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New insights into doping behavior of catalyst-free (In,Ga)As-based nanowires

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Abstract

This work provides a comprehensive study of the n-type doping characteristics of MBE-grown Si-doped InAs and GaAs nanowires on their electronic, structural and optical properties. Based on a wide set of nanoscale characterization techniques we elucidate direct correlations between chemically and electrically active dopant densities, their physical incorporation limits, as well as their role as surfactants enhancing growth. The study also gives insights into band gap tuning, and radiative recombination characteristics by active n-type doping.

1. Introduction

Freestanding (In,Ga)As-based nanowires (NWs) are attracting increasing attention due to recent advances in their integration on silicon (Si) and first demonstrations of proto-type devices for next–generation photovoltaics, integrated photonics, tunneling diode devices and high–performance vertical gate all-round III–V/Si NW transistors [1]. To tune NW-device performance it is essential to control the free carrier concentration, carrier diffusion lengths, lifetime, etc. by intentional doping. Thereby, doping is also expected to modify several electronic and optical properties, including band gap and band edges, carrier localization and non-radiative recombination mechanisms. While doping behavior is well established in planar III-V compound semiconductors, the unique 3D-geometry of NWs, their peculiar growth mechanisms, and presence of polytype crystal phases, give rise to doping characteristics that can be behave very differently from planar counterparts.

Here, we report recent understanding in the doping behavior of n-type (Si-doped) InAs and GaAs NWs grown in a completely catalyst-free (i.e., droplet-free) vapor-solid growth mode. In particular, our studies give insights into direct correlations between dopant incorporation distribution and their electrically activity, the effects of dopants on growth dynamics, and their influence on band gap, carrier localization, and recombination dynamics.

2. Experimental Details and Results

To investigate growth of catalyst-free, n-type doped (In,Ga)-based NWs, we employ a site-selective growth technology on Si substrate using molecular beam epitaxy (MBE). Hereby, we use Si (111) substrates covered with thin SiO_2 dielectric masks which are prepatterned by electron beam or nanoimprint lithography (EBL, NIL) to create periodic mask opening for subsequent selective area growth (SAG) of vertical, high-uniformity III-V NW arrays in MBE [1-3]. Si dopants are provided by a solid dopant cell (via thermal sublimation) with atomic Si dopant fluxes on the order of ~10^{11} -10^{12} $cm^{-2}s^{-1}$ [4,5].

In a first set of experiments, we elucidate the dopant behavior on growth dynamics, electrically active dopant concentrations, and corresponding optical properties of Si-doped InAs NWs. By varying the Si dopant flux under otherwise fixed growth parameters (In/As flux ratio, growth temperature), we find that neither morphology nor aspect ratio change upon Si doping, in the investigated range of Si dopant concentrations (~10^{17} – 5×10^{18} cm^{-3}). The Si-doped InAs NWs crystallize in a prominent wurtzite (WZ) phase

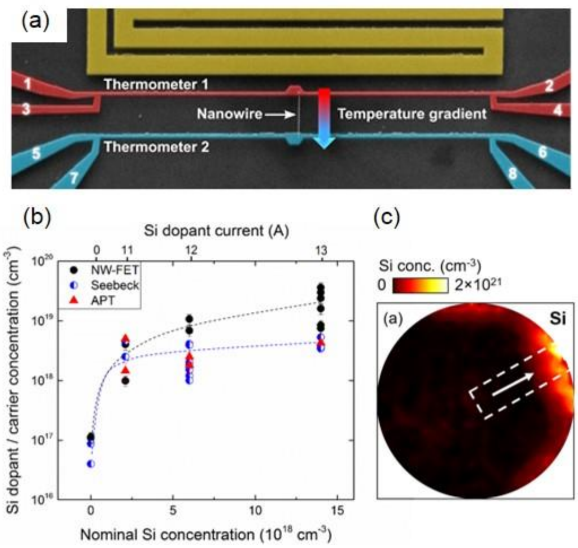

Figure 1. (a) SEM image of typical NW device for Seebeck effect measurement using lithographically defined heater and thermometers at both NW ends; (b) Comparison of bulk Si dopant concentration (APT data) and n-type carrier concentration (Seebeck and NW-FET data) as a function of nominal Si concentration; (c) APT reconstruction of a Si-doped InAs NW shown as projected 2D composition map, illustrating Si segregation at the NW sidewall surface [4].

with a high density of stacking defects, irrespective of the Si dopant concentration [4]. To directly compare the chemical and electrically active dopant concentrations in the Si-doped InAs NWs we performed correlated experiments using atom probe tomography (APT), Seebeck effect and NW-field effect transistor (NW-FET) measurements on individual NWs. Hereby, we find a characteristic saturation of the free carrier concentration in the mid-10^{18} cm^{-3} range which coincides perfectly with the actual Si dopant concentrations in the bulk part of the NW [4], see Fig. 1. This behavior suggests the absence of compensation effects in Si-doped InAs NWs. Importantly, however, we recognize excess Si dopants with very high concentrations ($>10^{20}$ cm^{-3}) segregating at the NW sidewall surfaces which confirms recent first-principles calculations and which results in modifications of the surface electronic properties as seen by NW-FET measurements [4].

The n-type carrier concentrations of the InAs NWs is further confirmed by photoluminescence (PL) spectroscopy, as extracted from Fermi-tail fits of the high-energy spectral region [5]. Here, we also find that with increasing carrier concentration the PL spectra exhibit a distinct blue shift (up to ~50 meV), ~2-3-fold peak broadening and red-shift of the low-energy tail, indicating both Burstein-Moss shift and band gap narrowing. The low-temperature bandgap energy (E_G) decreases from ~0.44 eV (n~10^{17} cm^{-3}) to ~0.41 eV (n~10^{18} cm^{-3}) following a $\Delta E_G \sim n^{1/3}$ dependence (see Fig. 2). Simultaneously, the PL emission is quenched nearly 10-fold, while pump-power dependent analysis of the integrated PL intensity evidences a typical *2/3*-power-law scaling indicative of non-radiative Auger recombination at high carrier concentration.

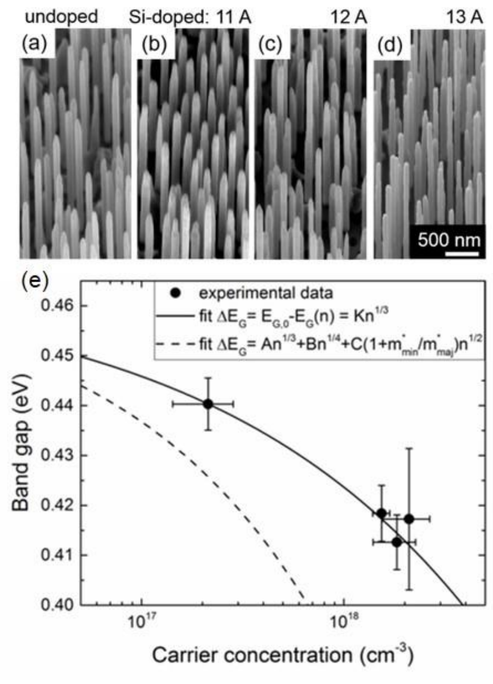

Figure 2. SEM images of undoped (a) and Si-doped (b-d) InAs NWs; (e) Band-gap as a function of *n*-type carrier concentration; best fit to the data gives the simple $\Delta E_G = Kn^{1/3}$ law [5].

Carrier localization and activation at stacking defects are further observed in undoped InAs NWs by temperature-dependent PL, but are absent in Si-doped InAs NWs due to the increased Fermi energy [5,6]. In particular, in undoped InAs NWs we recognize that carrier localization is very strong and governed by polytype crystal phase intermixing, i.e., wurtzite(WZ)/zincblende (ZB) stacking sequences. The optical transition energies are modelled for a wide range of WZ/ZB stackings using a Kronig-Penney effective mass approximation, where comparison with experimental results suggests that polarization sheet charges on the order of ~0.0016 –0.08 C/m along the WZ/ZB interfaces need to be considered to best describe the data [6].

The Si-doping studies are further extended to catalyst-free GaAs NWs grown in a vapor-solid growth mode. This is of particular interest, since all previous studies of vapor-liquid-solid (VLS) grown Si-doped GaAs NWs reported p-type conductivity due to the amphoteric nature of Si, whereas the conductivity of Si-doped *non*-VLS type GaAs NWs is expected to be n-type, although not yet proven. Using specific high-temperature surface treatments to the Si (111) substrate, we generate 1×1-As terminated surface reconstruction, and thereby allow for good vertical growth of [111]B-oriented GaAs NWs. Most interestingly, we find that the vertical NW growth yield of non-VLS GaAs NWs increases dramatically (> 98%) upon adding Si dopants [7]. The Si-doped GaAs NWs exhibit a high density of twinned ZB segments, indicating a twinning-induced growth mechanism leading to enhanced axial NW growth. We further present ongoing experiments using Raman spectroscopy and NW-FET characterization to verify the expected n-type conductivity of these types of NWs.

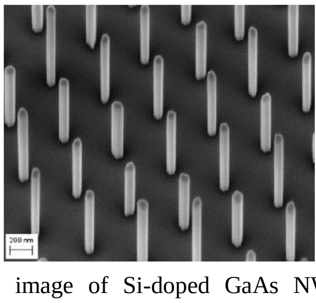

Figure 3. SEM image of Si-doped GaAs NWs grown by a non-VLS mechanism on Si(111) with high growth yield [7].

Acknowledgements

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References

[1] G. Koblmüller and G. Abstreiter, Phys. Stat. Sol.–Rapid Res. Lett. (Topical Review) **8** (2014), 11.
[2] D. Rudolph, et al., Appl. Phys. Lett. **105** (2014), 033111.
[3] J. Treu, et al., Appl. Phys. Lett. **108** (2016), 053110.
[4] J. Becker, et al., ACS Nano **12** (2018), 1603.
[5] M. Sonner, et al., Appl. Phys. Lett. **112** (2018), 091904.
[6] J. Becker, et al., Phys. Rev. B **97** (2018), 115306.
[7] D. Ruhstorfer, et al., in preparation (2018).