



III–V Integration on Si(100): Vertical Nanospades

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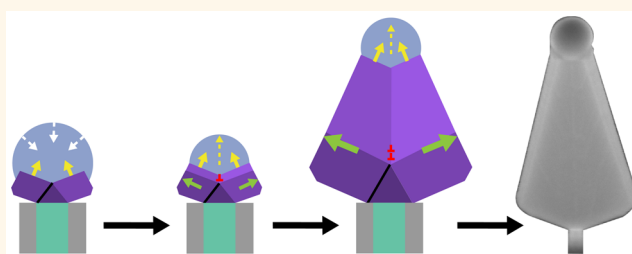
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ABSTRACT: III–V integration on Si(100) is a challenge: controlled vertical vapor liquid solid nanowire growth on this platform has not been reported so far. Here we demonstrate an atypical GaAs vertical nanostructure on Si(100), coined nanospade, obtained by a nonconventional droplet catalyst pinning. The Ga droplet is positioned at the tip of an ultrathin Si pillar with a radial oxide envelope. The pinning at the Si/oxide interface allows the engineering of the contact angle beyond the Young–Dupré equation and the growth of vertical nanospades. Nanospades exhibit a virtually defect-free bicrystalline nature. Our growth model explains how a pentagonal twinning event at the initial stages of growth provokes the formation of the nanospade. The optical properties of the nanospades are consistent with the high crystal purity, making these structures viable for use in integration of optoelectronics on the Si(100) platform.

KEYWORDS: nanospades, GaAs nanowires, nanowires, vertical growth, [100] growth, Si(100)



Because of their exclusive and intriguing properties, semiconductor nanowires (NWs) have drawn increasing interest among researchers for their potential applications in a diverse range of fields, from p–n junction and high-performance transistors^{1,2} to light-emitting diodes,³ solar cells,^{4–6} quantum computing,^{7–9} terahertz detection,¹⁰ and even biology.^{11,12} To complete their path toward electronic and optoelectronic applications, their up-scalability and their compatibility with modern semiconductor processing need to be tackled. There is currently a joint effort in the NW community to bring the technology closer to compatibility with CMOS technology. A first step was replacing Au as the liquid catalyst in the vapor liquid solid (VLS) mechanism,¹³ by other compounds, avoiding deep level traps in Si.^{14–16} Highly uniform arrays have been successfully obtained by a self-catalyzed VLS method,^{17–20} allowing Au-free opportunities for solar cells. Yet, those very promising results were exclusively obtained on Si wafers oriented in the [111] crystallographic direction, which is not the industry standard.

This work aims at implementing vertical, III–V-based self-catalyzed VLS-grown nanostructures on Si(100). Due to their preferential [111]B growth direction,²¹ NWs spontaneously grow at an angle of 35° with the (100) surface, which would strongly compromise their functionality.¹⁷ Several groups reported [100]-oriented III–V growth on III–V substrates using Au as a catalyst. This constitutes a limited number of systems, indicating the still open potential.^{22–25} So far, controlled, defect-free [100]-oriented growth has not been demonstrated on the Si platform nor in a Au-free manner.

Here, we propose an original way of engineering the contact angle from the initial stages of growth by patterning Si(100) substrates into oxidized nanoscale pillars. This is one of the key elements that we propose to obtain Au-free vertically [100]-oriented flat nanostructures on the (100) Si platform, with a yield of currently 10% (number of structures over the total

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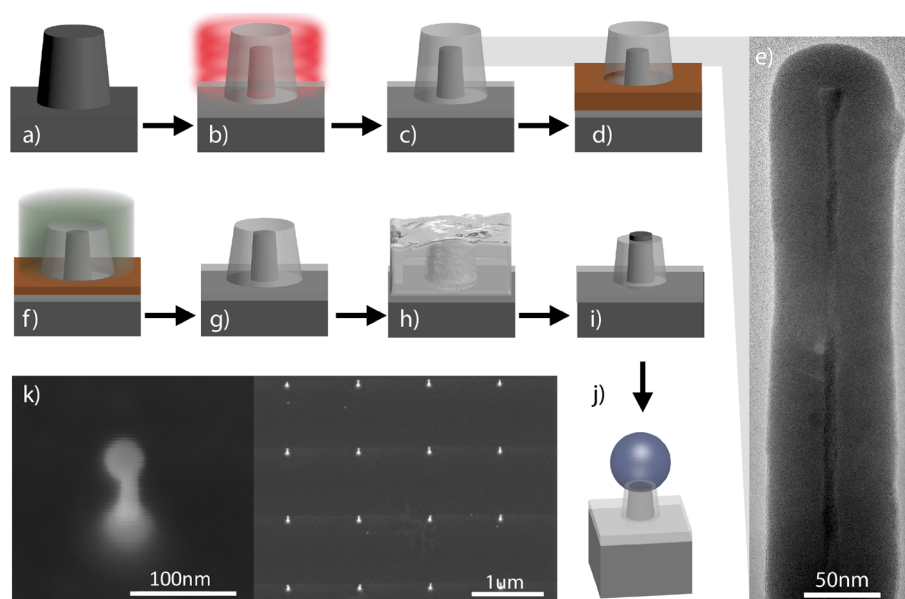


Figure 1. Scheme for the fabrication of the SiO₂ mask around (a) Si nanopillars. (b) A thermal oxidation is done at 900 °C (c) for nominal planar thicknesses ranging from 10 to 100 nm, as seen in the TEM micrograph (e). (d) A spin-coating of a polymeric protective layer and (f) a reactive ion etching offer a directional etching of the dielectric mask. (g) 5 nm is kept at the top of the pillar to keep the Si surface intact. A final hydrofluoric acid bath (h) permits uncovering the Si nanopillar's top. The sample is then introduced in the MBE chamber, and the growth is initiated with a liquid catalyst droplet predeposition (j). (k) SEM pictures of a Ga predeposition of 10 min on Si at 640 °C. The first picture depicts one pillar among the array shown in the second picture.

number of nucleation sites). These flat NW structures, called nanospades, exhibit high-quality crystalline structure with extremely few defects, rendering them suitable for photonic and energy-harvesting applications.

Several studies suggest that the configuration of the droplet catalyst determines the crystal phase,^{18,21} growth direction,²³ polarity,^{26,27} and uniformity.²⁸ Here, we engineer the liquid catalyst droplet in terms of size and contact angle before the VLS growth initiation itself to enable growth in the [100] direction. In doing so, a positive height-difference Si surface is crafted in the shape of a nanoscale pillar. Ga is then constrained at the tip using a SiO₂ mask. By varying the Ga predeposition time we make the droplet swell. This allows us to obtain contact angles that are higher than those expected for Ga on Si at equilibrium, the latter reported to be unstable for a reproducible NW growth.²⁸

The Si nanopillar arrays are produced using a process similar to that of Varricchio *et al.*²⁹ First, a dotted pattern is defined on a 4 in. Si wafer using electron beam lithography. Then the pillars are defined by RIE (reactive ion etching) using a mixture of SF₆ and C₄F₈, followed by a buffered hydrofluoric acid bath for resist stripping. The bare Si nanopillar heights vary between 150 nm and 1 μm, and their diameters from 300 to 30 nm. In this study we keep the pitch distance at 1 μm. The pillars are subsequently oxidized at 900 °C, the oxide providing the role of selective growth mask, as depicted in Figure 1. The tips of the pillars are uncovered by a second RIE using a mixture of SF₆ and CHF₃. Finally, a diluted HF bath is used for an isotropic etching, ensuring the uncovering of the silicon pillar tip; see Figure 1.

Given the geometry of the Si pillar, its oxidation should reach a self-terminating regime, resulting in a sub-10 nm diameter.³⁰ This is due to the build-in of internal stresses upon oxidation, limiting the reaction rate at the interface. The strain tends to be compressive due to the incorporation of oxygen in

the Si lattice.^{31–33} The thermal mismatch between both species is also expected to produce further internal stresses (tensile) during the cooling.³⁴ Walavalkar *et al.*³⁰ showed by finite element simulations that the overall built-in stress in the Si is likely to be tensile at room temperature. The nature of the strain in our pillars is not central to this work, and it will be further clarified in follow-up studies.

Figure 1e shows a representative BF TEM (bright-field transmission electron microscopy) micrograph of an oxidized Si nanopillar. The nominal diameter of this pillar is 75 nm, and the oxidation time is set for a nominal thickness of 100 nm, at a temperature of 1000 °C. The contrast between SiO₂ and Si is the result of dynamical scattering at the interface and in the bulk Si, which is enhanced by the aforementioned stress.³⁰ The oxide is thicker at the sidewalls than at the top due to the increased surface exposed to oxygen during the thermal process, but also to the radial tensile strain in the bulk oxide, easing the early supply of oxidants radially.³¹ The core Si pillar is 5 nm, indicating that the extent of the self-limiting oxide thickness can be reached in our system. The present work will focus on samples having a 15 nm Si core.

Several studies show that a deterministic contact angle engineering should serve in crystal phase engineering^{21,35} and growth direction.²³ Therefore, we focused on the mastering of the wetting angle of the Ga droplets on top of the pillars. In order to vary the contact angle, we increased the total volume of the droplet by changing the Ga predeposition time. The resulting contact angles have been measured by cross-sectional SEM (scanning electron microscopy). Pillars from 35 to 270 nm in diameter have been fabricated, oxidized, and loaded in the MBE (molecular beam epitaxy) chamber, where a Ga equivalent flux of 0.15×10^{-6} Torr is kept for 10 min under an ultrahigh vacuum. The manipulator temperature is set at 740 °C, which corresponds to a substrate temperature of 650 °C. Figure 2a shows SEM images, representative of the

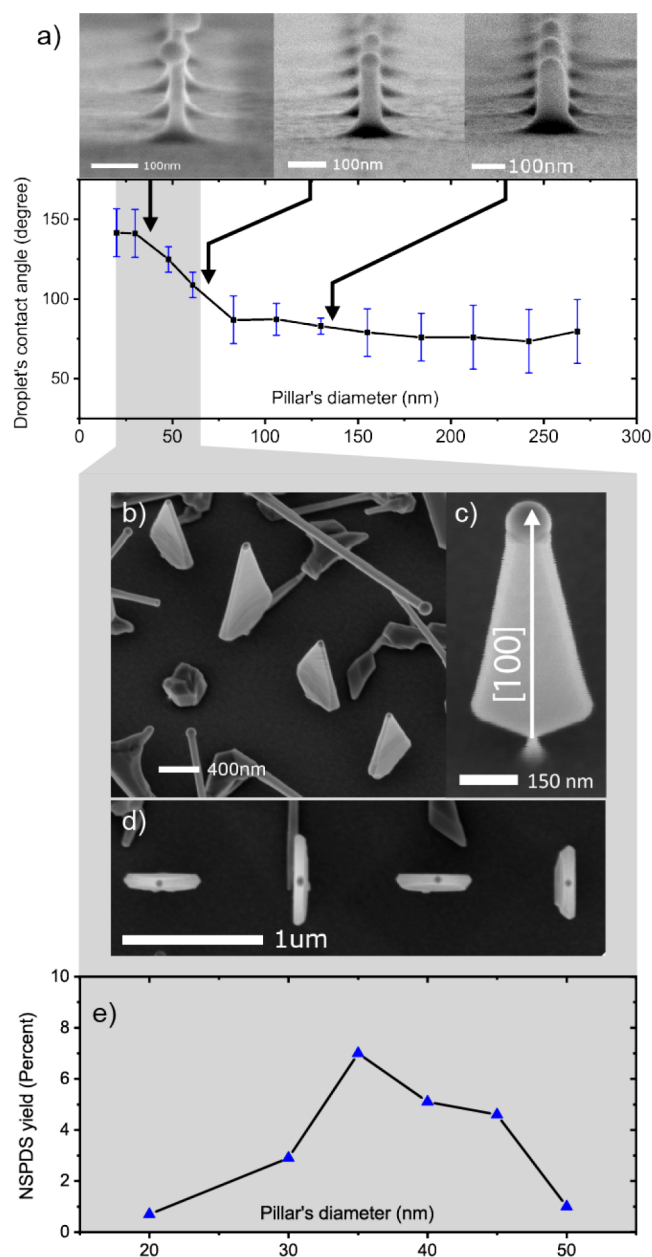


Figure 2. (a) Table showing the relation between Si pillars' diameter and the Ga droplets' contact angle, along with SEM images representing certain diameters. (b, c, and d) SEM pictures of GaAs nanospades on Si pillars and their growth range in the table. (e) Relation between the yield of nanospades (NSPDs) and pillar diameter for a 20 nm (nominal) oxide mask.

configurations obtained. We depict also the values of the contact angle as a function of the pillar diameter. We observe angles between 140° and 75° , from smaller to larger diameter pillars. There is a range between 40 and 100 nm where the contact angle varies almost linearly. For smaller pillars, the droplets fall down the side, which is expected to be detrimental for further MBE growth. For higher diameter pillars, the contact angle reaches the equilibrium value of liquid Ga on Si.³⁶ This variation of contact angle should translate to higher pillar diameters for longer deposition times, which shows the versatility and potential of this platform. It would be possible to tune the diameter and contact angle that one needs by

correctly adapting the process parameters and growth conditions.

Figure 2b to d highlight structures obtained in the range of contact angles marked in gray. They are oriented along the [100] direction. They exhibit a spade-like shape, substantiating their name. They can reach a high aspect ratio in two orthogonal directions. SEM pictures show the presence of a Ga droplet at the top, which confirms that they grow by the self-catalyzed VLS mechanism. However, their shape evolution throughout the growth appears to be a mixed contribution between VLS¹⁹ and VS (vapor–solid),³⁷ the former for the vertical elongation and the later for the horizontal elongation. The nanospades (NSPDs) presented here have been grown using a Ga predeposition step of 10 min as mentioned in Figure 2a, a Ga equivalent flux of 0.14×10^{-6} Torr, and a V/III ratio of 12. Figure 2e indicates the yield as a function of the pillar diameter. We can reach a maximum yield close to 10% for 35 nm diameter pillars. The other pillars contain [111]B-oriented GaAs NWs and parasitic growth. The yield drastically decreases for pillars larger than 50 nm, plummeting to a value of 1%. The low yield in smaller pillars can be explained by the Ga droplet falling down the side and, in larger pillars, by the energy of formation of the initial seed, as explained further below.

NSPDs have been transferred flat on a TEM grid and observed using an Cs-corrected TEM. Figure 3 shows a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) general overview of the studied nanospade in (a), details obtained on the tip in (b) and (c), and a color map showing the structure at the base in (d). Polarities have been resolved by an intensity analysis, as heavier atoms (As) appear brighter. The overall structure exhibits an original crystalline structure. The base is composed of several symmetrical twins and polarities, while the body consists of a bicrystal. Figure 3d shows the presence of a [100]-oriented domain (light blue) that is A-polar, Ga terminated, which is believed to be in epitaxial relation with the Si. This [100]A-oriented domain creates a truncated octahedron with (111)A facets where twin boundaries form upon further growth, showing a multiple-order twinning mechanism.³⁸ A similar mechanism has been observed in [111]B-oriented nanowire growth. It consists of the formation of successive twinning events in the three dimensions of space, resulting in well-defined modifications in the nanowire orientation with the substrate. Interestingly, after the first monolayer, one side exhibits a change of polarity (dark blue) with respect to the other side (red). To the best of our knowledge, this is one of the first reports of a polarity change during nanostructure growth. Due to its high energetic cost, this polarity change should be very unlikely to happen.³⁹ Its function is the conservation of the overall polarity in both sides of the truncated octahedral seed. This structure is similar to the InAs V-shaped membranes obtained by Conesa-Boj *et al.*,⁴⁰ where an [100]-oriented truncated octahedron is the seed of two [111]B-oriented “wings”.

In the case of NSPDs, the top of the seed exhibits the formation of two extra twins forming an angle of 70.53° with the vertical direction, giving rise to a pentagonal grain boundary structure. It is important to note that a regular pentagon would have angles of exactly 72° , while the {111} twinning happens at 70.53° . There is a 7.32° mismatch that is relaxed by the creation of dislocations in the first few nanometers of the vertical twin boundary. This fact is clearly

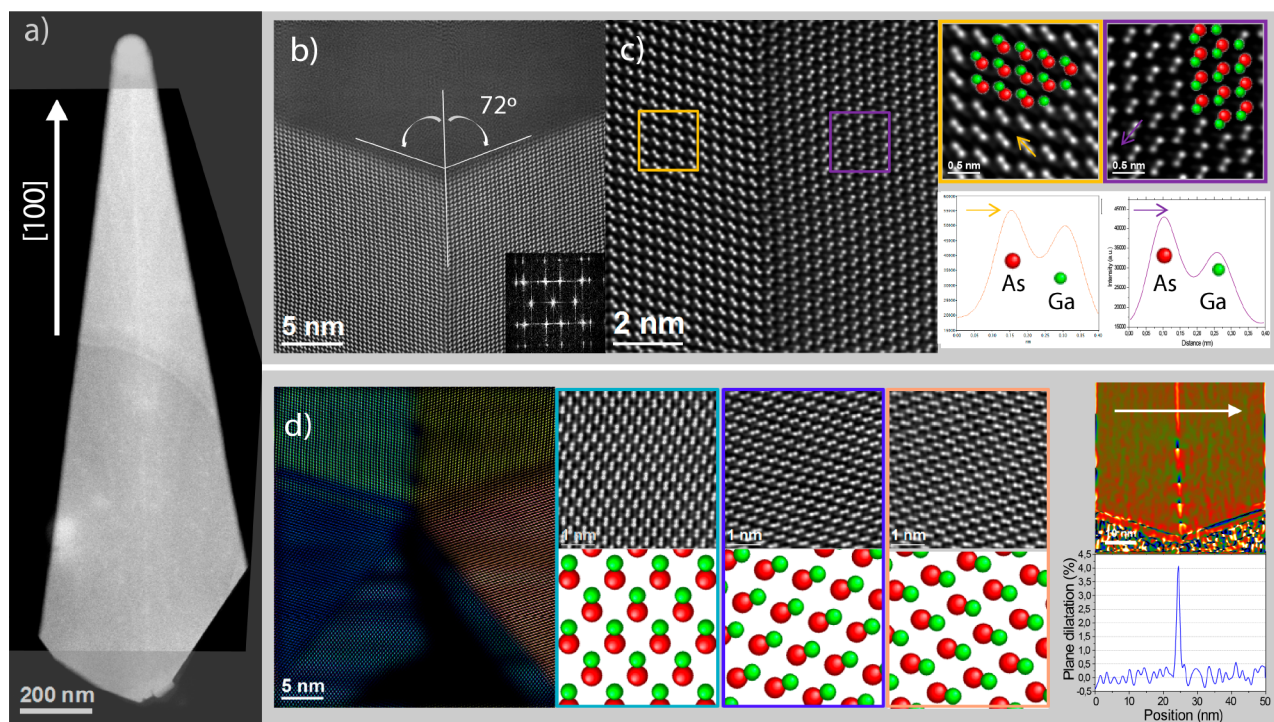


Figure 3. HAADF STEM study of the GaAs NSPD shown in (a). (b) Growth front. (c) Central vertical twin with the polarity of each side. (d) Color structural map of the penta-twin at the base of the NSPD and the resolved polarities of each grain. A geometrical phase analysis study at the base shows the plane dilatation on the vertical twin (the strain is around 4%), along with dislocations on this boundary. Far away from the base, after a partial relaxation, the remanent strain in the boundary along the $[100]$ direction is shown to be 2.5%.

visible in Figure 3d, where a GPA (geometrical phase analysis) study shows four misfit dislocations aligned on this domain boundary, and a plane dilatation of 4% is measured in the upper region. Figure 3c demonstrates that the structure succeeds in compensating for this mismatch, forming a virtually defect-free bicrystal.

Twinning with 5-fold symmetry has been observed in a variety of systems such as copper bulk⁴¹ and NWs,⁴² diamond,⁴³ Au,^{44,45} but also GaAs in a study by Däweritz *et al.*,⁴⁶ where RHEED (reflection high-energy electron diffraction) examinations of defects on GaAs(001) reveal a structure analogous to the nanospade pentagonal seed. L. D. Marks⁴⁷ presents modified Wulff constructions for twinned nanoparticles, including 5-fold symmetry twins. He divides the twinned particles into different segments bounded by the twin planes. Each segment possesses planes with given surface energies γ_x . For each twin boundary, the energy is divided into two fractions, $\alpha\gamma$ and $(1 - \alpha)\gamma$, respectively, for the segments sharing this twin, where α is defined as the partition coefficient. The lowest energy crystal shape is then determined by Wulff construction for each of the defined segments, with the twin boundaries included as pseudosurface facets. The volume partition and geometric constraints are also taken into considerations. If values of α_x can be found where the segments still assemble to a complete particle, a local energy minimum may be found. The symmetrical case of $\alpha = \frac{1}{2}$ and equal volumes for each segment is always a solution and proven to be a true minimum. In the case of a 5-fold symmetry twinned particle, a second solution arises by placing two asymmetric twin relationships, pushing the meeting point of the five segments well away from the particle center. This case resonates with the NSPDs, where the pentagonal twin is

located very close to the (100) substrate surface, *i.e.*, at the base of the structure. Despite the fact that our system is mainly kinetically driven, it is worth noting that such asymmetry can be caused by a difference in the twinning energies due to the polarity inversion.

Interestingly, Figure 3b shows the growth front formed by two $\{111\}$ planes that seem to grow simultaneously. This is known as the twin plane re-entrant (TPRE) mechanism, observed recently in the growth of GaAs NWs,⁴⁸ but also in other material systems such as ZnSe,⁴⁹ InSb,⁵⁰ and Si or Ge,^{51,52} but also in the bulk. Bulk TPRE configuration permits a fast expansion of platelets creating re-entrant edges, which at the same time serve as active nucleation sites. As elucidated by R. S. Wagner,⁵³ the TPRE mechanism in the bulk needs at least two twinning events to be stable. Otherwise, a single twin would rapidly outgrow itself. The platelet growth rate would then be limited by the nucleation at the ridge, which is significantly smaller. Nonetheless, Gamalski *et al.*⁵² showed that the nanoscale geometry allows steady-state growth based on a single twin boundary. Here, the growth rate of the structure is completely determined by the nucleation rate at the twin rather than at the triple-phase line. This prevents any of the sides of the twin from outgrowing the other. Thus, the structure remains symmetrical despite having one B-polar and one A-polar orientation, which are known to have different nucleation and growth rates.^{26,54–56}

One should note that contact angle engineering resulted into a maximized yield of 8%, which is relatively low. We believe this is related to the growth mechanism, combining both a polarity inversion and a 5-fold symmetry twinning. Nonetheless, we think that the yield could be further controlled. In particular, we believe the engineering of the pillar surface by nanofaceting could enable the TPRE mechanism without the

need of the pentagonal twin structure. In addition, introduction of impurities or change in the growth regime may as well increase the probability of 5-fold symmetry twinning and TPRE.^{57,58}

We now proceed with the proposal of a growth model for the NSPDs, combining our observations with other groups' results on the formation of penta-twins⁵⁹ and the *in situ* TEM observation of NW growth.^{52,54,60} Figure 4 depicts the model

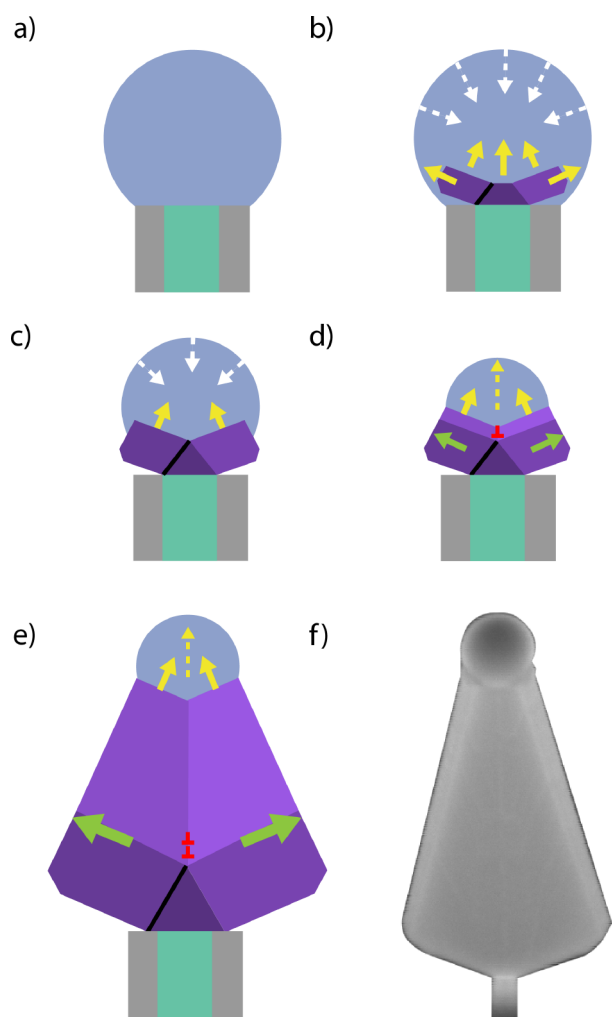


Figure 4. Schematic growth model depicting in (a) the Ga droplet pinning, (b) followed by the start of the growth with three VLS growth fronts: a [100]-oriented and two [111]-oriented. The droplet shrinks progressively, leading to a transient mode (c) that is followed by (d) the penta-twin formation. The growth is further continued by the VLS/twin plane re-entrant (TPRE) on top and the VS on the sides. The polarity inversion is highlighted by the dark line, the VLS growth by yellow arrows, and the VS growth by green arrows. Dislocations formed by the built-in strain are represented by inverted “T”-shapes. (f) Tilted SEM view of a generic nanospade.

we propose. The process starts with the pinning of the Ga droplet at the Si/oxide interface at the pillar tip. After a brief incubation time, the nucleation of GaAs layers starts. Initially, a [100] Ga-oriented pyramid forms (truncated octahedron), with the two opposite (111)A and (111)B facets. Overall, this results in five liquid/solid growth fronts, leading to a decrease in the size of the droplet due to Ga consumption. The [111]-oriented lateral fronts outgrow the (100) plane, reaching the

triple phase boundary, ceasing to be expanded by the VLS mechanism. After the termination of the [100]-oriented domain, a double-twinning event occurs, modifying the orientation of the growth front. As a consequence, the bicrystals constituting GaAs NSPD's main core are formed and grow perpendicularly to the substrate. The growth will proceed by the TPPE/VLS mechanism at the top, pushing the structure up. Additional VS growth expands the structure laterally, in two [110] directions (as is the case for typical NW growth).

The presence of twins and dislocations in semiconductor architectures could potentially reduce their viability for further applications. In order to assess the impact of the crystalline structure on the optoelectronic properties, we characterized them by luminescence. In particular, we were interested in obtaining signal of the defects at the NSPD base. For this, we increased the volume of the NSPDs by vapor–solid growth akin to ref 61. The thick NSPDs are then transferred flat onto a Au-coated Si substrate. Figure 5 shows in (a) the micro-photoluminescence (μ PL) spectra at 300 and 8 K and in (b) the cathodoluminescence (CL) spectra line scan.

In the RT (room temperature) μ PL spectra, an emission at 867 nm, which corresponds to the band gap of GaAs, can be seen, along with a secondary much weaker peak slightly above noise level between 900 and 930 nm. This secondary feature becomes almost invisible at 8 K, where the overall signal—corresponding to the free-exciton recombination emission in bulk GaAs at 1.51 eV and to an impurity-related band between 1.48 and 1.5 eV^{62–64}—is much higher. We attribute this weaker peak to defects at the base of the nanostructure. These defects exhibit energy levels with a limited density of states, as is usually the case for localized defects. As expected, emission from such states saturates with increasing excitation power, especially at low temperature, where recombination lifetimes are longer. By looking at the CL spectra in (b), the same feature is observed. The line scan along the NSPD unveils its origin at the base, close to the semiocahedron seed, the polarity inversion, and dislocations. It is concluded that those radiative transitions occur at the mentioned defects and are not observed in the rest of the structure. The CL spectra also show a decrease of the 819 nm exciton emission in the upper half of the structure. This is explained by the increase of the surface to volume ratio, quenching the emission by nonradiative recombinations at the GaAs surface. Further CL characterizations using AlGaAs shells and GaAs quantum wells are envisioned, along with a study on self-assembled quantum dots^{65,66} for assessing the impact of the NSPD structure on their formation.

CONCLUSION

To conclude, we have successfully designed and built an innovative Si platform for self-catalyzed VLS growth, consisting of etched nanopillars covered by a thermal oxide. The presence of a self-limiting oxidation effect permits a Si exposure in the chamber that is under 10 nm, enabling nonequilibrium growth conditions. The appearance of [100]-vertically oriented nanostructures, called nanospades, is a proof of the viability of this approach. A yield of NSPDs up to 10% has been obtained. This is expected to increase with further growth optimization. Overall, the NSPDs are mainly a bicrystal nucleated by penta-twins at the base. The optical properties are clearly consistent with high-quality GaAs. The penta-twin exhibits weak luminescence below the GaAs band gap, spatially

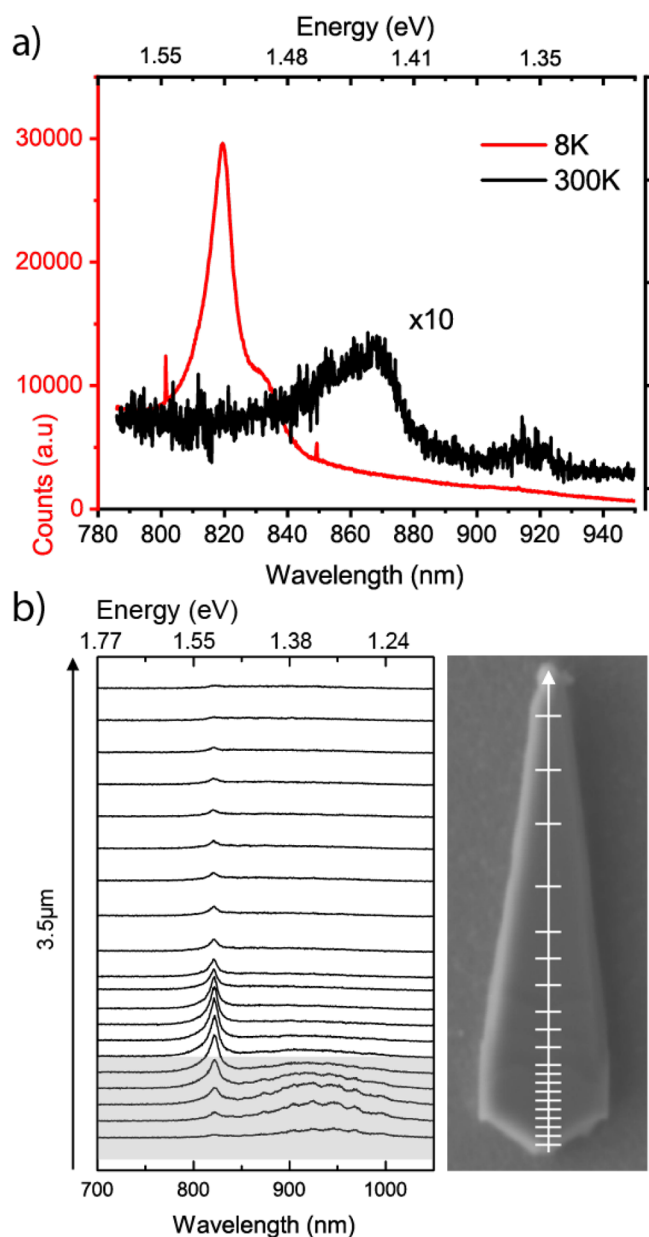


Figure 5. (a) Photoluminescence and (b) 10 K cathodoluminescence characterization of two different NSPDs. The vertical lines in the SEM picture show where the CL spectra have been acquired. Both studies show the presence of low-energy peaks linked spatially with the penta-twin and polarity inversion region.

localized at the base of the nanostructure. The NSPDs are promising structures for room-temperature lasing, energy harvesting, and photonic applications.^{61,67–71}

METHODS/EXPERIMENTAL

A 2 min 600 W O₂ plasma power in a TEPLA GigaBatch is done on a 100 mm Si wafer for surface activation before exposing it to e-beam lithography with a Vistec EBP5000ES and using Dow Corning HSQ 006 (hydrogen silsesquioxane) as a resist. The dose used is 2740 $\mu\text{C}/\text{cm}^2$ for all the pillars' diameters. The wafer is then developed using a commercial solution of Microposit[®] MF[®] CD26 for 2 min and rinsed sequentially with water, acetone, and propan-2-ol. A 2 min 600 W O₂ plasma power in a TEPLA GigaBatch is done for further cross-linking the HSQ. The wafer is then introduced in an Alcatel AMS200 DSE reactive ion etcher, where a customized recipe using SF₆ and C₄F₈ is used for creating the pillars. A buffered hydrofluoric acid (7:1) bath is

then used for 2 min to remove any trace of resist. A thermal oxidation is then done at 900 °C for a variable amount of time depending on the desired oxide thickness. After the oxide growth, a 20 nm styrene methyl acrylate based resist (ZEP) film is spin coated and heated for 2 min at 180 °C for polymerization. The sample is inserted in an Oxford Plasmalab system 80 PLUS using a mixture of SF₆ and CHF₃ at 100 W plasma power for 40 s to uncover the pillars. Ten minutes of O₂ plasma permits the removal of the resist, and a last cleaning involving a 5 min acetone bath, a 2 min propan-2-ol bath, and a 35 s HF bath at 1% concentration makes the sample ready for growth.

The growths are conducted in a DCA MBE chamber under a Ga BEP (beam equivalent pressure) of 0.14×10^{-6} Torr and an As BEP of 1.7×10^{-6} Torr for 45 min. The samples were characterized by SEM using a Zeiss Merlin and by HAADF STEM using a probe-corrected FEI Titan 60-300 equipped with a high-brightness field emission gun (XFEG) and a CETCOR corrector from CEOS. The μPL measurements were done using an in-house built setup using a 532 nm sapphire optically pumped semiconductor laser, and the CL using an Attolight Rosa 4634 SEM-CL microscope at 5 keV.

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Notes

The authors declare no competing financial interest.

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