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PAPER

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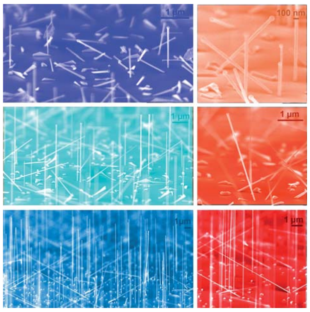

Nanowires grown under increasing V/III ratio. To obtain full vertical nanowires, temperature should also be changed.

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Suppression of three dimensional twinning for a 100% yield of vertical GaAs nanowires on silicon

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Multiple seed formation by three-dimensional twinning at the initial stages of growth explains the manifold of orientations found when self-catalyzed GaAs nanowires grow on silicon. This mechanism can be tuned as a function of the growth conditions by changing the relative size between the GaAs seed and the Ga droplet. We demonstrate how growing under high V/III ratio results in a 100% yield of vertical nanowires on silicon(111). These results open up the avenue towards the efficient integration of III–V nanowire arrays on the silicon platform.

A Introduction

The defect-free growth of III–V materials on silicon substrates would allow the integration of optoelectronic devices with CMOS technology, as well as the possibility of increasing the efficiency-to-cost ratio in solar cells.[1,2] The challenge of combining these two platforms is a consequence of: (a) the lattice-mismatch between III–Vs and silicon, and (b) the formation of anti-phase boundaries due to the mismatch in polarity between III–Vs and silicon. This area has gained a renewed interest, thanks to the possibility of obtaining defect-free III–V nanowires (NWs) on silicon or even germanium.[3–9] Although the self-organized growth of III–V NWs on silicon has been intensively studied in the last few years,[10–14] important issues such as those concerning the polarity mismatch between III–V NWs and the group IV substrate remain unsolved.

Recently, we have shown that multiple seed formation by three-dimensional twinning is responsible for the existence of a manifold of quantized orientations in self-catalyzed GaAs nanowires grown on silicon.[15] In this manuscript, we provide a detailed study about the occurrence of three-dimensional twinning with respect to the growth conditions. These results bring the necessary understanding for controlling the degree of complexity in nanowire arrays. In particular, we demonstrate the procedure by which a full yield of vertical GaAs nanowires can be obtained. This development is of great importance, as 100% yield vertical nanowires would for example avoid shortcuts in nanowire based solar cells or water splitting devices.[16,17]

B Experimental

Self-catalyzed GaAs nanowires were obtained on an undoped 2′ Si(111) substrate by the gallium-assisted method, in which a surface oxide is used to nucleate Ga droplets for the nanowire growth[18,19] using a DCA P600 MBE machine. The substrate temperature was previously calibrated by measuring the phase transition of the surface reconstruction of Si(111) from (7 × 7) to (1 × 1) at 830 °C.[20] The experiment is performed under an As partial pressure in the chamber below 10^{-13} Torr since an As exposure of the surface leads to a more stable Si(111):As (1 × 1) surface. The wafers were introduced directly in the MBE machine without any surface treatment or removal of the native oxide. Prior to growth, the substrates were degassed at 770 °C for 30 min. The nanowires were obtained under a rotation of 7 rpm at a temperature between 620 and 645 °C under a flux of Ga equivalent to a planar growth rate of 0.3 Å s^{-1}. The V/III beam equivalent pressure (BEP) ratio was varied between 15 and 60. The grown samples were then analysed by scanning electron microscopy (SEM) and aberration corrected high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM).[21] 3D atomic models have been obtained by using the Rhodius software package.[22]

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C Results

We start by presenting the occurrence of different growth orientations with respect to the substrate as a function of the growth conditions. Fig. 1 shows the SEM images of nanowires obtained under a V/III BEP ratio of 15, 30 and 60. The images have been taken at an angle of 30°. Nanowires grow directly on the substrate, with very little parasitic growth between them.[23] At the end of each nanowire, there is a gallium droplet leading the growth. We observe nanowires perpendicular to the substrate in all conditions. We also find many other orientations, especially for low V/III ratios. Particularly at the lowest ratio (V/III BEP = 15), we find many nanowires growing parallel to the substrate. As we increase the V/III ratio, the proportion of horizontal (crawling) nanowires decreases and is nearly null at a V/III BEP ratio of 60. A similar behaviour is observed for the other non-perpendicular orientations; they tend to be reduced for the higher V/III ratio but are still not zero at a V/III ratio of 60.

We have realized a quantitative statistical analysis of occurrence of the observed orientations. For this, we have combined cross-sectional and top view SEM measurements. As we have shown in our previous work, the analysis of the planar view allows us to realize a fast and reliable statistics on the occurrence of various angles. However, one of the disadvantages is that certain orientations cannot be distinguished unambiguously. This is the case for nanowires growing with a ±19° and 51° angle with the substrate. The histogram of orientations with respect to the surface for the three different growth conditions is shown in Fig. 2. We find six discretized orientations at angles: 0, ±19, 34, 51 and 90°. The occurrence of the particular angles different from 19 and 90° is a consequence of the formation of multiple seeds at the initial stages of growth combined with a 3D twinning phenomenon.[15] Several 3D animated atomic simulations of the growth mechanisms implying first and second order twinning can be found elsewhere.[24]

In order to understand the relative occurrence of the different orientations as a function of the growth conditions, start by recalling the structural relationship of the 111B orientations with respect to the underlying substrate. If nucleation takes place with a B polarity at the liquid–solid interface the NW will grow vertical to the substrate if no 3D twinning takes place. However if the droplet increases in size and expands beyond the top facet, 3D twinning will naturally take place in order to minimize the free energy and new 111B growth directions will start forming. Nanowire growth parallel to the substrate (0°) can be thought of as those which started from a GaAs B-polarized seed in the −19° 111B orientation and did not stop at the substrate surface but instead managed to continue growing crawling *via* a high order multiple twinning mechanism. For this reason we have put the −19° and 0° together in the histogram. A seed nucleating with A polarity results in a nanowire growing at 19° if it is free of 3D twinning. The angles 34° and 51° correspond to nanowires whose seeds have experienced a single 3D twinning phenomenon (marked II in the graph). The difference between them is the polarity in the nucleation, which is respectively B and A. We also observe one orientation typical of second order twinning after nucleation with A polarity, corresponding to nanowires marked with $\mathrm{III_A}$. Finally, all wires growing perpendicular to the substrate (90°) exhibit B polarity with respect to the substrate

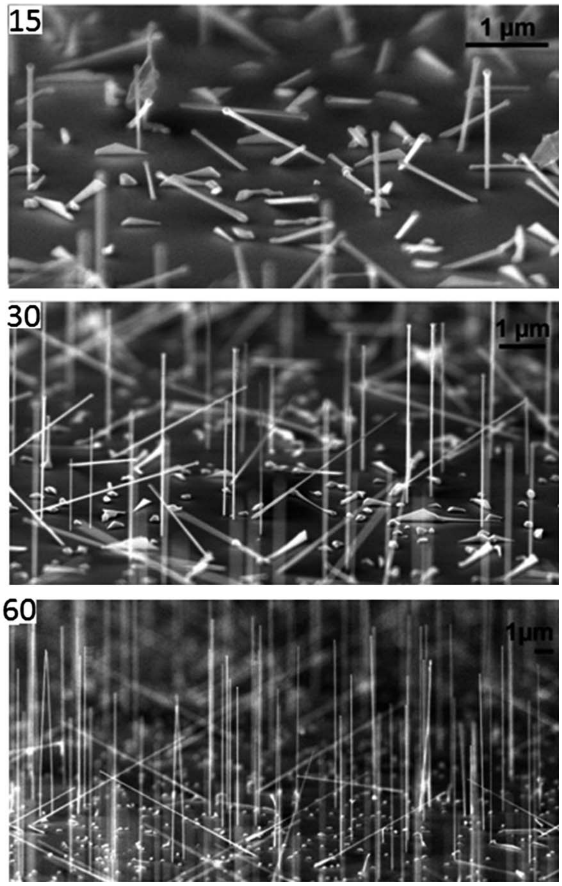

Fig. 1 Representative SEM micrographs of a field of nanowires grown at 620 °C under a V/III BEP ratio of 15, 30 and 60. The percentage of vertical nanowires increases.

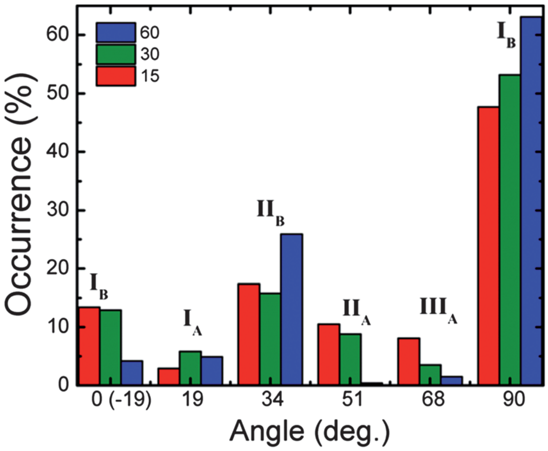

Fig. 2 Statistical analysis of the orientations of the nanowires with respect to the silicon surface as a function of the V/III BEP ratio. The labels I, II and III correspond respectively to first order nanowire growth and growth from second or third order seeds resulting from 3D twinning. The labels A and B refer to the polarity of the initial seed in contact with the substrate. The nucleation of seeds with A polarity decreases as the V/III BEP ratio is increased. Angles 0 and −19° are grouped together because crawling NWs start by growing towards the surface at −19°.

and have not suffered any 3D twinning phenomenon. From the results presented in the histogram, we deduce the general trend that the increase of the V/III BEP ratio results in the decrease of multiple twinning phenomena. Interestingly, we also find an important reduction in the initial seeds with A polarity. We speculate that the polarity of the initial seed might be linked to the time necessary for the formation of the seed. It seems that B polarity is favoured when this incubation time is reduced. This interesting phenomenon would require further theoretical investigations. Overall, we find an increase in the percentage of vertical wires, from 48 to 63%. Still, at the highest ratio the proportion of vertical nanowires is not 100%.

D Discussion

The characteristics of the seed formed in the initial stages of growth are intimately linked to the occurrence of orientations with respect to the substrate.[15] In the following, we try to elucidate the processes occurring in the initial stages of growth. We start by presenting a cross-section aberration corrected HAADF STEM micrograph of a nanowire and the substrate (Fig. 3). The interface of the nanowire and the substrate is not flat and abrupt. In fact, the GaAs penetrates about 5 nm inside the Si substrate. The interface at the bottom of this nanoscale hole is flat (parallel to the (111) orientation of the substrate). By analyzing the composition of the GaAs dumbbells at the GaAs/Si interface, we find that the polarity at the nucleation is B type (Fig. 3c and d). This is in agreement with the fact that this particular nanowire grows perpendicularly to the substrate and has not suffered any 3D twinning phenomenon.[15] We find the strain coming from the mismatch between GaAs and Si is released in the interface at the pinhole, allowing GaAs to grow perfectly relaxed (Fig. 3e).

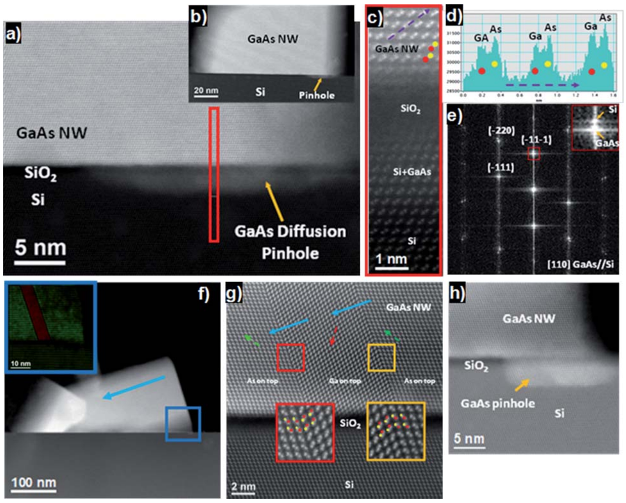

Fig. 3 (a and b) Cross-sectional aberration corrected HAADF STEM micrographs of a vertical nanowire, showing the formation of a nanoscale hole inside the silicon substrate; (c) magnified atomic resolution view of the red selected area in (a); (d) intensity profile obtained along the purple dashed arrow in (c); (e) power spectrum at the basis of the nanowire shows that the GaAs is completely relaxed; (f) cross-section aberration corrected HAADF STEM micrographs of a horizontal nanowire (−19 deg); the inset shows the formation of a twin boundary perpendicular to the growth direction; (g) magnified detail of the twinned area, polarity is kept along the twin boundaries; and (h) magnified detail of the pinhole region. Note that the final diameter of the nanowire is larger than the original pinhole because of the non-zero radial growth rate.

The formation of these nanoscale holes is not particular of the nanowire orientation, we have also observed it in nanowires growing in other directions (Fig. 3f and h). The size and morphology are in all cases quite similar. We believe that the formation of this nanoscale hole is related to the initial stages of growth in the following way: first, gallium gathers on the native silicon oxide forming droplets. Then, gallium pins at some defect of the native silicon oxide and reacts forming a highly volatile gallium oxide and silicon:[25]

$$SiO_x + Ga \rightarrow Ga_xO_y\,(\uparrow) + Si$$

As silicon is soluble in Ga at the growth temperature (1%),[26,27] gallium starts to dissolve the silicon thereby forming a nanoscale hole. By taking into account the solubility of Si in Ga, one can calculate that a 3 nm deep and 10 nm wide hole in the silicon can be obtained by the dissolution of a Ga droplet with a radius of 36 nm. This small calculation already hints at the possibility of having the Ga droplet larger than the initial GaAs seed. Finally upon supersaturation of the gallium droplet with As, growth starts at the interface with the substrate. For illustration, we have represented these steps in Fig. 4.

Given the picture of the initial stages presented here, one can try to depict in a qualitative way the role of the V/III ratio in the occurrence of 3D twinning. The first element to consider is the relative size between the Ga droplet and the GaAs seed. Indeed, as the V/III ratio is increased we might pass from a situation in which the Ga droplet covers completely the seed to the situation where it is just covering the top surface. Let us examine these two opposite cases, schematically drawn in Fig. 5a and b. Fig. 5c shows a model for the formation of horizontal (crawling) NWs (−19°, 0°) by following the growth mechanism proposed in (a) (initial octahedral seed). In Fig. 5d we show the growth mechanism for the formation of 34° NWs after a 3D twinning mechanism at the 2nd order.[28]

Let us consider what would be the shape of the seed with the minimal energy in each of the cases. Following Wulff's theory,[29] the equilibrium shape of the seed is given by the intersection of the lowest energy surfaces in the so-called 'gamma-plot'. It is not straightforward to apply Wulff's theory to solid–liquid systems out of equilibrium, but we can say that the thermodynamic driving force (the energy gain upon solidification per atom) is the greatest towards the corresponding 'Wulff shape' of the liquid–solid system. The system tends to form {111}B liquid–solid

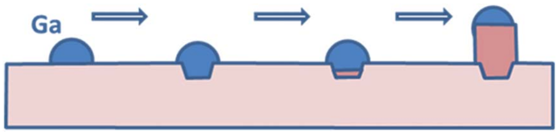

Fig. 4 Schematics of the initial stages of the Ga-assisted growth on a silicon substrate. The Ga droplet first pins on the substrate and, after dissolution of the native oxide, it dissolves the silicon forming a nanoscale hole. Upon saturation of the Ga droplet, the GaAs nanowire growth starts.

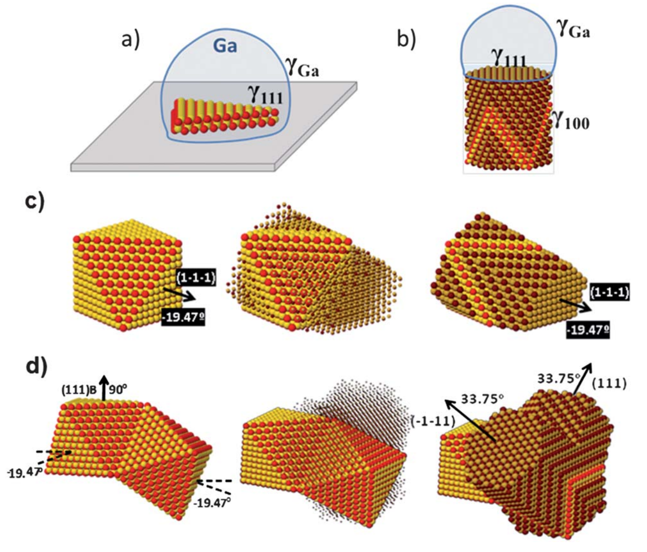

Fig. 5 Two different hypothetical case scenarios for the initial stages of nanowire growth. (a) For a low V/III ratio the Ga droplet covers the whole GaAs seed, thereby enabling the formation of octahedral seeds exhibiting (111) type of facets. (b) When the V/III ratio increases, the Ga droplet does not cover the totality of the GaAs seed, only the top (111) surface. In this case a hexagonal prism is energetically favorable. (c) Example of horizontal NW growth following the growth mechanism proposed in (a). (d) Growth mechanism following a second order twinning. See also the following link for 3D atomic animated simulations of the different twinning growth mechanisms: http://www.icmab.cat/gaen/research/160.

interfaces because this is the lowest free energy configuration of the system, however the choice of the 111B facet will depend on the relative size of the liquid phase. When the droplet is covering the seed and side facets, this is an octahedron. In the case where the Ga droplet is only covering the top surface of the seed, the most advantageous structure is composed of a top (111)B surface. The side facets which are not in direct contact with the Ga droplet pertain to the family {110}, as usually found experimentally.[30,31]

Now we turn to the important point of controlling the nanowire orientation with respect to the substrate. If we believe that the size ratio between the GaAs seed and the Ga droplet plays a role in the existence of multiple seeds, the substrate temperature could also be used for the further increase in the density of vertical nanowires. We have realized growths under a V/III BEP ratio of 60 at temperatures ranging between 620 and 645 °C. For our beam flux conditions the optimal substrate temperature is 645 °C. A typical SEM image of nanowires grown under a V/III BEP ratio of 60 and a temperature of 645 °C is shown in Fig. 6. Just with this small change in the growth conditions, we have obtained a 100% yield of vertical nanowires.

E Conclusions

We have presented a systematic study on the growth directions and occurrence of 3D twinning of MBE based Ga assisted growth of GaAs nanowires on silicon(111). We have shown how a small V/III ratio results in the existence of 3D twinning and a large percentage of quantized growth directions. We also demonstrate how a further optimization of the growth temperature results in a 100% yield of vertical nanowires.

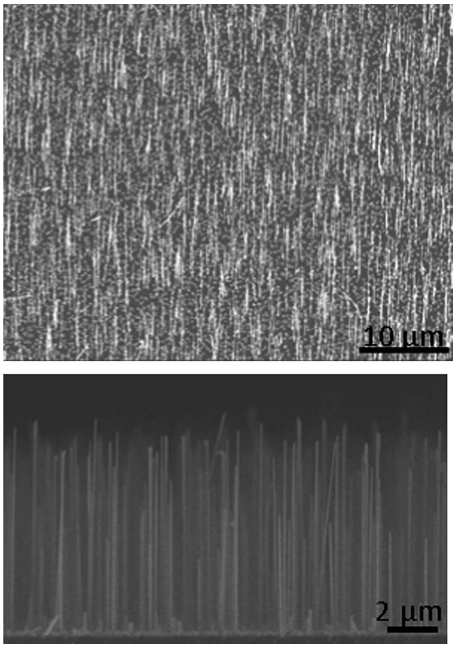

Fig. 6 Representative SEM micrograph of a field of nanowires grown at 645 °C under a V/III BEP ratio of 60 (top) and in cross-section (bottom).

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