AIP | Applied Physics Letters

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Citation: Applied Physics Letters **89**, 063119 (2006); doi: 10.1063/1.2336599
View online: http://dx.doi.org/10.1063/1.2336599
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/89/6?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **89**, 063119 (2006)

Catalyst-free growth of In(As)P nanowires on silicon

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(Received 30 May 2006; accepted 26 June 2006; published online 10 August 2006)

The catalyst-free metal organic vapor phase epitaxial growth of In(As)P nanowires on silicon substrates is investigated using *in situ* deposited In droplets as seeds for nanowire growth. The thin substrate native oxide is found to play a crucial role in the nanowire formation. The structure of the nanowires is characterized by photoluminescence and electron microscopy measurements. The crystal structure of the InP nanowires is wurtzite with its *c* axis perpendicular to the nanowire axis. Adding arsenic precursor to the gas phase during growth results in a bimodal photoluminescence spectrum exhibiting peak at the InAsP and InP band gap energies. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2336599]

The fabrication of one-dimensional nanostructures, or nanowires, has been under intense investigation due to their lucrative device applications.[1] One way of fabricating nanowires is by the vapor-liquid-solid (VLS) method[2] using metal organic vapor phase epitaxy (MOVPE).[3] Typically, the fabrication of III-V semiconductor nanowires by the VLS method has required the deposition of metal catalysts on the substrate either by evaporation, or from colloidal solutions or aerosols before actual growth. Very recently, Novotny and Yu[4] demonstrated the catalyst-free growth of InP nanowires on InP(111) substrates by changing the substrate surface reconstruction by annealing to support vertical nanowire growth at low temperatures. This catalyst-free method offers a possibility for totally self-assembled one-dimensional nanostructure fabrication without any preprocessing.

In this letter we have investigated the catalyst-free (or self-catalyzed) growth of In(As)P nanowires on Si(111) substrates using *in situ* deposited In metal droplets as seeds for nanowire growth in MOVPE. Growth of optically active III–V materials on silicon is important for applications combining optoelectronics and standard silicon electronics in small scale devices. Previously, III–V semiconductor nanowire growth on silicon has been demonstrated using gold nanoparticle catalysts.[5] However, gold nanoparticle mediated growth produces unwanted effects in silicon, such as introduction of deep levels[6] and gold migration on the semiconductor surface.[7] Since here gold is not required, contamination is avoided.

The nanowire samples were fabricated in a horizontal atmospheric pressure MOVPE reactor using trimethylindium (TMI), tertiarybutylphosphine (TBP), and tertiarybutylarsine (TBA) precursors for indium, phosphorus, and arsenic, respectively. For In droplet fabrication TMI was introduced to the reactor at 5 μmol/min for 15 s at 350 °C. However, at the extremely low temperature used here only a fraction of the metal organic precursors decompose. Nanowire growth was started by introducing TBP in the reactor immediately after droplet deposition. Nanowires were grown at 350 °C for 105 s. The reported temperatures are thermocouple readings and a few tens of degrees higher than the real substrate surface temperature. The samples were characterized using scanning electron microscope (SEM), transmission electron microscope (TEM), and room-temperature photoluminescence (PL) measurements.

In droplets deposited *in situ* by MOVPE on a Si(111) substrate are shown in the SEM image of Fig. 1(a). A top view is shown in Fig. 2(a). The droplets are semispherical in shape, having an average diameter of about 80 nm and an areal density of 1.4×10^8 cm^{-2}. Based on measurements on the image, the contact angle of all semispherical droplets with the substrate surface is about 125°. InP nanowires at the edge of a Si(111) substrate grown using the In droplets as

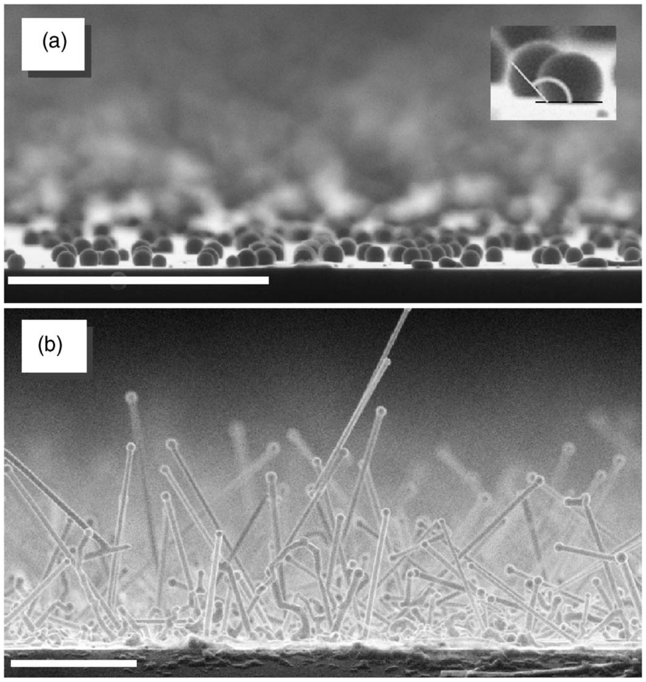

FIG. 1. SEM image of (a) In droplets and (b) InP nanowires at the edge of a Si(111) substrate. The inset shows a close-up image of a droplet and the contact angle. The scale bars correspond to 1 μm.

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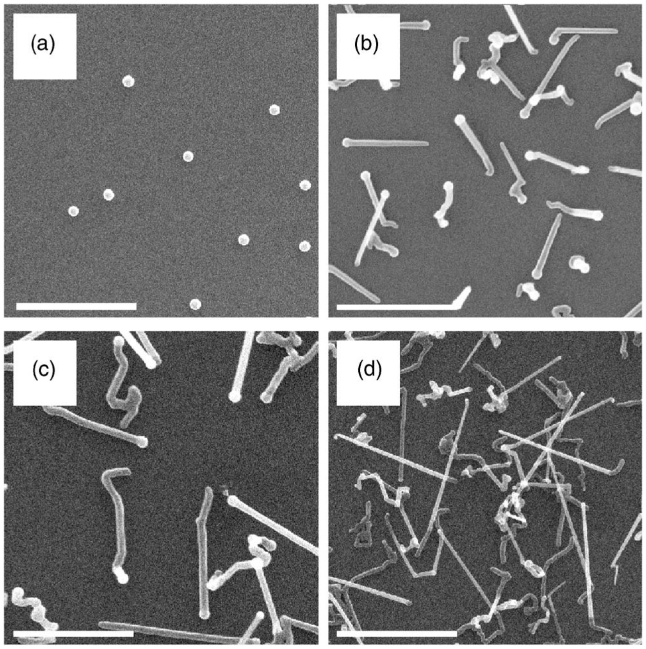

FIG. 2. SEM image of (a) a Si(111) surface with *in situ* deposited In droplets, (b) InP nanowires grown on Si(111) with a V/III ratio of 100, (c) V/III ratio of 200, and (d) V/III ratio of 300. The scale bar corresponds to 1 μm.

seeds are shown in the SEM image of Fig. 1(b). A top view of the same sample is shown in Fig. 2(c). Clearly, growth has resulted in nanowires pointing off the plane of the substrate. In addition to linear nanowires 1–2 μm in length, there are a number of curved and much shorter nanowires on the substrate. Curiously, no completely vertical nanowires can be observed. The average nanowire diameter in the figure is about 55 nm, and the average diameter of the droplet at the tip is about 90 nm.

Figures 2(b)–2(d) show top-view SEM images of samples with InP nanowires seeded by *in situ* deposited In droplets. The nominal V/III molar ratios used are 100, 200, and 300, respectively. It is clear that the tapering of the nanowire can be controlled with the V/III ratio. A small ratio produces reverse tapered nanowires, where the diameter is larger at the tip than at the base. Increasing the ratio reverses the behavior. In between there is an optimal ratio (here about 200) where nanowire tapering is negligible. All this is identical to catalyst-free growth of homoepitaxial InP nanowires reported by Novotny and Yu.[4] Also, the areal density and average base diameter of the straight nanowires seem to be a function of the V/III ratio. This suggests that there are more dynamics to the droplet formation than can be deduced from the image of the cooled-down droplet sample in Figs. 1(a) and 2(a). Introducing phosphorus after droplet deposition can and probably will affect the size and distribution of the droplets.

Further insight about the crystal structure of the nanowires was acquired by transmission electron microscopy. A TEM image of a single linear InP nanowire is shown in Fig. 3(a). In this particular case there are no signs of stacking faults. Figure 3(b) shows a high-resolution TEM image at the edge of the same nanowire. The inset shows a TEM diffraction image taken perpendicularly to the nanowire axis. Indexing the diffraction pattern reveals that the crystal structure of the nanowires is wurtzite and that the nanowire axis is perpendicular to the *c* axis of the lattice. This is common for GaN nanowires,[8] but has not been reported before for InP nanowires.

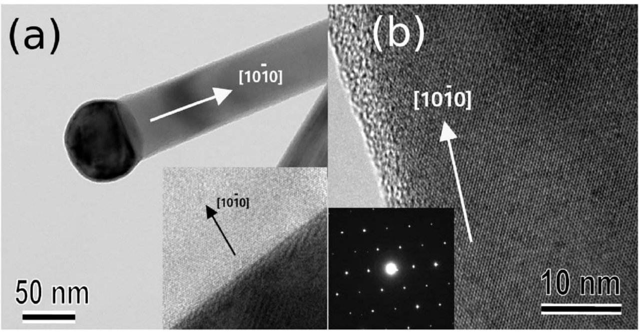

FIG. 3. (a) TEM image of a linear InP nanowire. The inset shows a close-up of the droplet-nanowire interface. (b) High-resolution TEM image of the same wire. The inset shows an electron diffraction pattern taken perpendicularly to the nanowire axis.

It should be noted that no special precautions were taken to remove the native oxide (~10 Å) from the substrates before nanowire growth. In fact, a sample treated with hydrofluoric acid and annealed at 800 °C under hydrogen before the droplet deposition exhibited no nanowire growth. This result is in contrast with results reported by Mårtensson *et al.*[5] on III–V semiconductor nanowire growth on silicon using gold nanoparticle catalysts. However, in our experiments here the native oxide alone was not enough to induce nanowire growth, since no nanowires were observed in samples where the droplet deposition step had been omitted. Also, no growth was observed on a 300 nm thick SiO_2 layer grown on silicon by plasma-enhanced chemical vapor deposition. This suggests that the In droplets actually penetrate the native oxide and that the nanowires start growing from the silicon-indium interface. Further studies are required to find out also whether catalyst-free nanowire growth on oxide-free silicon is possible using different growth parameters.

Room-temperature PL spectra measured from In(As)P nanowires detached from the substrate are shown in Fig. 4. The nominal TBP/III molar ratio was 200, and the nominal TBA/V molar ratio in the gas phase during growth is noted next to the spectra. Adding a small amount of TBA to the gas phase had no significant effect on the morphology of the nanowire samples (SEM images not shown). InP wires exhibit a luminescence peak at 1.35 eV [spectrum (i)] which equals the energy gap of zinc-blende InP. This is in contrast with the TEM results. Previously, we and other groups have proposed that the wurtzite modification in InP nanowires leads to a blueshift of the photoluminescence peak energy.[9,10] However, in these cases the growth direction of the nanowires has been along the *c* axis of the wurtzite structure. Further studies are required to find out whether here the lack of this blueshift is due to the different orientations of the nanowires with respect to the crystal axes, which could lead to different strain or surface effects. Since the nanowire diameter is larger than the exciton Bohr radius in bulk InP (~20 nm), no blueshift from quantum confinement is expected. The spectra (iii), (iv), and (v) in Fig. 4 also exhibit luminescence peaks at 1.18, 1.10, and 1.03 eV, respectively. We assume that these peaks originate from $InAs_xP_{1-x}$. The surprising result here is that the PL peak corresponding to bulk InP is present alongside the peak of InAsP. One expla-

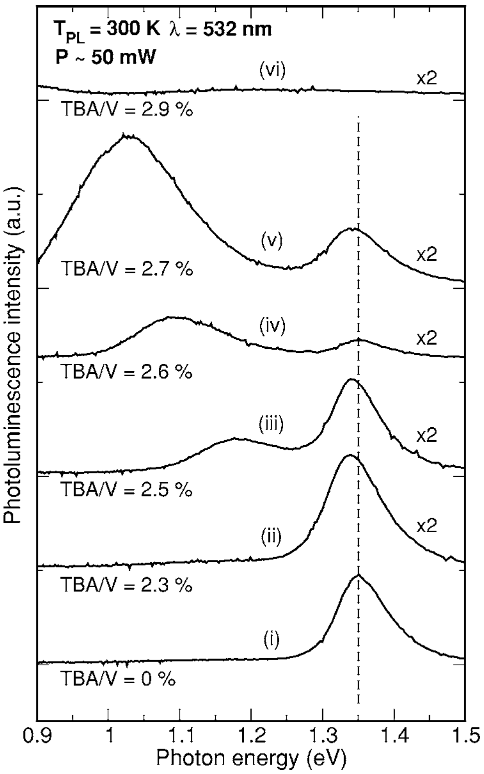

FIG. 4. Room-temperature photoluminescence spectra of In(As)P nanowires detached from the substrate. The dashed line is a guide for the eyes.

nation to this behavior is that the nanowires are actually so-called core-shell structures[11] having an InAsP core under an InP shell because the samples are cooled down in a phosphoric ambient. Compositional fluctuations in the axial direction are also possible. It can be seen from the spectra that as the As content is increased the PL intensity of the InAsP (InP) related peak increases (decreases). This can be understood as a result of more localized carriers in the InAsP parts with increasing As content and thus supports the existence of compositional fluctuations. For more compositional information, energy dispersive x-ray (EDX) analysis was conducted on one of the samples (EDX spectra not shown). The results confirmed that there are only segments of InAsP in otherwise pure InP nanowires, and thus support compositional fluctuations in the axial direction. We believe that this is the case in all samples where a bimodal PL signal is observed. However, when As content in the gas phase is further increased, no PL signal from InP is observed anymore [spectrum (vi) in Fig. 4]. No PL signal from InAsP is observed either, although it is possible that the emission of the As-rich nanowires falls outside the range of the germanium detector.

In summary, catalyst-free growth of In(As)P nanowires on Si(111) substrates was demonstrated. In droplets deposited *in situ* by MOVPE were used as seeds for off-substrate nanowire growth. The native oxide on the substrates was found to have a crucial role in the formation of the nanowires. No nanowire growth was observed on silicon without the native oxide or on a thick SiO_2 layer. The InP nanowires exhibited wurtzite crystal structure and room-temperature photoluminescence at 1.35 eV. The nanowire axis was found to be perpendicular to the *c* axis of the wurtzite crystal. Alloying the nanowires with As produced under certain conditions a bimodal spectrum exhibiting a PL peak at the energy of InAsP in addition to a peak corresponding to the energy gap of InP.

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