P-Doping Mechanisms in Catalyst-Free Gallium Arsenide Nanowires

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ABSTRACT Doped catalyst-free GaAs nanowires have been grown by molecular beam epitaxy with the gallium-assisted method. The spatial dependence of the dopant concentration and resistivity have been measured by Raman spectroscopy and four point electrical measurements. Along with theoretical considerations, the doping mechanisms have been revealed. Two competing mechanisms have been revealed: dopant incorporation from the side facets and from the gallium droplet. In the latter incorporation path, doping compensation seems to play an important role in the effective dopant concentration. Hole concentrations of at least 2.4 × 10^{18} cm^{-3} have been achieved, which to our knowledge is the largest p doping range obtained up to date. This work opens the avenue for the use of doped GaAs nanowires in advanced applications and in mesoscopic physics experiments.

KEYWORDS Nanowire, doping mechanisms, catalyst-free, Raman spectroscopy, electronic transport

Semiconductor nanotubes and nanowires have stimulated a new enthusiasm in the emerging field of nanotechnology by enabling extraordinary progress in applications such as single molecule sensing,1,2 functional nanoelectronic devices,3,4 high mobility field effect transistors,5,6 batteries,7,8 solar cells9,10 and thermoelectric devices.11,12 Additionally, in fundamental mesoscopic physics they have been the playground for the study of extremely interesting effects such as the possibility of electrostatically tuning the supercurrent,13 single electron transistor phenomena14 and quantum dot physics.15–17 Gallium arsenide (GaAs) has a long tradition in the history of mesoscopic physics.18–21 GaAs nanowires are a particularly interesting material system because of the possibility of extending the technology of mesoscopic physics directly in a one-dimensional system. Molecular beam epitaxy (MBE) can particularly contribute to this, thanks to the high purity and enablement of high quality axial and coaxial heterostructure fabrication.22–24 Doping of nanowires is an essential element for the realization of electronic and optoelectronic devices. In the case of quantum transport experiments, p-doped GaAs nanowires are a specially interesting system. Indeed, the expected spin coherence time in p-doped quantum dots can be strongly enhanced compared to n-doped case, due to the suppression of hyperfine interaction between the hole and the nuclei of the host material.25 Moreover, the hole–hole interaction is more pronounced than in the case of electrons.26 For this reason, p-doped GaAs nanowires are extremely suitable for the realization of electrostatically defined quantum dots with few electrons in the spin blockade regime and for the studies of the carrier–carrier interactions.27

There is an extensive literature on electronic transport properties of nanowires in many material systems such as InAs,27–29 InN,30,31 Ge,32 and Si.33 The doping mechanisms have been deeply investigated in the case of Vapor–Liquid–Solid growth of silicon nanowires by chemical vapor deposition (CVD). Indeed, it has been shown that differences in the precursor decomposition rates between the solid nanowire surface and the catalyst lead to the formation of a doped shell and a much lower doped core.34,35 Doping of III–V semiconductor nanowires has been demonstrated in the case of inclusion of magnetic impurities36 and by the inclusion of zinc in the growth process.37 Electrical doping and transport properties of GaAs nanowires have not been extensively investigated yet, mainly for two reasons: (i) the challenges in doping and (ii) the existence of a Schottky barrier between GaAs and the metal, which makes the realization of ohmic contacts challenging specially at low temperatures. One of the difficulties in controlled doping is the fact that dopants such as silicon and germanium are amphoteric in III-Vs. This means that their incorporation can lead to n or p doping, depending on whether they are incorporated in a substitutional III or V site.30,41 Furthermore, with respect to the doping mechanisms, the lessons learnt in studies of nanowires grown by CVD based methods cannot be directly applied to the case of III–V nanowires grown by MBE. The reason for that is that growth mechanisms differ to a large extent and the surface chemistry phenomena such as precursor decomposition are significantly less thermally activated.42–44

Recently, we have shown that it is possible to dope GaAs nanowire structures both p and n type. In particular, we
demonstrated a radial nanowire solar cell composed by an external n-type layer followed by an intrinsic and p-type layer toward the center of the nanowire. The device exhibited a 4.5% efficiency and a fill factor of 0.65 under illumination conditions of 1.5 a.m. These results let us think that doping in the core and in the shell of the nanowire is controlled and that the interfaces of the device exhibit high quality. While the growth on the nanowire facets is well understood, questions arise with respect to the core doping. First, it is not clear why should the doping be type p. Second, it is not clear if the dopants are incorporated from the side facets or from the nanowire tip. The purpose of this letter is to understand the doping mechanisms in catalyst-free gallium assisted grown GaAs nanowires. For that, we combine multicontact transport experiments and Raman spectroscopy on the same nanowire. The two techniques provide complementary information on the doping process: transport experiments give information on the electronic properties and doping activity of the incorporated impurities, while Raman spectroscopy reports on the incorporation sites of impurities and lends understanding to their distribution within the sample.

The p type GaAs nanowires were obtained by molecular beam epitaxy in a Gen II MBE system as described elsewhere. The nanowire growth was carried out at a nominal Ga growth rate of 0.25 Å/s, As partial pressure of 2.7 × 10⁻⁶ mbar, corresponding to Ga rich conditions, at a temperature of 630 °C and with 7 rpm rotation. Silicon was added to the growth process at the beginning of the growth process. A flux of ~1.62 × 10⁻¹² at. Si/(cm² s) was obtained by heating the Si cell with 13 Amp. In our MBE system, this typically leads to a concentration of ~6 × 10¹⁸ cm⁻³ in thin films obtained for a growth rate of 2.8 Å/s. The nanowire growth rate under these conditions is ~5.5 µm/h (15 Å/s). The nanowires were grown for 4 h, leading to nanowires 22 µm long and with a diameter ranging between 180 and 70–90 nm (from the bottom to the tip). Silicon is an amphoteric impurity in GaAs, which means that the incorporation of silicon can lead to n or p type doping, depending on whether it is incorporated in As or Ga sites. One should note that the type of incorporation depends on the growth facet and temperature. For {001} facets, n-type doping is mostly achieved, whereas for {111} and {110} facets, both types of doping can occur. We have analyzed the structure by high resolution transmission electron microscopy. We observe no difference in the structure between nanowires grown with and without silicon. The structure corresponds to 100% zinc-blende with single twins spaced between 30 and 500 nm.

Multiple electric contacts were fabricated regularly spaced along the entire nanowire. For this, the nanowires were transferred on an oxidized Si wafer, described elsewhere. The contacts were defined by a typical process of positive electron beam lithography. After the development of the resist, the samples were exposed to a short O₂ plasma cleaning, the oxide at the surface of the nanowires was removed by dipping the sample in a 1:2 HF solution for ~2 s. Immediately after, the metal layer consisting of Ti/Pd/Ti/Au (10/65/65/50 nm) was evaporated. The width of the contacts was varied between 250 and 1000 nm, for different samples. In order to enable a simultaneous measurement of the regions between contacts with Raman spectroscopy, the distance between two contacts was kept larger than the size of the illumination spot of ~800 nm. They were spaced between 0.8 and 1.3 µm. We did not observe any abnormal contact resistance increase by reducing the contact size, even for the thinnest contact of 150 nm.

The local nanowire resistance was measured both in two and four point configurations, R₂p and R₄p, respectively. In principle, the R₄p configuration has the advantage of avoiding the parasitic effect of the contact resistance. All of the transport measurements were performed at room temperature using a needle probe station equipped with a source meter unit used as a DC-polarization voltage source and DC-current meter and a high impedance voltage meter. The electrical contact scheme in R₄p configuration is shown in the Figure 1a: the polarization voltage was applied between the exterior contacts, while the voltage drop was measured with the high impedance multimeter between the two central contacts. Measurements in R₄p configuration are necessary in order to obtain an accurate value of the nanowire resistance. Indeed, in a two-point configuration the electrical circuit is constituted by two Schottky diodes in opposite direction with the resistance of the nanowire (R₉NW) in series. At a finite bias voltage, the potential drop occurs more importantly across the diode polarized in reversed mode and the nanowire. At a high enough bias, minority carriers can be injected through the Schottky barrier and the global resistance is then dominated by R₉NW. Nevertheless, in this high bias regime, a residual contact resistance is still
measured by comparing $R_{4p}$ and $R_{2p}$, even for a linear $V(I)$ characteristic ($\partial^2V/\partial I^2 = 0$). As a consequence, the values of the nanowire resistance obtained by measuring in $R_{2p}$ configuration generally constitute an overestimation of the real value. $R_{4p}$ was measured along the wire, with the exception of the first and last point, which for geometrical reasons cannot be realized in a $R_{4p}$ configuration. At the extremes of the nanowire, the resistivity is extracted from the measurement of $R_{2p}$ at high bias voltage.

We have measured the spatial dependence of the resistivity in 15 samples. The results of a representative nanowire are shown in Figure 2. The resistivity decreases along the nanowire from the nanowire tip to the bottom. This variation of the resistivity can be as high as 1 order of magnitude from one side to the other for a 20 $\mu$m long nanowire. The resistance per length can be as low as $2 \times 10^{10} \Omega \cdot m^{-1}$ for a diameter of $\sim 200$ nm, demonstrating the possibility of efficient doping in GaAs nanowires. As mentioned above, we have compared the resistivity mapping between nanowires obtained on the same run and with parallel identical runs. In all cases, there is a clear and constant decrease in the resistance per length up to factor 5, from 110 k$\Omega$ on one end to 20 k$\Omega$ on the other. They are all consistent, indicating an excellent reproducibility of the nanowire properties.

The variation in resistance of a semiconductor can be due both to a variation in doping and/or to a change in the carrier mobility. At room temperature, the mobility of GaAs is dominated by the optical phonon scattering and the crystalline quality, the effect of doping concentration remaining extremely small.47 As we have not observed any structural inhomogeneity in the structure of the nanowire, a variation in carrier mobility can in principle be excluded (see the Supporting Information for the structural analysis). The most plausible cause for the spatial dependence of the resistivity seems to be a non-homogeneous doping along the nanowire. At this point, the electrical transport measurements are insufficient to allow discrimination in the location of the dopants within the nanowire, e.g., in the more external part of the nanowire or core. In order to gain further understanding, a complementary investigation with alternative characterization techniques is needed.

To this end, we have measured Raman spectra along the nanowire between each electrical contact pair. Raman spectroscopy provides information about the material structure and also about the existence and relative concentration in impurities. The measurements were realized in backscattering geometry. The 488 nm line of an Ar$^+$Kr$^+$ laser was used for excitation. The laser was focused on the nanowire with a 100 $\times$ objective (0.95 NA). The power of the incident light was about 500 $\mu$W (equivalent to 25 kW/cm$^2$). Special care was taken to ensure that the nanowires were not heated. The scattered light was collected by a Trivista triple spectrometer with a multichannel charge couple device detector (CCD). The sample was positioned on a XYZ piezo-stage, which allowed the scanning of the surface (and therefore the nanowire) with a precision of 10 nm. Prior to the measurements, the contacted nanowires were located by imaging the surface through the microscope objective with a CCD. A typical Raman spectrum of a doped GaAs nanowire is shown in Figure 3a. The peaks at 264 and 288 cm$^{-1}$ correspond to the transverse optical (TO) and longitudinal (LO) phonon modes of GaAs. At wavenumbers around 393 cm$^{-1}$, a peak with lower intensity is present. It corresponds to the local vibrational mode (LVM) of silicon in GaAs. In particular, this mode corresponds to the presence of silicon in arsenic sites.
substitutional silicon in arsenic sites. The presence of Si in Ga sites would be detected in 384 cm\(^{-1}\). This implies that silicon should act as a p type dopant. In this measurement configuration, the intensity of the TO mode is proportional to the volume probed. The intensity ratio between the LVM and the TO mode \(I_{LVM}/I_{TO}\) should be proportional to the concentration of silicon incorporated in the volume probed by the laser beam. We should note here that the penetration depth at the excitation wavelength is \(\sim 40\) nm, meaning that Raman strictly reports on the relatively external shell. We have plotted the evolution of the \(I_{LVM}/I_{TO}\) ratio along the same nanowire of Figure 3b. The silicon concentration decreases along the nanowire from top to bottom. The decrease in resistivity correlates with an increase in the silicon incorporation in the external shell. Now, the question that arises is whether the incorporation is limited to an external shell or also extended to the nanowire core. Such a question is directly related to the growth mechanisms and preferential dopant incorporation paths of the nanowires.

The physical mechanisms leading to the dopant incorporation in the nanowire may be a combination of two extreme cases, which are schematically represented in Figure 4. The first incorporation pathway is the nanowire facets. This is especially relevant in the case where the dopants are not soluble in the droplet and/or where radial growth is non-negligible. Indeed, even for a slight radial growth, the silicon atoms impinging on the nanowire facets can be gradually incorporated during the nanowire growth. If doping should be a consequence of the nanowire radial growth, one would expect a higher number of dopants at the nanowire base and it should decrease monotonically when approaching the nanowire tip. The second incorporation pathway is the Ga droplet at the nanowire tip. In this case, the amount of dopants incorporated in the nanowire should be proportional to the concentration in the droplet; via the distribution coefficient. The doping concentration in the nanowire should be nearly negligible at the nanowire base and then increase monotonically toward the nanowire tip until the droplet achieves the equilibrium concentration.

We start considering the possibility of dopant incorporation through the side facets. The incorporation of silicon through the facets could be the natural consequence of the nonzero radial growth of the nanowires. In the case of gallium-assisted MBE growth of nanowires, the radial growth rate is about a factor of 1000 smaller than the axial. For a 20 \(\mu\)m long nanowire, the radial shell exhibits a thickness varying from 50 to 0 nm from the base to the nanowire tip. By taking into account geometrical factors of the flux toward the nanowire facets, the concentration in the shell should be \(6 \times 10^{19}\) cm\(^{-3}\). Such doping concentration is consistent with the resistances measured.

For the second dopant incorporation pathway, through the Ga droplet, the Si–Ga phase diagram and liquid phase epitaxy (LPE) data must be taken into account. In an LPE process, growth precursors are incorporated through a liquid–solid interface. Gallium-assisted growth of GaAs nanowires corresponds to an LPE process at the nanoscale. For single donors and acceptors in GaAs, the impurity concentrations in the semiconductor and in the liquid phase are proportional. Carrier concentrations well above \(10^{19}\) cm\(^{-3}\) have been obtained. Following the phase diagram, the solubility of Si in Ga is about \(\sim 1\%\) at 630 °C. Two elements determine if the droplet can be a significant pathway of incorporation, with respect to the side facet deposition: i) the steady state concentration at the droplet, given the growth conditions of silicon flux and nanowire growth rate, and ii) the incubation time for this process. The incubation time would correspond to the time necessary for the liquid droplet to achieve the steady state concentration of silicon. In a simplified model, the steady state concentration in the nanowire can be calculated taking into account the conditions:\(^{59}\)

\[
\frac{dc_{\text{Si}}}{dt} = \Gamma_{g-l} - \Gamma_{l-s}(c_{\text{Si}(l)}) = 0
\]

where \(c_{\text{Si}}\) corresponds to the silicon concentration in the droplet and \(\Gamma_{g-l}\) and \(\Gamma_{l-s}\) are, respectively, the silicon flux from the gas phase to the droplet and from the droplet to the nanowire. The silicon concentration in the liquid gallium and in the GaAs nanowire are related via the distribution coefficient \(k\), in the form: 

\[
k = \frac{c_{\text{Si}(l)}}{c_{\text{Si}(s)}}
\]

The values are well known for the Si–Ga (l)/GaAs(s) system. The distribution coefficient of silicon in the GaAs solid/liquid system at 630 °C is 0.1 for silicon incorporated as an acceptor, and 0.06 as a donor. As a result of simultaneous incorporation of silicon as acceptor and donor, compensation will exist. At 630 °C, the incorporation of Si occurs preferentially in As sites (p-type doping) in a ratio 5:3, given by the different values of \(k\) for acceptors and donors.\(^{59}\)

For nanowires growing at 5.5 \(\mu\)m/h and under the silicon flow used in this study, \(c_{\text{Si}(l)}\) is equal to \(1.06 \times 10^{18}\) Si at. cm\(^{-3}\), and \(c_{\text{Si}(l)} = 0.015\%\) in the droplet. The incubation time...
will correspond to the time necessary for the droplet to achieve \( c_{\text{Si}} = 0.015\% \), about 3 min for the given conditions. As a consequence, already after 3 min of growth the silicon concentration in the droplet would be high enough to result in a non-negligible precipitation into the nanowire. Given the total growth time of 4 h, this is a nearly negligible nucleation time. The point here is that due to the high compensation, the effective doping should be of \( 2.6 \times 10^{17} \text{ cm}^{-3} \). One should note here that the calculated doping concentration in the core corresponds to an upper boundary and that it is 2 orders of magnitude lower, with respect to what is expected in the most external part of the nanowire. As a consequence, the doping throughout the shell dominates the total conductivity under these conditions. Additionally, one should also note that the predominance of shell vs core doping will also depend on the growth rate of the nanowire.

The steady increase of resistivity toward the tip of the nanowire is in good agreement with the hypothesis that dopants are mainly effective incorporated on the side facets. Also from the theoretical considerations, elevated effective doping incorporation through the gallium droplet seems extremely unlikely for nanowires grown at the growth rate of 5.5 \( \mu \text{m/h} \), for the given silicon flows. In order to find one more element of consistency, we have scaled the resistance of the nanowire with two different geometrical factors: (i) the total nanowire section and (ii) the shell thickness, which can be approximately determined from the diameter tapering along the nanowire axis. In Figure 5, the spatial dependence of the resistivity of a typical nanowire is plotted. On the same graph, we plot the resistivity scaled assuming the two extreme models. The resistivity is calculated by taking the whole the section of the shell and of the entire nanowire. By assuming that silicon is mainly incorporated in the shell, one obtains a quasi-constant resistivity along the nanowire. The same trend was obtained from all the nanowires measured. In conclusion, for relatively high growth rates, the model of doping through the facets is predominant.

For the sake of completeness, it is important to consider the possibility of doping through the gallium seed in more detail. For this, we have grown nanowires under the same conditions but with a reduced nanowire growth rate. For example, for growth rates of 1 \( \mu \text{m/h} \), the \( c_{\text{Si}} \) would be 0.083 \%, leading to a silicon and effective doping concentration to the nanowire respectively of \( 5.8 \times 10^{18} \) and \( 1.46 \times 10^{18} \text{ cm}^{-3} \). This effective doping concentration is just about 1 order of magnitude below the doping concentration expected in the shell, meaning that it will have a stronger influence in the spatial dependence of the conductivity. Such nanowires should exhibit a different surface doping and resistivity dependence along the nanowire, as dopant incorporation through the droplet should be higher.

We have grown nanowires under identical conditions for a growth time of 8 h, and lowering the nanowire growth rate by a factor of 5.5. The lower growth rate is obtained by lowering the \( \text{As}_{4} \) pressure by the same factor.44 We should note here that lowering the axial growth rate by a factor 5.5 does not result in a lowering of the radial growth rate.44 Results on the Raman and resistivity mappings are presented in Figure 6. Within the error bars, we observe that the resistivity along the whole nanowire length is much more homogeneous than in the case of the nanowires grown at 5.5 \( \mu \text{m/h} \). Additionally, the silicon concentration at the nanowire shell as measured by Raman spectroscopy shows a diminution of a factor 3 from the base to the nanowire tip. As Raman spectroscopy of GaAs at 488 nm is only sensitive to the first 40 nm, the Raman measurements indicate the gradient in the thickness of the doped shell along the nanowire and not on the nanowire bulk concentration. In this sense, the Raman spectroscopy measurements are consistent with the existence of shell doping (through epitaxial growth on the facets). However, the spatial dependence of the resistivity is contradictory with a model that...
only considers incorporation of dopants through the nanowire facets. Indeed, if the resistivity is approximately constant along the nanowire, the only solution is that dopants are also getting incorporated in the nanowire core in the part closer to the tip. More detailed studies of the conductivity and silicon concentration as a function of growth conditions are necessary for obtaining more details in the doping mechanisms and are currently in progress. In particular, one should find a method to measure the material grown in the last stages (e.g., for the first type of nanowires 1 h of growth corresponds to 5.5 μm, while for the second this is just 1 which is not possible to measure either electrical contacting or by Raman spectroscopy). Moreover, the microstructure of the nanowire should be taken into consideration to account for the small spatial variation of the resistivity. Such studies are in progress and will be the subject of future publications.

Finally, we would like to point out the importance of the concept of distribution coefficient in the case of gallium-assisted growth of GaAs nanowires. Indeed, the different temperature dependence of k for p and n type incorporation of silicon could potentially be used in the future for controllably fabricating doped junctions in nanowires with one single type of dopant. In particular, k is higher for n type than for p type at high temperatures like 750 °C and smaller at temperatures lower than 650 °C. This means that one could potentially obtain an axial p-n and/or a gradient junction by just changing the operating temperature during the growth.\(^\text{1b,61}\)

In conclusion, we have analyzed the dopant and resistivity distribution of nanowires for the understanding of the doping mechanisms of catalyst-free MBE grown GaAs nanowires. Two complementary experimental approaches have been used: resistivity mapping and Raman spectroscopy for the measurement of silicon incorporation. Two competing doping mechanisms have been outlined: incorporation from the side facets and from the gallium droplet. Additionally, doping compensation seems to play a major role in the incorporation of silicon through the liquid phase. Doping concentrations of at least 2.4 × 10\(^{18}\) cm\(^{-3}\) have been obtained. Finally, one should note that the possibility of extremely high doping in GaAs nanowires opens the avenue for using these nanowires in low temperature mesoscopic physics experiments and modern nanoscale devices.

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**Supporting Information Available.** Additional HRTEM figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) To ensure that the silicon flux did not have any perturbation in the nucleation of the nanowires, the silicon shutter was opened 15 min after the start of the deposition process, which effectively corresponds to 10 minutes of growth, as the incubation time is approximately 5 min.


(48) In this equation we neglect the incorporation of silicon by diffusion through the nanowire walls and the desorption of silicon from the droplet, silicon has an extremely low pressure in these conditions.
