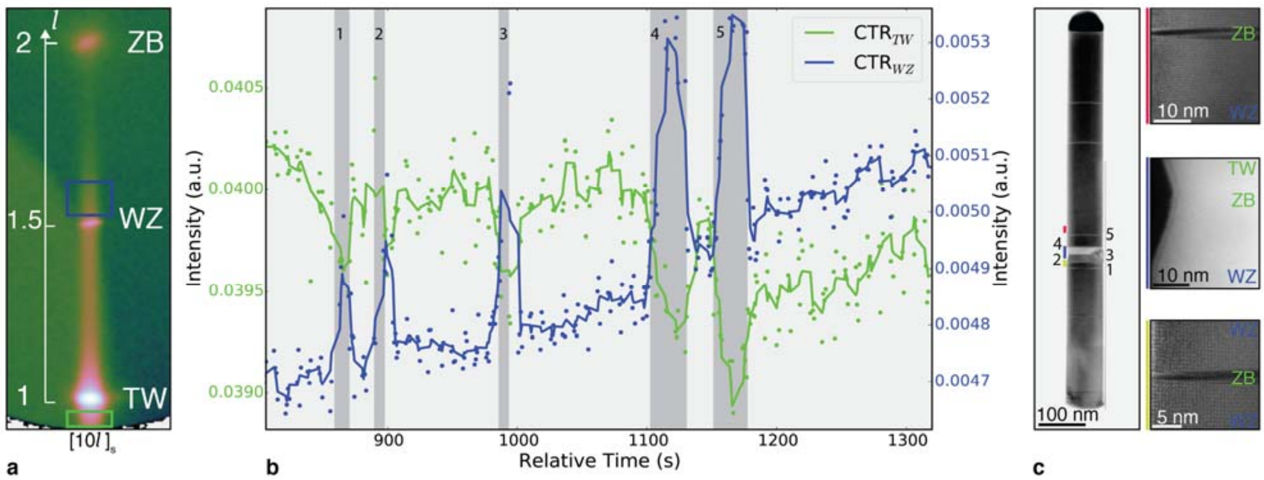


Figure 2 a) Reciprocal space model overlaid to a snapshot of the actual recorded data (time 800s). Miller Indices follow the surface-index notation. b) CTR intensities from the marked regions in a) as a function of growth time for a selected growth period. In flux is on during in darker shaded areas. The CTR intensities are proportional to the area of the thin slabs of the respective structures [1]. The observed trends suggest that an increase in In pressure favors the formation of thin WZ slabs and ZB to WZ reconstruction, whereas for strong reduction (i.e. turning the flux off) the opposite holds true. c) An example of a TEM images of a NW from the growth experiment shown in (b), where the identification correlation have been determine by several different TEM measurements. The timestamps and corresponding changes in the crystal structures are highlighted by the numbers. Right insets, top and bottom: HRTEM showing the sharp interfaces created by the formation of a thin ZB slab. Middle inset: STEM image of the neck region of the nanowire where a sharp transition from WZ to ZB and formation of twinned ZB is noticeable. The reported phase changes are correlated with the opening/closing the indium flux as highlighted by the matching numbers in figure b and c.

The deposited SiO_2 film on the substrates prevented epitaxial growth but still parasitic growth spreading from the root of the nanowires is observed suggesting that a better family of substrates for in-situ studies could be silicon <111> with SiO_2 oxide film though the growth of InAs NWs on this kind of substrates is still far from being optimized.

Nonetheless the parasitic growth crystal structure is characterized with reciprocal space maps and is found to be composed of slabs of varying thicknesses, increasing with growth time, with high symmetry facets, mostly {11-1} and {31-1}. The time derivative of the scattered intensity dI/dt corresponds to the instantaneous growth rate and can be used to identify changes in growth of different structures. Laue fringes were observed next to the TW and ZB peaks (Fig 1a) in the d*I*/d*t* signal, meaning that the substrate growth takes place forming slabs of the uniform thickness in the measured area. Moreover, the frequency of the fringes increases in time, suggesting that the linear growth rate (ML/s) increases, whereas the volumetric growth rate stays constant. This is possible in case of the pyramid formation, where thicker slabs grow at the top in order to conserve the volume.

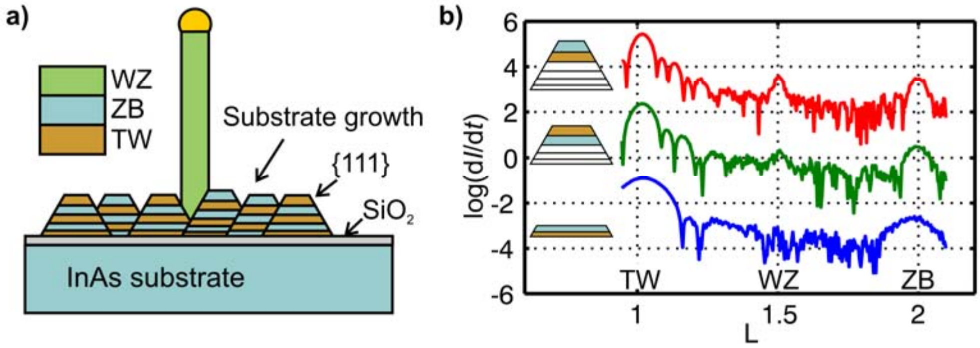


Figure 3. a) Schematic diagram showing the morphology of the parasitic substrate growth consisting of the pyramidal islands of ZB with multiple twin faults. b) Laue fringes next to the TW Bragg peak show increasing thickness of the TW/ZB slabs towards the top of the islands.

In conclusion we have studied the dynamics of the growth of nanowires and parasitic growth separately, thanks to the oxide layer deposited on the substrates.
We find out that it is possible to create abrupt crystal phase changes in InAs NWs by solid phase reconstruction transitions.

4. References

0. Feidenhans'l, R. Surface structure determination by X-ray diffraction. Surface Science Reports 10, 105–188 (1989).
1. Krogstrup, P. et al. In-situ x-ray characterization of wurtzite formation in GaAs nanowires. Appl. Phys. Lett. 100, 093103 (2012).
2. Krogstrup, P. et al. Impact of the Liquid Phase Shape on the Structure of III-V Nanowires. Phys. Rev. Lett. 106, (2011).