Electronic Supplementary Information

Phase Transition Induced Vertical Alignment of Ultrathin Gallium Phosphide Nanowire Arrays on Silicon by Chemical Beam Epitaxy

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Fabrication of GaP & Si NW Arrays: CBE and CVD were performed in an ultra-high vacuum (UHV) system. The background pressure was kept at 1×10^{-10} mbar. The Au was deposited by MBE on a hydrogen terminated Si substrate with a surface temperature of 350°C, then, transferred *in situ* to the growth chamber and heated by a backside hot-plate radiation with a calibrated temperature control. A 40 sccm 5 % silane (SiH_4) + Ar mixture gas was lead into the chamber for Si NW growth as a standard UHV-CVD. The Si NWs were grown at 450 °C with 0.5 mbar SiH_4 partial pressure. Precursors of tertiarybutylphosphine (TBP) and trimethylgallium (TMG) were used for GaP growth with a controlled low-pressure (1×10^{-6} ～ 1×10^{-4} mbar) CBE manner. Considering the thermal stability of TBP, a home-made gas cracker which could be heated up to 1000 °C was connected to the outlet, resulting in a high growth efficiency with low substrate

temperature (450°C～500°C) after the predecomposition of TBP. The TMG and TBP were introduced successively with partial pressures of 1×10^{-5} mbar and 1×10^{-4} mbar respectively with the substrate temperature increased to 470 °C. The TBP was introduced with a 1.5 min delay after the TMG. The CBE growth was kept for 4 min. The post-anneal process was heating at 600 °C for 10 min *in situ*.

Instruments: The structural characterizations were carried out *ex situ* with a field-emission scanning electron microscope (FE-SEM JEOL 6701) and a high-resolution transmission electron microscope (HR-TEM JEOL 4010). The photoluminescence spectroscopy was measured by a Hitachi F4500 fluorescent spectroscope with the excitation at a wavelength of 475 nm. The spectral resolution of the detector was 0.2 nm. The optical excitation was generated by an OPO laser pumped by a mode-locked high-energy Nd:YAG laser (PL2143) with a repetition rate of 10 Hz. The laser pulse duration was 20 ps and the excitation wavelength could be selected from 450 nm to 540 nm. Time-integrated emission spectra were recorded by a synchroscan streak camera connected to a monochromator. The excitation picosecond laser pulse was focused on the sample by a lens with focal length of 150 mm with a grazing incidence between the incident light and the normal of the sample plane. The light emission from the sample was collected with a home-built lens system into the spectroscope which was connected to the streak camera. The whole detection system gives a time resolution about 20 ps and spectral resolution of 2 nm, respectively. The experiment was performed at room temperature.

Identification of Au-Ga phases:

	Au_7Ga_2	Au_2Ga	AuGa	$AuGa_2$
Sys.	Hexagonal	Orthorhombic	Orthorhombic	Cubic
a;b;c (Å)	7.724;7.724;8.751	18.02;3.199;6.999	6.266;3.421;6.399	6.075
3.4 (Å)	3.53;3.53;3.34 {111;121;200}	3.50; 3.44;3.26;3.20 {002;102;202;501}	3.20;3.42 {002;010}	3.51 {111}
2.2 (Å)	2.16;2.19;2.20;2.23 {301;004;203;300}	2.15;2.17;2.19;2.20;2.25;2.26; 2.26;2.28;2.28 {801;303;610;312;800;203; 511;212;602;}	2.13;2.17;2.19;2.24; {003;211;112;202}	2.15 {220}
90 (°)	{200}-{004} 90	{002}-{800} 90	{010}-{202};{003} 90	{111}-{220} 90
Dir.	[010]	[010]	[101]; [100]	[112]

Table S1. Comparison of lattice parameters for different Au-Ga phases with the measured values (in bold) of the sample. For the two measured planes, considering the limited resolution, all the real planes within the ± 5% errors of the measured values are listed respectively. All the possible combinations of the two planes possessing the observed 90° in between were listed below the thick line. The calculated viewing directions are listed in the last line.

The calculated images compared with the real HRTEM image using the software JEMS (P. Stadelmann, CIME-EPFL, CH-1015 Lausanne, Switzerland). Only the phase $AuGa_2$ viewed in [112] direction fits.

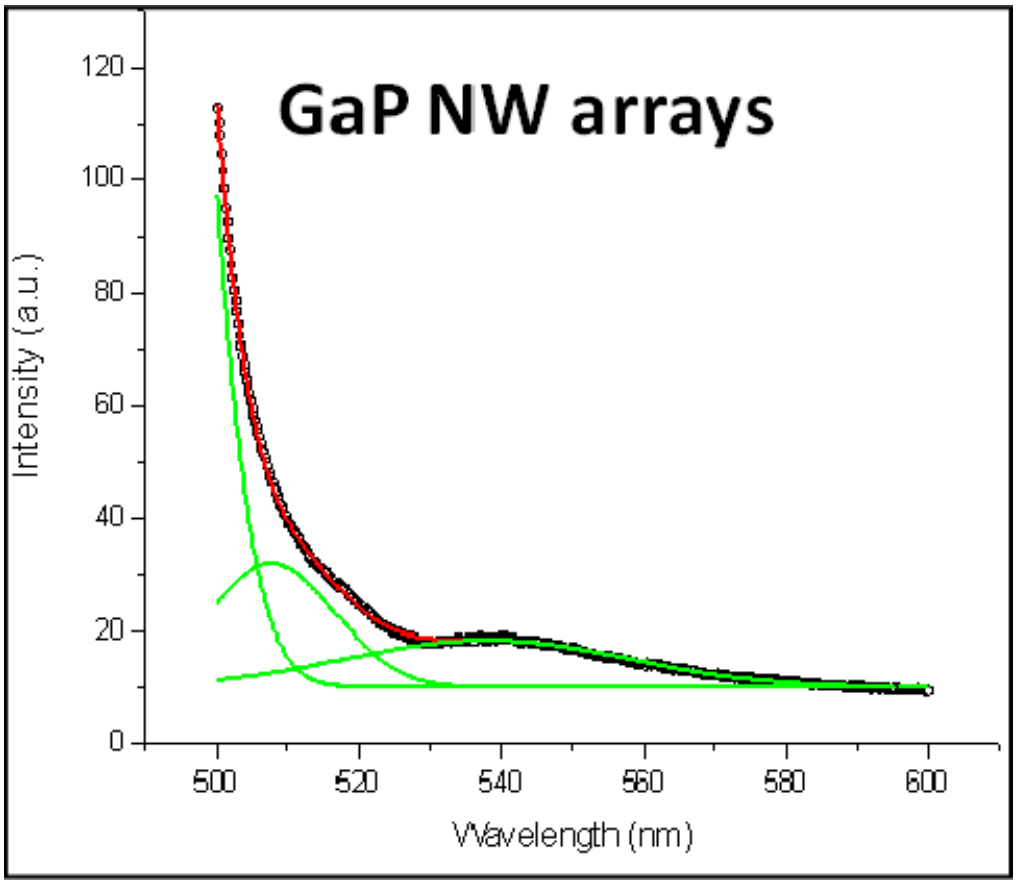

Figure S1. The Gaussian peak fit of photoluminescence of a sample with high-density Au-catalyzed sub-10 nm diameter GaP NW arrays on Si (111) substrate, the light emission peaks are at a wavelength of 539 nm with a half width of about 20 nm and at 508 nm corresponding to a smaller half width of about 10 nm.

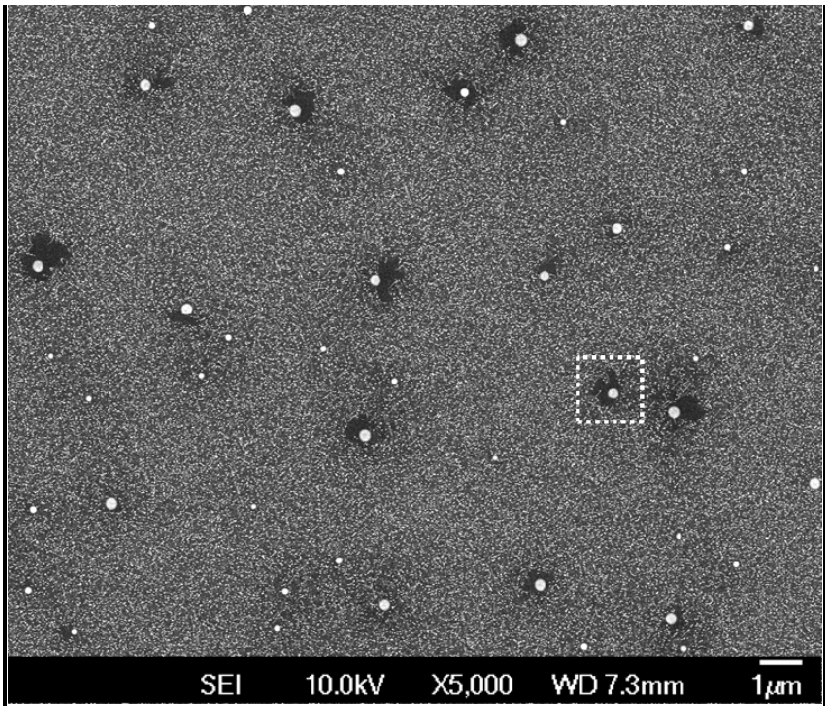

Figure S2. SEM image shows dashed lines, which are the edges of Fig. 2a. The phenomenon we observed in the experiment with and without annealing was used mainly to explain the influence of annealing on the control of vertical growth direction. Since the collection of Au particles occurs mainly around the big Au droplets, the average diameter of GaP NWs' bases with Au annealing was almost the same with the one without annealing. Indeed, the thin gold film undergoes some rapid annealing before the start of NW growth, which is the reason why we found the NWs' bases were 8-11 nm in diameter, although the Au nanoparticles were smaller (around 7 nm in diameter) synthesized directly by the hot-surface MBE method.

For the ab-initio calculations the release 1.3.31 of elk (elk.sourceforge.net) was used. Lattice parameter a for ZB was 5.15 a.u., Ga 0, 0, 0; P 1/4, 1/4, 1/4. K-point offset was 0.5, 0.5, 0.5 and number of k-points 8, 8, 8. Spinorb and spinpol were set to true. For WZ the parameter u was set to the ideal value of 0.375, Ga at 2/3, 1/3, 0 and P at 2/3, 1/3, 3/8. c/a was the ideal value of 1.633, and a 7.2832 a.u. (1 a.u. is about 52.9177 pm). K-point

offset was 0, 0, 0.5 and number of k-points was 8, 8, 8. Spinorb and spinpol were set to true.