

Rocking chair defect generation in nanowire growth

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We report the observation of a different defect generation phenomenon in layer-by-layer crystal growth. Steps at a nanowire liquid-solid growth interface, resulting from edge nucleated defects, are found to cause a gradual multiplication of stacking faults in the regions bounded by two edge defects. In the presence of a twin boundary, these generated defects continue to propagate along the entire nanowire length. This rocking chair generation mechanism is a unique feature of nanoscale layer-by-layer growth and is significantly different from well-known defect multiplication mechanisms in bulk materials. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4739948>]

Semiconductor nanowire (NW) growth is seeded by a liquid eutectic particle in an epitaxial layer-by-layer fashion.^{1,2} Such crystal growth at the nanoscale is distinguished by a single nucleation event for each succeeding atomic layer.^{2,3} Perfection is governed by interface properties that determine the driving forces for nucleation of a certain crystal phase⁴ or formation of defects.⁵ Therefore, nucleation, propagation, and interaction of defects in NWs can be dramatically different from those in bulk materials. We report here new defect generation mechanism in layer-by-layer crystal growth. This generation mechanism is mediated by atomic steps at the liquid-solid interface, which result from surface nucleated defects. When a new layer nucleation event switch between steps of surface nucleated defects, a gradual generation of stacking faults (SFs) in the regions bounded by these surface nucleated defects emerges. This rocking chair defect generation mechanism is a unique feature of NW layer-by-layer growth and contrasts well-known defect multiplication mechanisms in bulk materials such as Frank-Reed, cross-glide, climb or grain boundary-emission.⁶

Layer nucleation in a vapor-liquid-solid (VLS) grown NW emerges at the triple-phase-boundary (TPB) as illustrated in Figure 1(a).^{4,7} In the presence of SFs or twin boundaries (TBs), it is energetically favorable to nucleate a new layer at the interface between the SF or TB with the TPB (Figure 1(b)).⁸ In the case of a SF, nucleation is pinned at the SF/TPB (Figure 1(b)) until the SF exits the NW at the opposite edge, whereas for a single TB running parallel to the NW growth direction, nucleation is pinned at the TB/TPB throughout the NW length.⁸ With high supersaturations in the growth seed, nucleation of a new SF from the surface of the NW becomes possible. In the presence of two SFs in the NW, the probability of nucleation of a new layer at either SF is equal. As nucleation switches to the preexistent SF (SF1 in Figure 1(c)), fast ledge propagation—characteristic of VLS growth—encounters an atomic step at SF2, and a new fault forms within a couple atomic distances of SF2 (Figure 1(c)). We observe this mechanism in GaAs NWs and expect its applicability to other NW systems. The GaAs NWs were grown by metal-organic chemical vapor deposition

(MOCVD) in a horizontal reactor (Aixtron 200) on GaAs(111)B substrates using 40 nm diameter Au colloids at a temperature of 430 °C, pressure of 50 mbar and a V/III ratio of 14.25.⁹ Structural characterization was performed using a high-resolution transmission electron microscope (HR-TEM, 300 keV FEI Tecnai F30) and Gatan Digital Micrograph software was used to identify defects in the GaAs NWs.

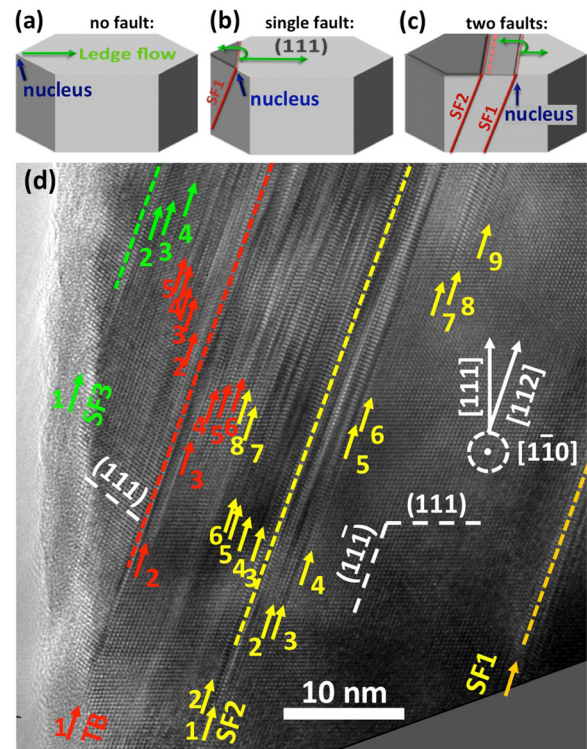


FIG. 1. Perspective view of nucleation and ledge flow in NWs at their faceted surface and triple-phase boundary (a) in the absence of defects (b) at the triple-phase intersection with stacking fault, marked by blue arrow, (c) and at triple-phase intersection with one of two SF2 leading to a new stacking fault (dashed red line) near SF2. (d) HRTEM image of a GaAs NW with multiple surface-nucleated SFs and a TB marked by dashed lines. In any region bounded by two faults, a successive increase in the density of SFs (numbered ≥ 2) outgoing from the surface-nucleated SFs or SF/TB is observed.

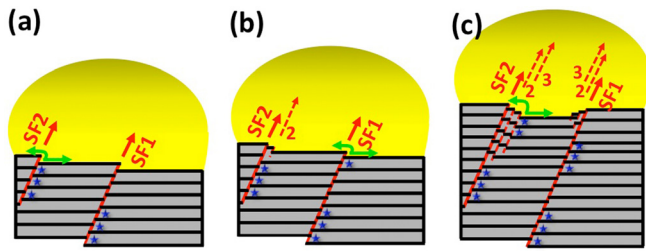


FIG. 2. Schematic representation of the generation mechanism: (a) Layer nucleation (blue star) at SF2 and subsequent layer growth in a NW with two defects. (b) Switching nucleation to SF1 and subsequent ledge propagation toward SF2 encounters a step at SF2 resulting in the generation of an additional SF (marked 2) near SF2. (c) Repetition of the process in (b) leads to generation of successive SFs in between the two surface-nucleated SFs.

Figure 1(d) shows a HRTEM image of a GaAs NW showing three surface nucleated stacking faults (SN-SFs) and a surface nucleated twin boundaries (SN-TB) illustrating this mechanism. Multiple SFs are generated in regions bounded by SN-SFs or a SN-SF/SN-TB. In the first ~ 70 (111) bi-layers to the left of TB (red dashed line), there are no additional generated SFs. When SF3 emerges (green dashed line), successive nucleation of multiple SFs is observed (green and red arrows numbered in sequence of formation). All regions bounded by SN-SFs show a consistent behavior: SFs emerge near SN-SF and SN-TB and their density increases periodically toward the center of the bounded region between them.

In the postulated SF generation mechanism (Figures 1(c) and 2(a)–2(c)), the nucleation energy for the next layer is lowest at TBP intersection of the SF and NW surface (blue arrows in Figures 1(b) and 2(c) and stars in Figures 2(a)–2(c)) and this leads to one additional bi-layer, above blue star in Fig. 2(a) that stacks to preserve the underlying structure. Following a nucleation event at SF1 (Figure 2(b)), fast ledge propagation on the (111) surface encounters a surface step (Figure 1(c)), resulting in formation of a new SF near SF2 (dashed red line in Figure 1(c) and arrow in Figure 2(b)). Random switching of nucleation between the two SFs leads to alternating generation of SFs as illustrated in Figure 2(c) and observed experimentally in Figure 1(d). It is possible to nucleate simultaneously at SF1 and SF2 at high supersaturations in order to create an inward step at SF1 or to balance the line tension at the TPB on opposite edges of the NW.

This defect generation mechanism can explain in part the presence of dense stacking faults and lamellar twins previously observed during the growth of groups IV (Ref. 10) and III-V (Ref. 11) semiconductor NWs. While these SFs spread on one of three {111} slip planes that are 19.5° from the [111] growth axis (Figure 1(d)), the TB leads to distortion of the force balance at the TPB and NW kinking to a new [112] growth orientation.⁸ With the new [112] orientation (Figure 3(a)), the generated SFs run parallel to the NW growth axis and are as such preserved throughout the length of the NW (Figure 3(b)). For the generated SFs to the right of SF2 in Figure 1(d), we noticed that these SFs did not propagate throughout the NW length. Additional TEM analysis has shown that these particular SFs recover as SF1 annihilates (Figure 3(c)) before it exits the NW at the right edge. It is worth noting that superlattice structures along NW axes

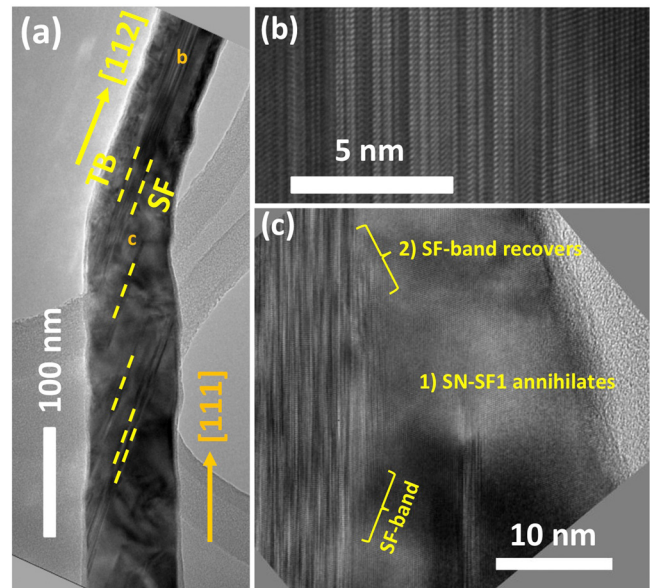


FIG. 3. (a) TEM image of the GaAs NW of Figure 1 showing multiple surface-nucleated stacking faults running in [112] direction and are therefore preserved as the NW kinks from a [111] to a [112] orientation. (b) HRTEM image showing that the generated defects prevail in the newly kinked wire. (c) HRTEM image showing that SN-SF1 annihilates just before the kink (marked “c” in panel (a)).

that are formed with such mechanism contrast those perpendicular to NW axes frequently found in III-V NWs.⁵ It is possible that missing planes of either group III or IV could exist at these SFs but this could not be confirmed in this present study.

In summary, we reported the observation of a new defect generation mechanism in semiconductor NWs. This mechanism stems from the characteristic layer-by-layer growth at a liquid-solid growth interface. Steps that are formed by surface nucleated defects lead to the generation of additional SFs in regions that are bounded by those defects.

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