Au-free Epitaxial Growth of $InAs_{1-x}P_x$ Nanowires

B. Mandl, J. Stangl, M. Brehm, T. Fromherz, G. Bauer

Institute for Semiconductor and Solid State Physics, University of Linz, A-4040 Linz

T. Mårtensson, L. Samuelson, W. Seifert

Department for Solid State Physics, S-221 00 Lund University, Sweden

InAs and $InAs_{1-x}P_x$ nanowires have been grown by the use of a metal-organic vapor phase epitaxy. The nanowire growth is initiated by a thin SiO_x layer deposited on the substrate prior to growth. The wires exhibit a non-tapered shape with a hexagonal cross section. Further the growth of InAs on Si is demonstrated as well as the growth on a pre-patterned InP (111)B substrate.

Introduction

Semiconductor nanowires as one-dimensional structures and building blocks for nano-devices have received increased attention in recent years. Controlling the one-dimensional growth on a nanometer scale offers unique opportunities for combining materials, manipulating properties, and designing novel devices. We present a general method to produce epitaxial nanowires of InAs, without using Au-particles as catalyst. It has been shown that InAs nanowires can easily be contacted and gated. With inbuilt barriers (e.g. InP), the functionality of such structures in single electron transistors [1] and resonant tunneling devices [2] has been demonstrated.

Moreover, InAs has a high potential to be used complementary in combination with Si for high-mobility applications. For this purpose, however, nanowires grown Au-assisted impose severe restrictions due to the introduction of deep-level defects into Si. We show in this report that InAs nanowires can be obtained epitaxially on various substrates without any metal catalyst when one covers the substrates by a thin layer of SiO_x ($x \approx 1$) prior to InAs growth. X-ray diffraction measurements indicate that the wires form in part in the wurtzite modification and grow spontaneously in c-direction [000.1], equivalent to the cubic [111] direction.

Experimental

For wire-growth we used low pressure metal organic vapor phase epitaxy (LP-MOVPE) at a pressure of 10 kPa, with trimethylindium (TMI), arsine (AsH_3), and phosphine (PH_3) as precursor materials, transported in a flow of 6000 ml/min of H_2 as carrier gas. For the precursors typical molar fractions of 2×10^{-6} for TMI and 2×10^{-4} for AsH_3 were used. For TMI also higher molar fractions were tested, but had no significant effect on the growth rate. The molar fractions for PH_3 were varied between 3.5 and 15×10^{-3}. As substrates we used epitaxy-ready III/V wafers and Si wafers. In case of Si substrates, the native oxide was removed by an HF dip. Before loading the substrates into the growth chamber, a thin SiO_x layer was sublimated onto the surface. The substrates were then heated to the growth temperature between 520 °C and 680 °C in H_2 atmosphere. As soon as growth temperature was reached, the precursors were switched on simultane-

ously. The growth was stopped by switching off the TMI source, and the samples were cooled under AsH_3 flow, or for $InAs_{1-x}P_x$ deposition, under additional PH_3 flow. To characterize the wires we employed scanning electron microscopy (SEM) and x-ray diffraction (XRD). SEM investigations were performed using a JEOL 6400 and a LEO 150 microscope. From SEM we obtain the length, orientation, shape, and density of the wires.

XRD experiments have been performed at beamline 10B (Troïka II) at the ESRF in Grenoble, to get information on the orientation of the wires relative to the used substrate and relative to each other, about the lattice constant and the crystalline structure of the wires. SEM images of InAs wires grown at different temperatures on InP (111)B surfaces, covered by 1.3 nm SiO_x prior to growth, are presented in Fig. 1. We observe the following trends:

(i) The wires grow spontaneously on the InP(111)-surface and appear epitaxially oriented, i.e., they are standing vertically on the surface and grow in continuation of the substrate [111]B orientation. Remarkably, the wires are homogeneously thick, i.e., in contrast to typical MOVPE wire growth [3], [4], we cannot determine any measurable tapering and also no thickening at the wire foot/substrate connection.

(ii) In general, the growth temperatures are much higher than for Au-assisted growth of InAs nanowires in MOVPE, where growth suddenly ceases when the temperature exceeds 500 °C. The wire length is not a linear function of time: in parallel investigations, not presented here, we have seen that the length growth rate starts with a high value and decreases then over time according a power law $R \sim t^n$ ($n \approx -0.5$). This fact can be seen as a hint on the growth mechanism.

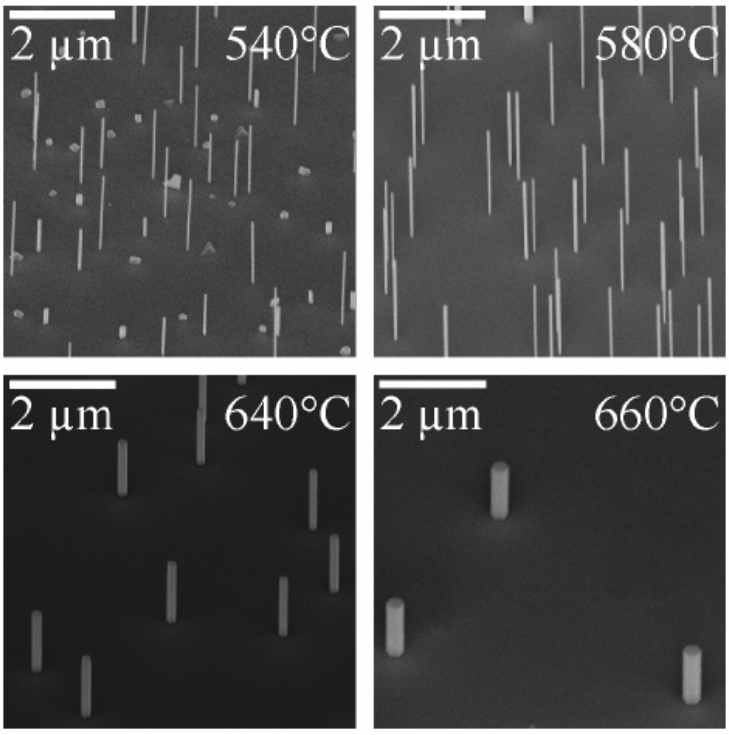

Fig. 1: SEM images (45° tilt) of InAs wires grown on InP (111)B at different temperatures, growth time was 60 s [5].

(iii) The wire density is also a function of growth temperature. In general, the density decreases with increasing temperature. This indicates that there are relations to

the general laws which govern the nucleation kinetics of clusters on surfaces, where the density ρ of critical nuclei follows the general proportionality ρ ~ R/D(T), with R the deposition rate and D(T) the temperature-dependent coefficient of surface diffusion. This result indicates that clusters may be involved in pre-stages of wire growth. At higher temperatures these clusters grow anisotropically and form one-dimensional wires. At lower temperature only a part of the clusters adopts this growth mechanism, others grow by isotropic expansion instead. In fact, we find that at low temperatures the wires compete with InAs-clusters on the surface (see the 540 °C sample in Fig. 1).

(iv) In parallel to the decreasing density, the aspect ratio length/width of the wires decreases with increasing temperature: At higher temperatures the radial growth on the side facets gets more and more important. At the highest growth temperature of 680 °C, the aspect ratio dropped down to below 1 and we obtained epitaxially grown hexagonal platelets.

(v) The morphology of the nanowires is rod-shaped with a regular hexagonal cross-section. The top of the wires is flat, visible at least in case of the thicker wires grown at higher temperatures. From x-ray diffraction experiments performed at ID01 at the ESRF Grenoble it follows that the structure of the wires is in part wurtzite, which is the thermodynamically metastable modification of InAs.

By using different materials as substrate, the influence of the lattice mismatch on the wire growth was investigated. For this study different epiready III-V (111)B substrates (InAs, InP, GaAs, and GaP) as well as Si (001) substrate are used. With these substrates, a range of lattice mismatches up to 12% (InAs/Si) is covered, with all substrates, epitaxial wire growth along [111]B could be demonstrated, indicating that the lattice mismatch poses no restriction for the wire growth.

Position controlled nucleation of InAs nanowire is demonstrated when using a pre-patterned InP (111)B substrate. The pattern is defined by electron beam lithography, SiO_x and a subsequent e-beam resist lift-off. For structured substrates, a slightly different growth sequence was used, in that the precursors are activated at 500 °C during the heating of the samples to 580 °C, wires are growing on the positions defined by the SiO_x patches. Such a patterned nucleation can be seen in Fig. 2(a). It has to be mentioned that the wires are nucleated by patches remaining on the substrate surface, in difference to processes where openings in a SiO_2 layer are used to control the growth position of III-V nanowires [7].

Another result of this study is the successful growth of InAs nanowires on Si (001) and Si (111), nucleated using a 1.3 nm thick SiO_x layer instead of Au as nucleation centers [8]. Before the deposition of the SiO_x layer, the native oxide is removed by a HF etch. The wires grow in the four incline [111] directions on the Si (001) substrate. For the growth on such substrates, the exposure of the substrate to Oxygen prior to the growth is critical. Such a growth mechanism opens the possibility to use InAs as high mobility semiconductor on Si, without making use of Au particles that are detrimental for the performance of Si based electronics.

Further, the growth of $InAs_{1-x}P_{x,}$ as a III-V alloy is demonstrated. The growth is done similar to InAs, on a InP (111)B substrate with a 1.3 nm thick SiO_x layer. As precursor material Phosphine is used in addition to TMI and Arsine. The growth results in wires very similar to those of InAs, with a constant diameter, showing no tapering and no thickening at the wire foot/substrate interface and show a hexagonal cross-section, again the wires grow in the <111>B direction, continuing the substrate orientation. The wires are shown in Fig. 2(a). In photoluminescence and XRD measurements a change of the energy gap and the lattice constant as a function of the Phosphine flux is found, demonstrating a significant phosphorus incorporation into the wires [9]. The maximum concentration of P in the wires so far achieved is estimated to be x = 0.17.

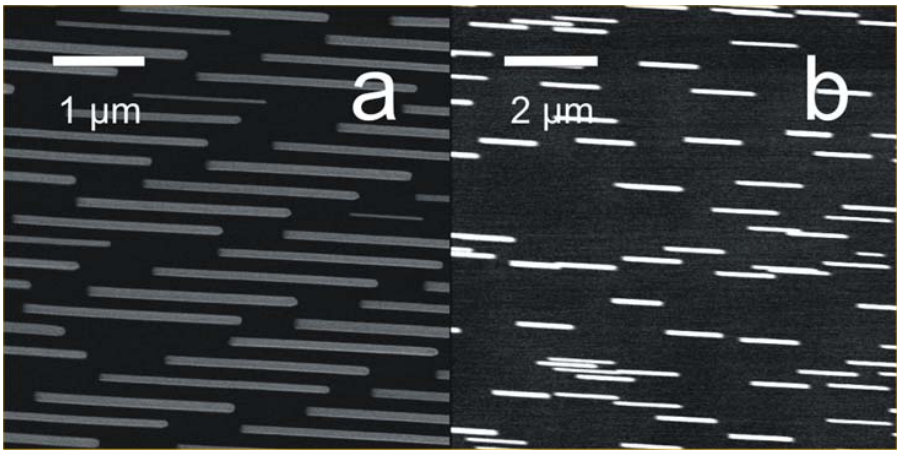

Fig. 2: 45° tilt SEM images of a) InAs nanowires grown using a pre-patterned SiO_x layer on an InP (111)B substrate. b) SEM image of $InAs_{1-x}P_x$ nanowires (45° tilt) grown at InP (111)B at 620 °C for 60 s [9].

Conclusion

We demonstrate a novel mechanism for the growth of InAs and $InAs_{1-x}P_x$ nanowires which relies on a SiO_x layer deposited at the substrate surface. This growth mechanism shows epitaxial grown wires with homogeneous shape. The wire growth rate is depending on the growth temperature and growth time. Also, the density of the wire nucleation is depending on the growth temperature indicating a growth initialized by clusters formed on the substrate prior to wire formation. In addition the wire length to width ratio is found to be temperature dependent. From XRD measurements the existence of a wurtzite phase together with the zinkblende phase is found for the wire crystal structure. Additional to the growth on InP, various III-V and even Si substrates were used, showing no influence of strain on the wire growth. The demonstrated growth of InAs wires on Si substrates in the absence of metal catalysts opens a promising route for integrating III-V high mobility devices with standard Si based electronics. In addition, the growth of wires on a pre-patterned substrate is demonstrated with a high yield for the wire nucleation on pre defined positions. Also, the growth of $InAs_{1-x}P_x$ wires is demonstrated, opening the possibility to grow additional III-V materials and heterostructures by this method.

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