EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Investigation of the inverse piezo-electric effect in single GaAs nanowires	**Experiment number**: HC887
Beamline:	**Date of experiment**: from: 27/11/2013 to: 02/12/2013	**Date of report**: 18/08/2014
Shifts:	**Local contact(s)**: Tobias Schülli	*Received at ESRF:*

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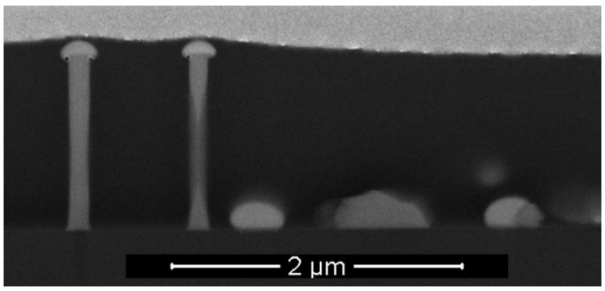
Report title: From the 'investigation of the piezo-electric effect' to the 'impact of strain induced by BCB polymer curing' in embedded GaAs nanostructures

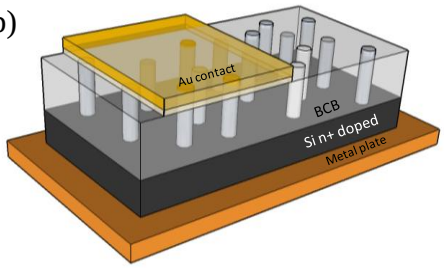
Report Summary:

Future electronic application require the use of semiconductor nanowires (NWs), whose structural parameters, such as phase composition and lattice strain, influence most of the final properties of the devices. Aim of the performed experiment was the investigation of the inverse piezoelectric effect in ensemble and single free standing GaAs semiconductor nanowires. Due to high aspect-ratio of NWs, a dependence on the NWs diameter may be expected. In addition, the presence of wurtzite crystal phase in NWs will likely lead to a different piezoconstant compared to bulk (zinc-blende structure). The initial aim of the experiment was therefore to access via X-ray diffraction (XRD), zinc-blende and wurtzite structural units and extract the piezo-electric coefficient via the *in-situ* application of an external electric field. A special sample configuration was needed for the application of the mentioned external electric field, and it included the embedding of the NWs in a benzo-cyclobutene (BCB) polymer matrix. XRD revealed the effect of such polymer in terms of strain on the embedded objects; effect which is one order of magnitude higher than the piezo-electric one.

Experimental details:

The XRD characterization was performed on GaAs NWs (diameter of ~100 nm and length of ~ 1µm), grown by molecular beam epitaxy (MBE) on a highly n-doped Si substrate (resistivity of 10^{-3} Ω/cm) in the Paul-Drude Institute, Berlin. The NWs have a number density of $10^8/cm^2$. Among them, the parasitic growth of GaAs clusters took place as well (Fig. 1(a)). In order to apply an electric field to the NWs under investigation, an embedding benzocyclobutene (BCB) polymer was used to fill the spaces between the NWs. The BCB-based polymer belongs to the series CYCLOTENE 4000 from Dow Chemical, which has wide applications in GaAs electronic circuits [1]. The planarization procedure included the spin coating of the fluid polymer, a UV exposure of 1.3s duration and a final thermal annealing for 30 min at 250˚C [2]. In modern electronic applications [3], the last curing step is crucial for the hardening of the polymer, to induce the crooslinking of the polymer chain. In order to be able to apply an electric field, and avoid a direct electrical contact and breakdown current, the thickness of the deposited spin coated polymer was kept ~40 nm higher than the mean length of the NWs (Fig. 1(a)). Then two 10nm Ti/150nm Au contacts were deposited onto the front and back sides of the sample, as top and back electrodes (Fig. 1(b)). The contact on the front side had a 0.5 mm to 1 mm diameter and the contact on the back side was covering the whole surface.
The prepared sample was measured at beamline ID01 at the ESRF in Grenoble, France, using a monochromatic beam with an energy of 15keV with the initial aim to measure the piezoelectric effect.

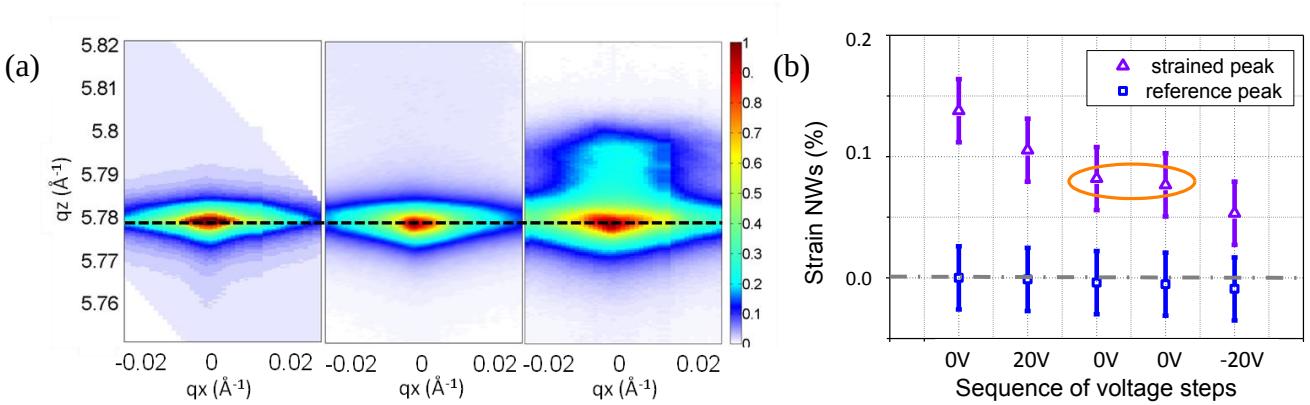
(a) 

(b) 

(a) SEM image of embedded GaAs NWs and parasitic clusters on the growth substrate, embedded in a BCB polymer layer, and covered by a metallic contact. (b) Sketch of the GaAs NWs embedded in the BCB polymer matrix.

Firstly, the symmetric (333) reflection was probed for ensemble and single NWs, by applying an alternating electric field in the 100 Hz regime. An alternating field was first chosen in order to reduce the failures, likely to be produced by electro migration in a static field. The selection and the analysis of a single NW was performed using a nanofocused X-ray beam. With the available Fresnel Zone Plate setup a focal size of 400x700nm² was achieved, providing the required spatial resolution. Longitudinal scans of the selected reflection were performed with an avalange photodiode detector, allowing the data collection from several cycles of the AC field using a synchronized detector-readout, for an improved statistics. Subsequently, the peak profile along the value of the wave vector transfer parallel to the [111] surface normal was extracted. The application of an electric field should result in a reversible shift of the diffracted signal, however at this step of the characterization no effect was detected.
Secondly, in the absence of an external electric field, ensemble NWs, were probed with a (300x300)µm² sized beam, obtained using a pair of motorized slits in front of the sample. Fig. 2(a) shows three 2D reciprocal space maps, measured with a 2D Maxipix detector, around the (333) reflection of samples at different steps of the preparation process. One was measured for the as-grown nanowires, a second for the embedded sample without the last annealing step at 250˚C, and a third for an embedded sample after complete preparation. In the third map (from left to right) an additional signal at higher q_z angle ($\Delta q_z \sim 0.02 Å^{-1}$) is visible. The position of that signal compared to the most intense one (from the unstrained NWs, black dashed line in Fig. 2(a)) allowed to quantify the strain state of the amorphous polymer indirectly, by measuring the strain of the crystalline NWs. The average (compressive) strain state induced by curing was ~ -0.2%. That strain affected only part of the diffracting free standing nanowires and GaAs parasitic clusters embedded and planarized by BCB. We estimated, through the intensity ratio of the two signals, that less than 4% of the total volume of the measured nanowires and GaAs clusters was actually compressed. This strain state was due to the different thermal expansion coefficients of BCB (~ $52 \cdot 10^{-6}$/°C) and GaAs (~ $5.73 \cdot 10^{-6}$/°C).

Thirdly, a voltage was applied to the sample up to |20|V, resulting in a static effective electric field ranging between $6.6 \cdot 10^5$ V/m and $1.3 \cdot 10^7$ V/m. A variation of strain as function of the applied voltage was observed: the strain always decreased, towards the unstrained limit, and it was independent of the sign of the electric field. We interpret the observed behavior as the effect of the combined X-ray radiation and the application of an external electric field, which results in the scission of the BCB polymer chains and the polarization of the generated polar sub-molecules. This process lead to a local release of the pre-compression in the polymer with resulting strain decrease in the embedded NWs. The decoupled application of an electric field and an extended exposure to X-rays have been tested as well, and revealed no measurable effects. For example, the region marked by the orange ellipse in Fig. 2(b), shows that two consecutive measurements of the same region on the sample without application of an electric field kept a constant strain state.



(a) From left to right, comparison of reciprocal space intensity maps for: as-grown NWs, embedded NWs before and after last curing step. The dashed black line indicates the reference unstrained GaAs position. The intensity is normalized to the respective maximum in each map. The maps are drawn in terms of lateral and vertical momentum transfer, given by q_x, the lateral component in the scattering-plane, and q_z, along the growth direction, respectively. (b) Strains values extracted from the X-ray diffraction data in one area on the sample. The data set around the value zero (blue squares) was calculated from the Bragg peak position of the unstrained GaAs NWs (main signal). The second data sets (purple triangles) was calculated from the Bragg peak position of the strained NWs, and showed a decrease in the strain during the application of the voltage cycle.

Additional characterization is needed to understand whether the polymer changes are reversible or not. Within this context, we can exclude the possibility of detecting lattice expansion due to the piezo-electric effect, which is expected to be one order of magnitude smaller than the strain state detected.
The presented data are now part of a submitted manuscript [4].

References:

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[2] E. Dimakis, U. Jahn, M. Ramsteiner; A. Tahraoui, J. Grandal, X. Kong, O. Marquardt, A. Trampert, H. Riechert, L. Geelhaar Nano Letters **14**(5), 2604–2609 (2014).

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[4] Bussone G.; Dimakis E.; Grifone R.; Biermanns A.; Tahraoui A.; Carbone G.; Geelhaar L.; Schülli T. U. and Pietsch U. Impact of strain induced by polymer curing in benzocyclobutene embedded semiconductor nanostructures (submitted).