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InP Nanowires and nanotubes for bottom-up nanoelectronics

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1. Introduction

One-dimensional structures, such as semiconducting nanowires are attractive building blocks for bottom-up nanoelectronics [1]. The electronic structure of nanowires is determined by the chemical composition and the diameter and additionally these wires can be n-type or p-type doped [2]. The size confinement for nanowires with a homogeneous composition, which still have macroscopic dimensions in one direction, is clearly less than for quantum dots. The confinement effect in one-dimensional structures can be enhanced by the formation of tubes instead of wires. In this paper the synthesis of crystalline InP nanowires and nanotubes is reported. The temperature during growth establishes the shape of the resulting nanostructures and can be used to tune the electronic properties. The optical properties of the nanowires and nanotubes are discussed. In addition, we demonstrate the principle of epitaxial growth of III-V nanowires on a group IV substrate. For this study, InP nanowires were grown on Ge(111), which relates to the preferential growth direction for these nanowires, and on Ge(100) substrates, which corresponds to the standard orientation for silicon technology. Although the InP/Ge crystal lattice mismatch is large (3.7 %), the as-grown wires are monocrystalline and virtually free of dislocations. In addition, we show that a low-resistance electrical contact can be obtained between the wires and the substrate.

2. Results

For VLS nanowire growth [3], the substrates were provided with the equivalent of a 2 Å gold film by thermal evaporation. Upon heating, the gold film breaks up into small particles from which the nanostructures grow. A top-view scanning electron microscopy (SEM) image of a Ge(111) substrate with as-grown InP wires is shown in Fig. 1a. The wires have a uniform diameter and a length of ~1μm. There are three clearly noticeable orientations with in-plane components parallel to the sides of an equilateral triangle. Some wires are oriented perpendicular to the surface, and in this top view they appear just as small bright spots. The observed preferential orientations correspond to the four ⟨111⟩ directions typical for a (111) oriented crystal. The fact that nanowires have well-defined orientations consistent with the substrate's crystal symmetry is a clear indication of epitaxial growth. To substantiate this claim further we have performed X-ray diffraction (XRD). The crystallographic relation between the Ge substrate and
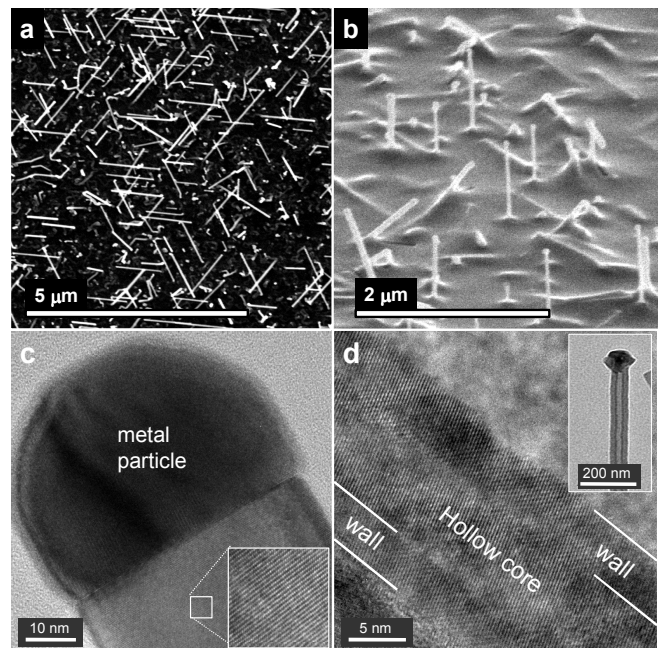
Fig. 1. Electron microscope images of InP nanostructures **a** SEM topview image of InP wires grown on Ge(111), showing that the wires are aligned according to the crystal symmetry of the substrate. **b** SEM sideview image after spin-coating of a PMMA layer.**c** TEM image of an InP wire with the gold particle at the top. The inset is a high-resolution TEM of the wire. **d** HRTEM image from a InP nanotube grown at 520°C by the use of an InP target doped with 0.1 mol% Zn (inset) overview TEM image of an InP nanotube

(a large number of) InP nanowires was studied by XRD pole figure measurements. Pole figures were measured for the (111) and (220) reflections of the substrate and the wires and illustrate that InP wires were grown epitaxially on Ge(111) and Ge(100) [4]. Electrical transport measurements through individual wires [5] were performed in an atomic-force microscopy (AFM) set-up. A platinum-coated AFM tip was scanned in contact mode over the surface, while a tunable dc voltage was simultaneously applied between the tip and the back of the Ge substrate. A non-zero current through the substrate was measured when an electrical contact was established between the tip and the catalytic metal particle at the top of a nanowire. Current-voltage characteristics of tens of individual wires were measured, yielding resistance values down to a few kΩ, which
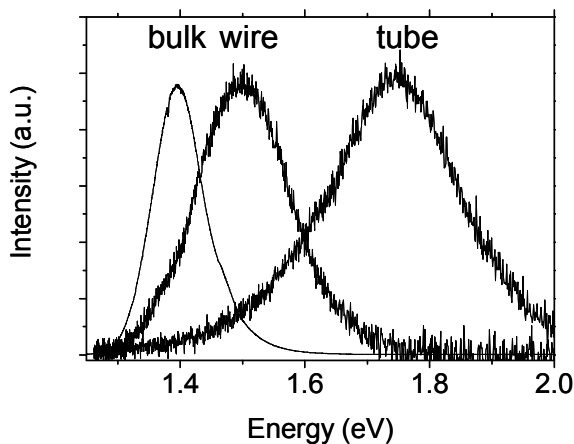
Fig. 2 Photoluminescence spectra of a bulk InP crystal, an InP nanowire, and an InP nanotube demonstrating the enhanced size quantization effect for the tube compared to the wire.

corresponds to a very low InP/Ge contact resistivity of less than $\sim 10^{-8}$ Ωcm^2. When, during synthesis, the substrate temperature was in the range 425-500°C and an undoped InP (6N) target was used, single-crystalline InP nanowires were formed. The growth direction and the crystal structure were determined from high-resolution TEM (fig. 1c). The long axis of the wires was perpendicular to the (111) lattice plane and each wire was terminated by a particle containing Au and an amount (typically 40%, determined by EDX) of InP, indicating that the wires grow via the VLS mechanism [3]. The diameter of the nanowires is initially determined by the thickness of the Au film. However, the substrate temperature during growth affects the resulting diameter as well. When higher temperatures (>500°C) were applied InP nanotubes were formed [6]. A closer examination by TEM, presented in figure 1d, showed that hollow tubes were formed. Judging from the contrast from both bright field TEM and HAADF (high-angle annular dark field) imaging it was clear that there was no material present in the core of the tubes. The tubes were terminated by a particle, (inset fig. 1d) which contained gold; this indicates that the tubes grow from the liquid InP-Au phase via the VLS mechanism. The diameter of the tubes was uniform along their length. Upon tilting the sample with respect to the electron beam, diffraction fringes were seen to move over the entire width of the tubes, implying a cilindrical shape of the crystals. The observation that the diffraction contrast is most pronounced in the walls again confirms the hollow nature of the tubes. The thickness of the wall of the nanotube shown in the HRTEM image in figure 1d was approximately 4 nm.

Photoluminescence measurements were performed on individual nanostructures. Effective-mass-approximation calculations predict that the size quantization effect for a solid one-dimensional structure is determined by the diameter, whereas the size quantization for a hollow tube is determined by the wall thickness. In figure 2 the emission

spectra of a bulk InP crystal, an InP nanowire (d~15 nm), and an InP nanotube (d~30nm, wall thickness~4nm) are plotted. The emission intensity is normalized for easy comparison. Other emission bands at lower energies were not observed, demonstrating that defect states, for instance at the surface of the structures, do not dominate the optical properties. The maximum of the measured emission of bulk InP is at a slightly higher energy than the bandgap energy of InP reported in the literature. Probably, this is caused by the limited sensitivity of the spectrophotometer at wavelengths > 900 nm. The emission maximum of the wire has blue-shifted by ~100 meV, whereas the tube emission has blue-shifted by ~400 meV. This enhanced blue-shift clearly demonstrates the strong size quantization effect for the tube. The width of the emission band has increased for the nanostructures with respect to that of the bulk InP crystal. This might be due to fluctuations in the diameter or the wall thickness, for the wire and the tube, respectively.

3. Conclusions

In summary, we have synthesised crystalline InP nanowires and nanotubes by using the VLS growth mechanism. These tubes give the opportunity to tune the opto-electronic properties of these one-dimensional structures in an even wider range. Additionally, the epitaxial growth of InP wires on germanium substrates in combination with the current progress in growing strain-relaxed germanium layers on silicon wafers [7] implies that III-V semiconductor nanowires can be combined structurally and electrically with silicon technology. This represents a first step towards the final goal of bringing new materials and hence new device architectures into silicon-based integrated circuits The VLS growth of ternary compound semiconductor nanowires [8] may be a way to engineer the lattice parameter and overcome possible limitations coming from an exceedingly high lattice mismatch. Based on the results of this work, and the versatility of the VLS method, we believe that the growth of III-V semiconductor wires directly on silicon is now a step closer.

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