

Supporting information for:

Nanobeam X-ray fluorescence dopant mapping reveals dynamics of in situ Zn-doping in nanowires

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S1. Consistency of the results

In the main text, we only report data for one nanowire per sample. However, for each sample 2-3 nanowires were measured in order to assess the consistency of the result. In Figure S1 we show the Zn concentration profile for three nanowires of the p-i-n InP sample and two nanowires of the barcode InP sample. The concentrations were assessed with the same methodology, demonstrating excellent consistency with variation between samples below noise level.

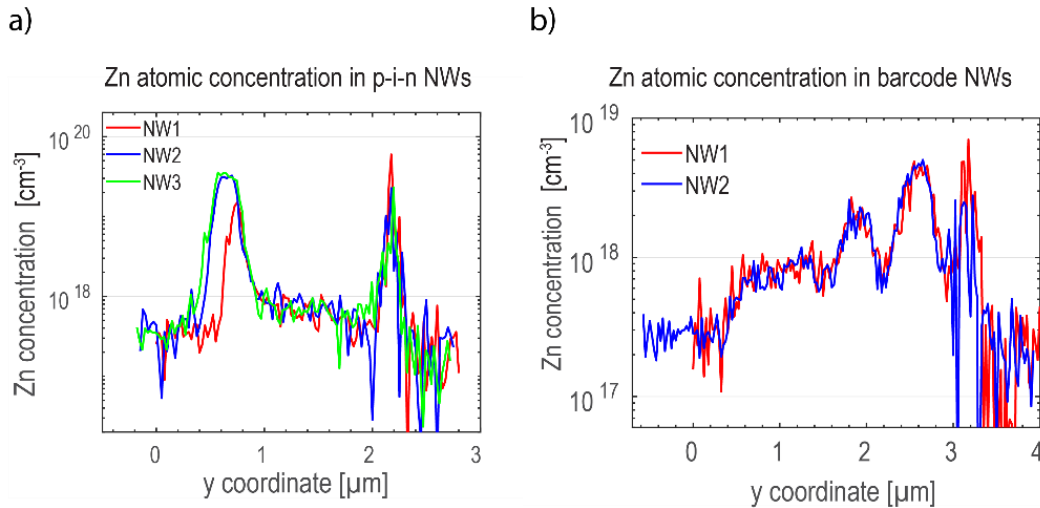


Figure S1. Consistency of the doping evaluation on nanowires of the same batch. a) Zn doping concentration of three different nanowires of the p-i-n InP nanowires sample. NW1 shows a lower concentration because part of the p-segment broke off during deposition. b) Zn

doping concentration of two different barcode nanowires measured during the nano-XRF experiment.

S2. Detection limits details

A complete harmonization of the definition of detection limit is not yet achieved, depending mostly on the specific technique. Here we provide the highlights of our calculation of detection limit, which was performed considering the IUPAC recommendations.

The detection limit was calculated in function of the variance of 30 independent measurements on the blank σ_B . Assuming a normal distribution for these measurements, one can define the detection limit L_D as the minimum detectable signal which gives a probability α of making an error of the first type (false positive) and a probability β of making an error of the second type (false negative). A false positive would consist in the detection of a dopant when in reality it would not actually be present, whereas a false negative would happen if the dopant would not be detected, whereas in reality it is present in the sample. This value can be calculated with a statistical hypothesis testing, which in case of a normal distribution is a Student's t test.

One can first consider the false positive error by defining a critical limit L_C :

$$L_C = t_{\nu, 1-\alpha} \sigma_B$$

Here, t is the Student's t , ν is the degree of freedom and α is the significance level. We can combine this result with the probability β of making an error of the second type, thus defining the detection limit:

$$L_D = L_C + t_{\nu, 1-\beta} \sigma_B$$

In our case we consider $\alpha = \beta = 0.05$ and $\nu = 30$ (the number of measurements), which gives:

$$L_D = 2t_{\nu, 1-\alpha} \sigma_B = 3.4\sigma_B$$

The probability values $\alpha = \beta = 0.05$ were chosen in order to get a confidence level $1-\alpha$, corresponding to 95%. This value is recommended by IUPAC (IUPAC recommendations, 1994) and allows to easily compare our study with others, since it is a confidence level commonly used in most statistical tests.

S3. Nano-XRF mapping of a p-i-n InP nanowire

A chemical map of a p-i-n InP nanowire is shown in Figure S2. The image was taken with a beam energy of 10.5 keV. The red channel represents the In count rate, the green represents the Au, whereas the blue channel shows the Zn count rate. The p-doped segment is clearly visible at the bottom of the nanowire. This map shows the imaging capability of the technique which can be exploited in future in more complex sample design, e.g. when the nanowire is patterned with contacts in a real device setup.

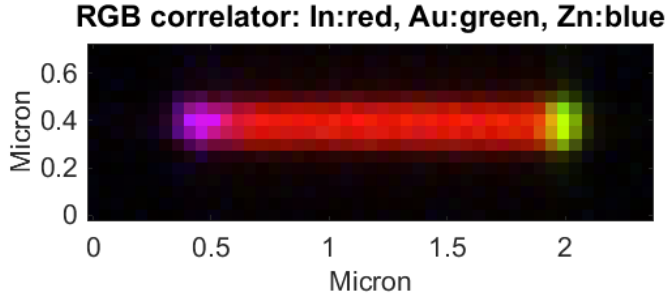


Figure S2. Nano-XRF RGB map for a p-i-n InP nanowire. 50 nm step size and 1 s counting time.

S4. Reservoir model of the Zn doping

Here, we present a model for obtaining the doping concentration profiles along the nanowire, when switching on and off the dopant source. In this model, we assume that the dopant is incorporated from the liquid seed to the solid through the liquid-solid interface area without involvement of diffusion. We also assume that there is no competition in nanowire site occupation between the dopants and the nanowire constituents.

The concentration of dopants in the liquid is $c_L = \frac{N}{V}$, where N is the number of dopants. V is the volume of the seed particle, which remains approximately constant during the growth because the dopant atoms constitute only a small fraction of the total volume. The dopant concentration in the solid, c , is proportional to c_L : $c = kc_L = k \frac{N}{V}$, where k is the segregation coefficient. Thus, the dopant concentration in the solid is proportional to the number of dopants in the seed particle.

Due to mass conservation, the rate equation for the dopant atoms in the seed particle is:

$$\frac{dN}{dt} = J_{VL} - J_{LS}$$

Here J_{VL} is the flux of dopants from the vapour to the liquid phase, and J_{LS} is the flux of dopant incorporation from the liquid to the solid state. The flux of dopants into the solid at the liquid-solid interface can be rewritten as:

$$J_{LS} = Av_g c = Av_g \frac{k}{V} N,$$

where A is the liquid-solid interface area and v_g is the nanowire growth rate. This leads to:

$$\frac{dN}{dt} = J_{VL} - J_{LS} = J_{VL} - \left(Av_g \frac{k}{V} \right) N$$

Assuming a constant growth rate, we get:

$$\frac{dN}{dx} = \frac{dN}{dt} \frac{dt}{dx} = \frac{dN}{dt} \frac{1}{v_g} = \frac{J_{VL}}{v_g} - \left(A \frac{k}{V} \right) N \quad (i)$$

By defining the characteristic length as $l = V/kA$, equation (i) can be rewritten as:

$$\frac{dN}{dx} = \frac{J_{VL}}{v_g} - N/l$$

which can be converted into an equation for the solid concentration using $c(x) = \frac{k}{V}N(x)$:

$$\frac{dc}{dx} = \frac{k}{V} \frac{dN}{dx} = \frac{k}{V} \left(\frac{J_{VL}}{v_g} - \frac{V c(x)}{l} \right) = \frac{k J_{VL}}{V v_g} - \frac{c(x)}{l}$$

This differential equation has the general ansatz $c(x) = \alpha + \beta e^{-x/l}$ (ii). The solution has to be divided into the two cases of leading and trailing edge, since these have different boundary conditions.

After switching on (leading edge)

Just as the dopant source is switched on at $x = 0$, we have $c(x = 0) = \alpha + \beta = c_I$, where c_I is the concentration in the preceding i-segment. At large x , the number of dopants saturates at $c(x = \infty) = c_\infty = \alpha$, and

$$\frac{dc}{dx} = \frac{k J_{VL}}{V v_g} - \frac{c_\infty}{l} = 0$$

from which it follows that $c_\infty = \alpha = l k J_{VL} / V v_g$. Thus, the steady-state concentration is proportional to the flux J_{VL} . The solution of the equation is:

$$c(x) = c_\infty + (c_I - c_\infty) e^{-x/l} \quad (iii)$$

After switching off (trailing edge)

After switching off the dopant source, we assume that dopant flux from the gas phase is zero, i.e. $J_{VL} = 0$, and there is an initial concentration $c(x = 0) = \alpha + \beta = c_0$. For large x , the concentration drops to the background concentration of the undoped segment, which is

$$c(x = \infty) = c_I = \alpha. \text{ It follows that } \beta = c_0 - c_I.$$

Thus, the solution of Eq. (ii) after switching off the dopant source is

$$c(x) = c_I + (c_0 - c_I) e^{-x/l} \quad (iv)$$

Note that l and c_I are the same as in eq. (iii) in this model.

Combined solution

The equations (iii) and (iv) are equivalent but with different constants due to the boundary conditions. For sake of simplicity and compactness, in the main text we merged equations (iii) and (iv) in the following expression:

$$c(x) = c_1 + (c_2 - c_1) e^{-x/l} \quad (1)$$

This function was used for the fitting of the measured signal, with three free parameters c_1, c_2 and l . Note however that c_1 and c_2 have different meanings for leading and trailing edges.

S5. Sum of Ga and In atomic concentrations.

The concentrations of Ga and In in the $\text{Ga}_x\text{In}_{1-x}\text{P}$ nanowire estimated with nano-XRF were summed up (Figure S3) to cross-check the measured concentrations. The sum of Ga and In was constant over the whole nanowire as expected from stoichiometry.

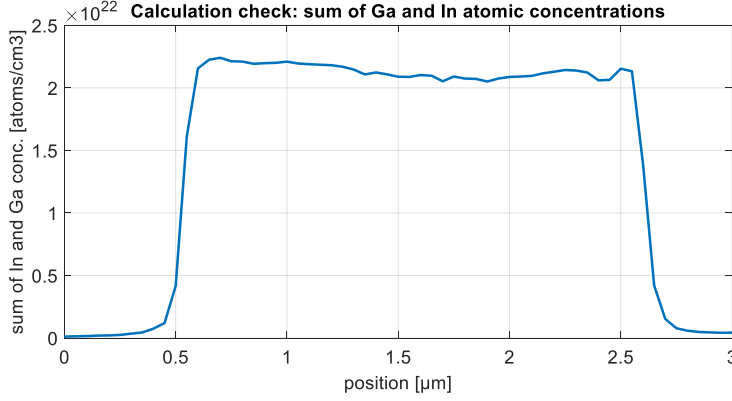


Figure S3. Sum of Ga and In atomic concentrations over a $\text{Ga}_x\text{In}_{1-x}\text{P}$ nanowire.

S6. $\text{Ga}_x\text{In}_{1-x}\text{P}$ nanowire measured at 17.5 keV

In order to have a reference for the Zn concentration in the InP nanowires, we performed a XRF line scan of the $\text{Ga}_x\text{In}_{1-x}\text{P}$ nanowires sample at 17.5 keV (Figure S4) in addition to the measurement at 10.7 keV. Note that in this case the In concentration is constant in this line scan, which is unphysical since it implies that the total Ga+In concentration would change. The reason is that the nanowire was not aligned perfectly horizontal, such that the excited volume decreased from left to right. The sample in the main text, measured with a monochromatic beam, was aligned better and did show a constant Ga+In composition.

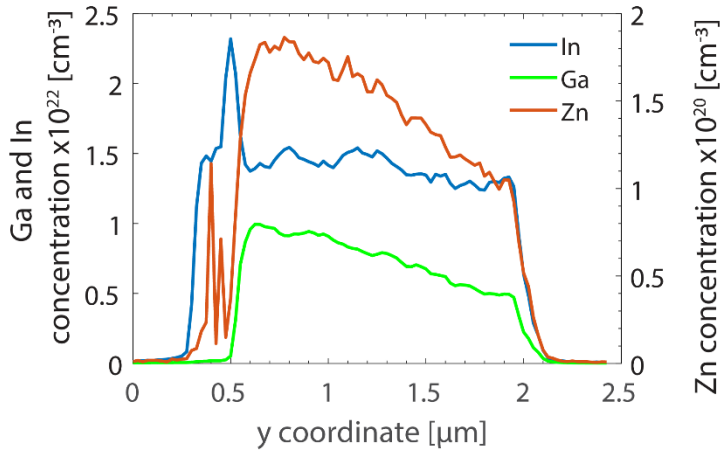


Figure S4. Concentrations of In, Ga and Zn in a $\text{Ga}_x\text{In}_{1-x}\text{P}$ nanowire measured with an X-ray energy of 17.5 keV.