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Critical diameter for III-V nanowires grown on lattice-mismatched substrates

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The authors report the experimental observation of a critical diameter (CD) of III-V compound semiconductor epitaxial nanowires (NWs) grown on lattice-mismatched substrates using Au-catalyzed vapor-liquid-solid growth. The CD is found to be inversely proportional to the lattice mismatch. NWs with well-aligned orientation are synthesized with catalysts smaller than the CD. Well-aligned InP NWs grown on a Si substrate exhibit a record low photoluminescence linewidth (5.1 meV) and a large blueshift (173 meV) from the InP band gap energy due to quantization. Well-aligned InAs NWs grown on a Si substrate are also demonstrated. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2436655]

Monolithic integration of semiconductors with different lattice constants has excited much interest because of its promise to combine the best performance of different material systems.[1] In particular, it is desirable to integrate compound semiconductors onto a Si substrate, where Si is the prevalent platform for microelectronics and compound semiconductors for light emitting diodes and lasers. Past attempts failed due to high defect densities resulting from large lattice mismatches (LMs) and high temperatures required for typical epitaxial synthesis ($\sim$600 °C).[2,3] Nanowires (NWs) grown by the vapor-liquid-solid (VLS) mechanism[4] are promising because of the substantially lower temperatures reported (400–500 °C).[5–12] Typical Si complementary metal-oxide semiconductor back-end processes require temperatures below 450 °C. Recently, theoretical calculations on equilibrium limitations for coherent growth of strained NWs were reported.[13] Here, we report the experimental observation that there exists a critical diameter (CD) for epitaxial NWs grown on lattice-mismatched substrates, up to as large as 11.6%. Below the CD, well-aligned NWs with bright photoluminescence can grow, while above the CD, spiky structures form. We report well-aligned InP NWs on Si with a very narrow photoluminescence linewidth of 5.1 meV, indicating excellent optical quality. This linewidth is the narrowest reported for III-V NWs.[12] Furthermore, we show an inverse dependence of CD on the LM, which agrees well qualitatively with the theoretical results.[13] This may serve as a guideline to synthesize defect-free compound semiconductor NWs on Si substrates with a low-temperature process.

We use colloidal Au nanoparticles (NPs) as catalysts in a low-pressure metal-organic chemical vapor deposition reactor under the VLS growth mode. Five material combinations and various sizes of Au NPs are used to study the growth as a function of LM and catalyst size. The material combinations are listed in Table I. The Au NP size ranges from 10 to 160 nm. In this study, the growth temperature (430–470 °C), pregrowth annealing temperature (610–660 °C), V/III ratio, growth rate, growth pressure, and substrate orientation were the experimental parameters. More than 120 growth runs, including many with repeated conditions, were conducted. To derive the size-dependent information, Au NPs with different sizes were placed on different parts of the same substrate for a given growth run. Metal-organic sources used in this work were *tert*-butylphosphine, *tert*-butylarsine, and trimethylindium. All as-grown NW samples were inspected under scanning electron microscopy (SEM) to derive CD information.

Figure 1(a) shows a typical (20°-tilt) SEM picture for InAs NWs grown on a (111) Si substrate, with 11.6% LM. The widest epitaxial NW found has a 26 nm diameter. The Au NP size was determined by SEM in a separate, anneal-only run to be nominally 20 nm, with a wide size distribution from 10 to 40 nm. Hence we deduce that the maximum epitaxial NW diameter of 26 nm was due to the existence of a CD. Figures 1(b)–1(d) show (20°-tilt) SEM images for InP nanostructures grown on a (111) Si substrate using nominal (b) 20, (c) 60, and (d) 120 nm Au NPs, respectively. With 8.1% LM, only the 20 nm Au region supports epitaxial NW growth with vertically aligned NWs along the [111] direction. In the 60 and 120 nm Au NP regions, spiky starlike structures are created. For this case, the CD was found to be 36 nm.

Figure 1(e) shows a typical transmission electron microscopy (TEM) image for a 17 nm InP NW on Si. No dislocations were observed along the 450 nm length of the NW. Furthermore, the period between the lattice planes is 3.4 Å throughout the full length of the NW, in agreement with the period for fully relaxed InP (111) planes.

TABLE I. Material combinations used in this letter for obtaining different LMs.

NW/substrate	InAs/Si	InP/Si	InP/GaAs	GaP/Si	InP/InP
LM (%)	11.6	8.1	3.8	0.4	0

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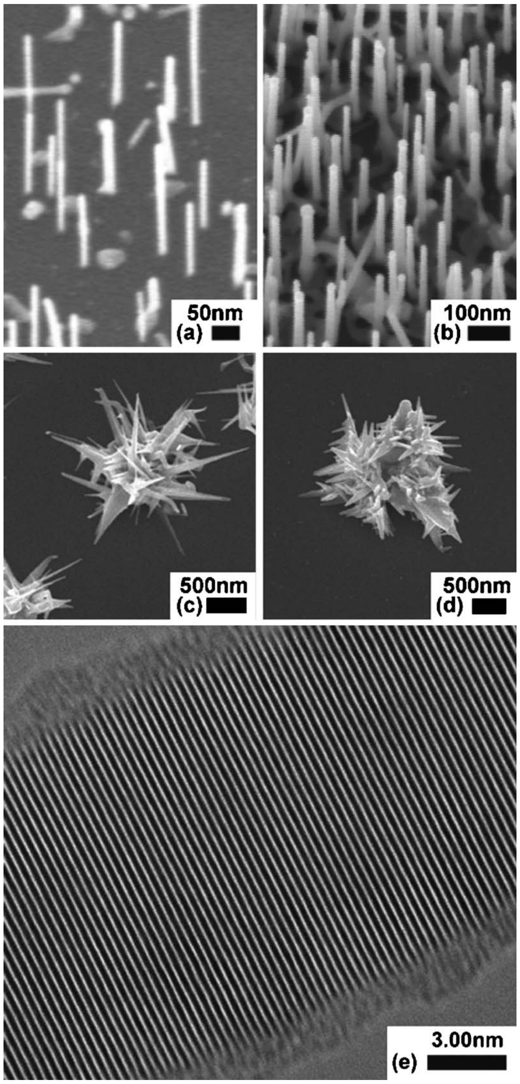

FIG. 1. 20°-tilt SEM pictures for nanostructures grown on (111) Si substrates. (a) InAs NWs with nominal 20 nm Au NP catalysts. (b) InP NWs grown with nominal 20 nm Au NPs. [(c) and (d)] Starlike InP structures using nominal (c) 60 and (d) 120 nm Au NPs, respectively. (e) TEM image of a 17 nm diameter InP NW showing clear (111) planes perpendicular to growth axis with 3.4 Å spacing. No dislocations were observed along the entire 450 nm NW length.

Figure 2(a) shows the SEM picture of InP NWs grown on a (111)B GaAs substrate with a mixture of nominally 20 and 60 nm Au NPs. With 3.8% LM, well-aligned, epitaxial NWs are obtained with both 20 and 60 nm Au NPs. A clear bimodal distribution of NW diameters appears in this region, supporting that the dominant factor for NW size is the catalyst size as long as it is less than the CD. In the 120 nm Au NP region [shown in Fig. 2(b)], branching is again observed. The CD in this case is 96 nm.

For GaP NWs on Si, epitaxial NWs could grow even with the largest Au NPs used, about 100 nm in diameter. For the InP-NW-on-InP experiment, epitaxial NWs as wide as 480 nm were obtained. For both experiments, we confirm that wide epitaxial NWs can be synthesized, with no CD constraint observed within the NP size limits used.

Figure 3 summarizes these growth results. The black dashed curve in this figure is the theoretical curve of the misfit-dislocation-free CD (CD_{MDF}) taken from Ref. 13 for comparison. An equilibrium model similar to the Matthews critical thickness model[14] was used to calculate CD_{MDF}.

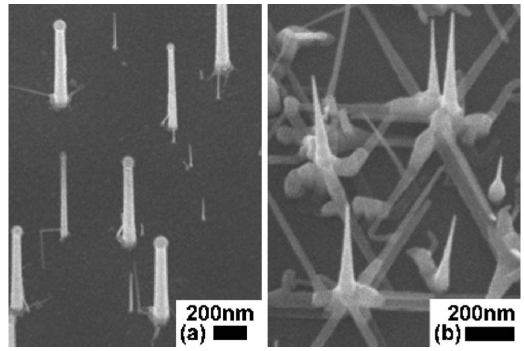

FIG. 2. 20°-tilt SEM pictures for InP NWs grown on a (111)B GaAs substrate with (a) a mixture of nominal 20 and 60 nm Au NP catalysts. (b) Region with nominal 120 nm Au NP catalysts. The branching of NWs is clearly seen.

When the NW diameter is less than CD_{MDF}, the NW will be coherent everywhere solely via lateral relaxation. The epitaxial NW CDs experimentally obtained in this work were fitted by the solid blue curve. It shows a similar trend to the CD_{MDF} curve, but the magnitude is approximately two times larger for a given LM. We attribute the difference to the fact that the CD_{MDF} was calculated assuming equilibrium growth, while the epitaxial NWs grown in this work have kinetic growth factors not considered in the calculation.[15,16] Similar experiment-to-theory deviations were also reported for strained thin film growth.[17] In addition, epitaxial InP NWs on Si with wider diameters (~70 nm) have been reported.[9] We believe that the discrepancy could be due to the growth condition difference which leads to different kinetic factors.

The linewidth and intensity of photoluminescence (PL) are key indicators of the material optical quality. The PL linewidth is particularly critical as its broadening often results from structural fluctuations and defects. A broad PL linewidth has deleterious effects on devices such as lasers.[18] Hence, it is crucial to obtain a narrow linewidth for optoelectronic applications. Figure 4 shows microPL (μ-PL) results of as-grown InP nanostructures on (111) Si at 4 K, with an excitation laser beam size of ~1.5 μm. The excitation source is a diode-pumped solid-state laser at 532 nm. The

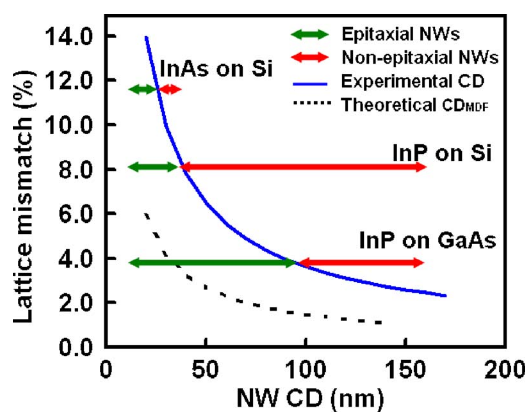

FIG. 3. (Color online) Experimental NW CD's and theoretical NW CD_{MDF}'s as a function of LM. Three CD data points were experimentally obtained in this work and then fitted. CD_{MDF} curve was taken from Ref. 13 for comparison. Green arrows denote that epitaxial NWs within this size range were observed. Red arrows denote that Au NPs within this size range were used as catalysts but no corresponding epitaxial NW could be found. Hence the boundary between a green arrow and a red arrow is the experimental CD for that particular LM.

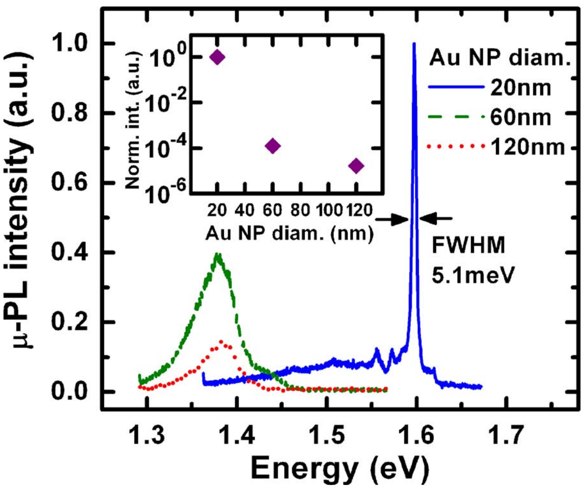

FIG. 4. (Color online) Low-temperature (4 K) μ-PL spectra of InP nanostructures on (111) Si for NWs (20 nm Au NP catalyst) and star structures (60 and 120 nm Au NPs). A single NW PL shows a sharp peak with a 5.1 meV FWHM, the narrowest reported for a single NW, with a 173 meV blueshift from the InP band gap. The inset shows the μ-PL intensity normalized to nanostructure volume.

power used was extremely low: 120 nW, corresponding to a power density of 6.8 W/cm^2. Figure 4 compares typical μ-PL spectra for NWs (20 nm Au catalyst) and starlike structures (60 and 120 nm Au catalysts). A sharp peak at 1.597 eV with a full width at half maximum (FWHM) of 5.1 meV is observed for a single NW. This FWHM is the narrowest reported to date by a factor of 4.[12]

The single NW PL shows a 173 meV blueshift from the InP band gap (1.424 eV) due to quantum confinement. This was also the most significant blueshift ($\Delta E/E \sim 12\%$) ever reported in NWs. Furthermore, the brightness of this emission, when normalized to the volume of the NW, is comparable with that of a standard GaAs/AlGaAs multi-quantum-well sample. The μ-PL spectra for starlike structures have a broad FWHM ($\sim$60 meV). The inset shows the PL intensity normalized by the nanostructure volume. The brightness of the NW is over four orders of magnitude higher than that of the starlike structures, which attests to the good optical quality of the NWs.

In conclusion, we report the experimental evidence of a CD for epitaxial NWs on lattice-mismatched substrates, with NWs smaller than this value demonstrating extremely narrow PL linewidths and bright PL intensity. We show that CD is inversely dependent on the LM. The CD can serve as a general guideline in heterogeneous material growth for obtaining high brightness, well-aligned III-V NWs on Si or other dissimilar substrates. This observation will be important for monolithic integration of optoelectronic and electronic devices with highly mismatched lattice constants.

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