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InP nanobridges epitaxially formed between two vertical Si surfaces by metal-catalyzed chemical vapor deposition

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The heteroepitaxial growth of III-V compound semiconductors on Si would enable the integration of high-performance III-V materials with Si technology. We report epitaxial growth on (111)-oriented Si surfaces of highly aligned, single crystalline InP nanowires by chemical vapor deposition catalyzed by Au. We demonstrate laterally oriented InP nanowires bridging between vertical (111) Si surfaces formed by anisotropically etching a (110)-oriented Si substrate or the top Si layer of a silicon-on-insulator wafer. This method of connecting nanowires offers a facile way of integrating nanoscale III-V optoelectronic and photonic devices with Si. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357890]

The growth of III-V compound semiconductors onto Si substrates has been a long sought goal because the integration of high-performance III-V materials with current Si technology could open many applications in optoelectronics and photonics. However, the epitaxial growth of planar layers of III-V compound semiconductors on Si substrates remains challenging because of materials incompatibilities, such as large lattice and thermal expansion coefficient mismatches and differences in crystal structure.[1,2]

With recent rapid progress in the growth of various inorganic nanowires (NWs) using the vapor-liquid-solid (VLS) growth method developed by Wagner and Ellis in the mid-1960s,[3] there have been several studies on the growth of NW heterostructures such as InAs/InP (3.1% lattice mismatch),[4] GaAs/GaP (3.1% lattice mismatch),[5] Si/SiGe,[6] and Si/Ge (4% lattice mismatch).[7] These results indicate that the lattice misfit can be effectively accommodated in NW heterostructures. Recently, Mårtensson *et al.* reported the epitaxial growth of oriented GaP, GaAs, and InP NWs on Si (111) substrates.[8] Although GaP NW growth on Si (less than 0.4% lattice mismatch) was investigated using high-resolution transmission electron microscopy (TEM), the crystalline quality of highly lattice-mismatched (8.1%) InP NWs grown on Si was not addressed.

In this letter, we report the epitaxial growth of highly aligned InP NWs on Si substrates. High-resolution TEM measurements show that InP NWs are single crystalline and of high quality. We show bridging of InP NWs between two vertical, (111)-oriented Si surfaces. Forming the connections during the NW growth provides a facile method of making robust connections between the nanowires and microscale structures, which can be developed into electrodes of nanoelectronic and photonic devices.

Two different types of samples were used to investigate the epitaxial growth of InP NWs on Si substrates. For the growth of vertically aligned InP NWs on unpatterned (111)-oriented Si substrates, a nominally 1-nm-thick Au film was deposited by electron-beam evaporation onto HF-cleaned Si (111) substrates.

For the growth of bridging InP NWs between vertical Si surfaces, a trench bounded by (111) vertical surfaces was formed in a (110)-oriented Si substrate or the top layer of a silicon-on-insulator substrate by conventional optical lithography and wet etching. After forming the vertical (111) surfaces, Au was deposited by electron-beam evaporation onto the vertical surfaces of the etched trenches. Details of the preparation of the patterned samples were reported previously.[9,10]

The InP NWs were grown in a vertical metal-organic chemical vapor deposition reactor equipped with a close-coupled showerhead. The reactor was typically operated at 76 Torr with a total H_2 flow of 10 slm (standard liter per minute). Substrates were annealed at 650 °C in H_2 for 10 min to form Au catalyst nanoparticles from the deposited Au film. The reactor temperature was then lowered to the typical nanowire growth temperature of 450 °C, and trimethylindium and phosphine were introduced into the reactor to initiate the growth of InP NWs. The typical growth rate was 0.1 μm/min.

Figure 1 shows a cross-sectional scanning electron microscope (SEM) image of InP NWs grown on a (111)-oriented Si substrate. The InP NWs typically have diameters of 20–80 nm. InP and other III-V NWs are known to grow preferentially along $\langle 111 \rangle$ directions, and observing vertically aligned InP NWs indicates epitaxial growth on the (111)-oriented Si surface. Although the majority of InP NWs

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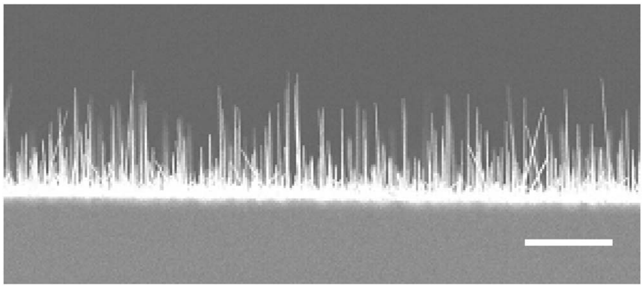

FIG. 1. Cross-sectional SEM image of highly aligned InP nanowires grown on Si (111). The marker corresponds to 3 μm.

shown in Fig. 1 grew nearly normal to the substrate surface, some NWs grown at angles of 30°–50° relative to the $\langle 111 \rangle$ direction are noticeable. Most of these misaligned NWs are shorter than the vertically aligned NWs. It is possible that a thin layer of native oxide, which remained after annealing in H_2 at 650 °C prior to the NW growth, hampered the epitaxial growth of NWs. We observed that the fraction of vertically aligned NWs was lower for aged samples stored in a glovebox for a longer period between Au deposition and nanowire growth than that for samples with freshly deposited Au.

In order to verify the crystalline quality of InP NWs epitaxially grown on Si substrates, we investigated the NWs using high-resolution TEM. Figure 2(a) is a low-magnification TEM image of an InP NW showing a hemispherical catalyst nanoparticle at the tip, indicating that NWs were grown via the VLS growth process. The high-resolution TEM image in Fig. 2(b) clearly shows lattice fringes perpendicular to the NW growth axis and indicates the high crystalline quality of the NW. The average spacing between the lattice fringes is 0.344 nm, which agrees well with $d_{111} = 0.338$ nm for bulk InP. These results indicate that the strain induced by the large lattice mismatch between InP and Si (8.1%) can be relieved effectively because of the small cross section of a NW.

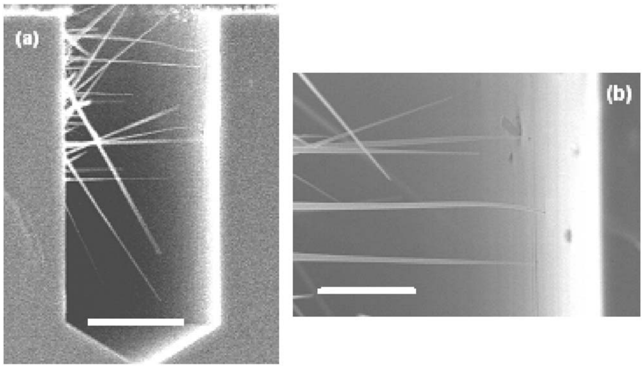

FIG. 3. Cross-sectional SEM images of (a) lateral epitaxial growth of InP nanowires across a 4-μm-wide trench and connecting to an opposite sidewall. The marker corresponds to 2 μm. (b) Details of impinging ends of InP nanowires. The marker corresponds to 1.5 μm. The growth direction is from left to right in both (a) and (b).

For fabrication of nanoelectronic and photonic devices integrated onto Si substrates, it is highly desirable to form connections during the growth of NWs. This approach could greatly reduce the complexity of the overall device fabrication process involving the positioning and alignment of NWs. Figure 3(a) illustrates Au-catalyzed InP NWs grown laterally from one (111)-oriented Si surface to the opposite sidewall of a trench etched into a bulk Si (110) wafer. When the NW reaches the opposite surface, it bonds to the surface, forming a mechanical connection, as shown in Fig. 3(b). The strength of the connection is indicated by the NWs breaking along their length, rather than at the connection point when they are stressed to mechanical failure. Since the growing NWs have Au at their tips, catalyst is transported across the trench by the growing NWs. If the growth continues after the NWs impinge on the opposing sidewall, the transported catalyst can lead to additional nucleation of nanowires, as shown in Fig. 4.

In order to fabricate nano-optoelectronic devices integrated onto Si substrates, it is necessary to grow nanobridges between electrically isolated electrodes so that the electrical properties of the nanobridges can be assessed and they can be integrated into a practical device structure. A single Mg-doped InP nanobridge was grown between isolated Si electrodes, which were formed on a Si-on-insulator wafer with a heavily doped, (110)-oriented top Si layer (Fig. 5). The amount of Au deposited was reduced to achieve the selective growth of NWs from the vertical sidewall, with no growth on horizontal surfaces.[10] Bis(cyclopentadienyl)magnesium was used as a precursor for Mg doping. Secondary ion mass spectrometry (SIMS) was carried out on samples containing a large number of nanowires to measure the Mg concentration in the nanowires. The Mg concentration determined by SIMS measurements was $\sim 1 \times 10^{19}$ cm^{-3}. Preliminary electrical measurements showed nonlinear current-voltage characteristics, suggesting that the connections between the InP NW

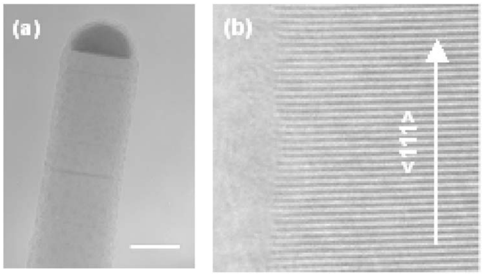

FIG. 2. (a) Low-magnification and (b) high-resolution TEM images of InP nanowires. The marker in (a) corresponds to 20 nm.

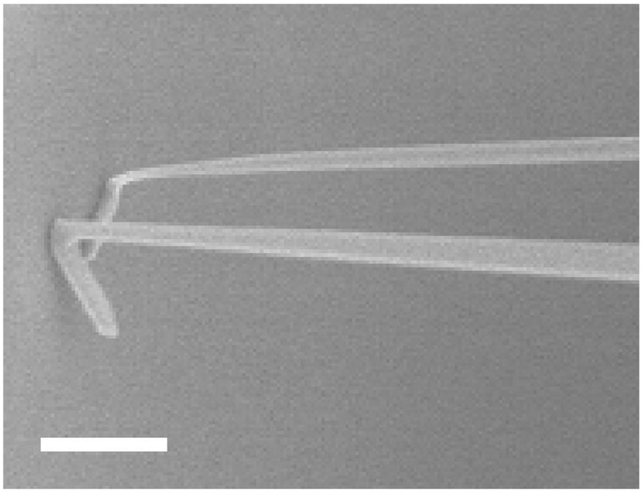

FIG. 4. SEM image showing secondary growth of nanowires near the impinging ends of bridging nanowires. The growth direction is from right to left. The marker corresponds to 300 nm.

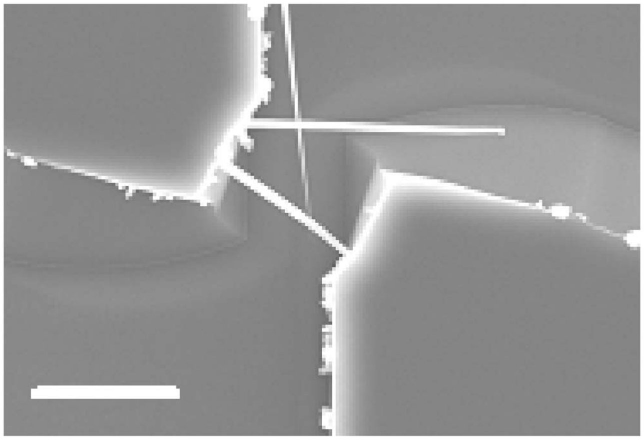

FIG. 5. Single InP nanobridge formed between isolated Si electrodes. The horizontal surfaces are free of nanowires. The marker corresponds to 10 μm.

and the Si electrodes limited the current. The effects of band gap offsets and interface states at the InP–Si heterojunction need to be considered carefully. Detailed crystallographic and electrical studies of the InP nanobridge-Si interfaces would reveal the nature of the interfaces at the two ends of a nanobridge and suggest methods of controlling the band alignment at these interfaces to form the desired electrical connections, perhaps by suitable band gap engineering.

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