Role of liquid indium in the structural purity of wurtzite InAs nanowires that grow on Si(111)

The epitaxial growth of vertical InAs nanowires (NWs) on Si(111) substrates offers the possibility to integrate monolithically the two semiconductor classes maintaining a high quality interface despite of the large mismatch between their lattice constants and thermal expansion coefficients. However, the general susceptibility of III–V NWs to structural polytypism when they are grown along the [111] crystallographic orientation can affect basic properties of any device application. Extensive experimental investigations, also supported by classical nucleation theory models, have shown that it is possible to control the polytypism when the NWs are grown in the Au-assisted, and to a lesser extent in the self-assisted, vapor–liquid–solid (VLS) mode by tuning the supersaturation or the contact angle of the catalyst particle (via the growth conditions). In contrast, the freedom to tune the polytype of choice is limited in the vapor–solid (VS) growth mode, where the (111)B top facet of the NWs is directly exposed to the vapors.

Executing an *in situ* growth experiment at SPring-8, we developed a procedure to monitor the temporal evolution of the zincblende (ZB) and wurzite (WZ) polytypes as well as the presence of liquid indium during the growth by molecular beam epitaxy (MBE), based on time-resolved X-ray scattering and diffraction measurements [1]. Assisted by Masamitsu Takahashi and his team the experiment has been performed at beamline **BL11XU**, using the MBE system integrated with a surface X-ray diffractometer [2]. The geometrical configuration of the X-ray experiment is shown in Fig. 1. The glancing angle of the primary X-ray beam ($\lambda = 0.620$ Å, size: 0.3×0.3 mm^2) was fixed smaller than the critical angle of the silicon (111) substrate in order to reduce the diffuse scattering from the substrate, whereas the large footprint of the X-ray beam on the surface ensures that a large number of nanowires is illuminated. The X-rays diffracted from the WZ $(10\bar{1}1)$ and the ZB (101) InAs Bragg peaks were collected by a 2D-CMOS detector. Also we detected a characteristic powder-like scattering signal of liquid Indium formed at any stage of the growth by placing the detector close to angle of its maximum scattering (see inset Fig. 1). The scanning electron microscopy (SEM) inset in Fig. 1 illustrates that the substrate surface is mostly covered by InAs NWs, 300 nm in length and 250 nm in diameter, whereas a few InAs structures of larger diameter and multiple facets (henceforth referred to as parasitic islands) are also present.

Figure 2 shows the temporal evolution during the growth of InAs NWs of (a) the scattering signal from liquid Indium and (b) the diffraction signals from the two polytypes of InAs. The growth started at $t = 0$ s by initiating the supply of Indium, whereas the supply of As_4 had been initiated several minutes in advance. Despite the As-rich conditions, we detected the formation of liquid Indium phase during the first 1000 s

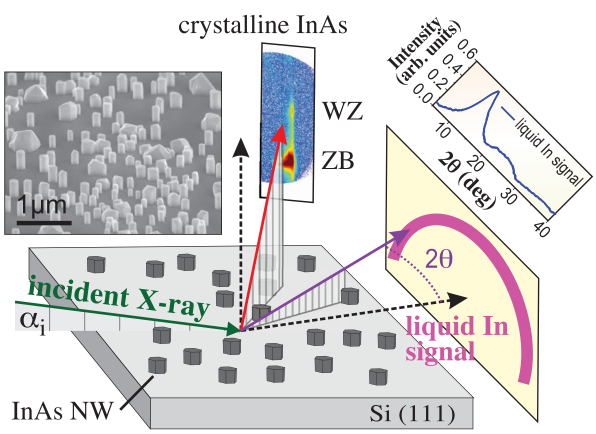

Fig. 1. Diffraction geometry within the MBE chamber. The incident X-ray beam illuminates the sample surface under a shallow angle of $\alpha_i = 0.07°$. Liquid indium causes a powder-like scattering signal at small scattering angles. The diffraction from crystalline InAs can be observed using a two-dimensional detector. The inset shows an SEM image of the grown NWs and parasitic crystallites after 1800 s of growth.

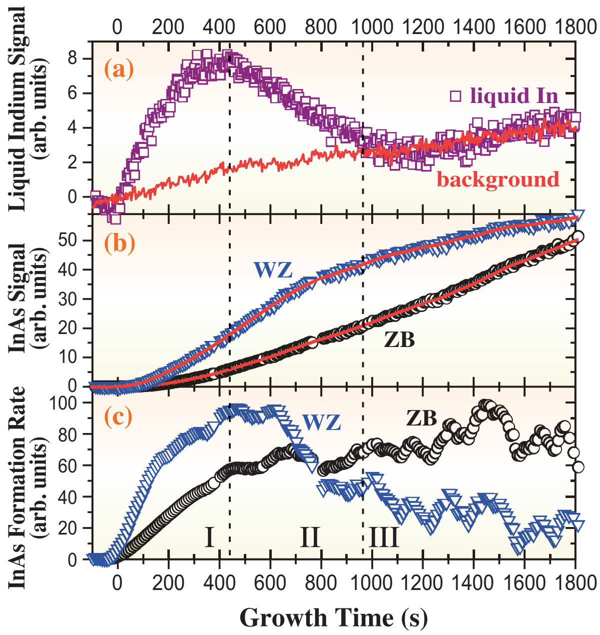

Fig. 2. **(a)** Evolution of the liquid indium signal (open squares) during NW growth, showing a maximum ~440 s after opening the In shutter at t=0 s. **(b)** Evolution of the crystalline WZ (triangles) as well as the respective ZB signals (open spheres) as function of growth time. Solid lines represent a running average of the data. **(c)** Growth rates of ZB and WZ materials, obtained as derivative of the solid lines in (a), showing a good correlation with the liquid In signal.

of the growth. Based on the signal behavior with time, we define three regimes. Regime I is characterized by the monotonic increase of the signal of liquid Indium, which reaches its maximum at t ≈ 440 s. Then, the signal drops continuously and eventually diminishes within regime II, following the background-noise level for the rest of the growth duration (regime III). The continuous increase of the background-noise level with time is attributed to the additional material deposited on the substrate.

The actual role of liquid Indium in the nucleation of InAs NWs emerges from the study of the structural dynamics of the two InAs polytypes. The diffraction intensity from the WZ polytype increases during the first 440 s, followed by a tendency to stabilize for the remaining of the growth (Fig. 2(c)). Because the diffraction intensity is proportional to the amount of material growing in the respective phase, the formation rate of the polytype can be calculated from the time derivative of the intensity. From the result shown in Fig. 2(c), we see that the behavior of the WZ formation rate correlates well with the three time regimes that were defined previously for the presence of liquid Indium. In regime I, the WZ formation rate increases continuously, reflecting the increase of the number of InAs NWs that nucleate on the substrate. The formation rate slows down to half of the peak value in regime II, manifesting not only the completion of the nucleation stage, but also the fast degradation of the WZ purity of the growing NWs that were nucleated within regime I. Thus, we conclude that the locally Indium-rich conditions that formed spontaneously on the substrate in the beginning of the growth promoted the nucleation of InAs in the WZ phase (regime I), whereas the subsequent transition to As-rich conditions defined the end of the nucleation stage (regime II) and accounted for the decrease of the WZ purity in the growing NWs (regimes II and III). All these findings are fully consistent with the model that we already suggested in Ref. 3, which was based though only on indirect observations. The diffraction signal and the respective formation rate from the ZB polytype in Figs. 2(b,c) exhibited a different behavior than the WZ ones. The formation rate increased monotonically throughout the growth duration, with a faster increase in regime I and a significantly slower one in regimes II and III. Unfortunately, safe conclusions about the temporal evolution of the ZB polytype inside the NWs cannot be drawn because the InAs NWs and parasitic islands grow simultaneously on the substrate surface, and they both contain ZB segments. The smooth transition of the ZB formation rate between regimes I and II, unlike the WZ peak at 440 s, suggests that the ZB signal in regime I reflects mostly the InAs islands, which nucleate and grow solely in VS mode. The ZB formation rate practically stabilized outside regime I, suggesting that the nucleation phase of the parasitic islands completed at the end of regime I, in coincidence with the nucleation phase of the NWs.

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