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Imaging Defects in Nanometer-scale Semiconductor Crystals: Statistical Nucleation Events are Few in Small Crystals, but can Control Growth

W.MoberlyChan, G.Seryogin, I.Shalish, C.Wen, S.Hu*, X.Guo**, V.Narayanamurti, & F.Spaepen
Harvard University, DEAS & CIMS, Cambridge, MA 02138. *NNDL, Hsinchu. **IPAS, Taipei.

Defect control in semiconductor devices is as important for present-day nanometer-diameter fibers and devices as for single crystal silicon. TEM images 3 types of growth defects in small fibers: dislocations, stacking faults, and twins. (Point defects are not easily imaged by TEM. Grain boundaries are rare as the nanometer-scale devices are smaller than even a single grain wants to be.) Near-by free surfaces enable most dislocations to grow out of small-diameter crystals. However, stacking faults and twins may occur in these zincblende/wurtzite/diamond-based crystal structures, with interdependence to the growth orientation.

Small crystals have been processed by many methods [1]. Ideal catalysts (neither consumed nor altered during growth) can limit location and diameter of crystal; and CVD may grow semiconductor phases at low temperature without damaging neighboring microdevices. Figure 1a is an SEM image of hexagonal-2H-c-axis-GaN fibers grown on sapphire using patterned Ni/Au as catalysts [2]. BF-TEM (Fig. 1b) depicts dendritic defects. Having lost catalytic control, these sub-fibers grow along $[0\bar{1}10]$, normal to the [0001] main fiber. The smaller fibers fatten; however, the noncentrosymmetric GaN structure limits polarity-controlled growth [3] only "upward" [0001] (not $[000\bar{1}]$). Now [0001] growth nucleates stacking faults and twin defects; and coalescence of two nuclei forms out-of-plane defects. The 2H structure changes to 3C-cubic, and fibers curve upward due to tensile stress. Such defects are readily visible in $[\bar{2}110]$ HR-TEM or diffraction, Fig. 1c & 1d. However, if the curved and defected 2-phase fiber is rotated 90°, [0001]-TEM images a "straight" fiber and diffraction views a "single crystal".

Figure 2a is a cross-section lattice image of shape, surface facets, and internal defects of Si fiber (courtesy of Shu-Fen Hu & Xing-Jian Guo). Plane-view imaging and diffraction ease sample preparation and statistical analysis of such defects. However, judicious TEM tilts are needed to analyze these {111} faults, (30° along the growth axis, Fig. 2b). For an FCC crystal, with {111} twins extending along entire $\langle\bar{1}10\rangle$ fiber, there is "no" orientation normal to the fiber that readily depicts the twin by diffraction. A (111) fault is invisible along [111], and the orthogonal $\langle 11\bar{2}\rangle$ axis exhibits no twin symmetry. For random normal TEM (neither [111] nor $[11\bar{2}]$), the fault(s) are inclined to the beam ; being difficult to discern by HR-TEM and having less BF-fringe-contrast in smaller fibers. However, double diffraction through an inclined twin is distinct (e.g. the 1/3<224> reflections in FCC-Cu films.) Figures 3a, 3b ($\langle 1\bar{1}0\rangle$, $\langle 11\bar{1}\rangle$) calculate double diffraction (Desktop Microscopist) of an inclined {111} twin plane. Fig. 3b represents many general cases with only one twin close to a major zone; however, the inclined twin plane enables double diffraction (1/3<224>). Figure 4 models growth of a crystalline fiber with defects. The catalyst cap constrains the "diameter". (Note final fiber is typically facetted, Fig. 2a.) In general, the crystal may nucleate anywhere beneath catalyst and also with any crystal growth orientation; although heteroepitaxy can insure a growth normal to the substrate (Fig. 1a). The fiber develops energetically favorable side facets. The catalyst interface plane need not be normal to the growth axis; however, this "growth plane" and side facets do cause a specific growth orientation. (Small fibers may macroscopically curve, as planes easily "bend".) Multiple nuclei are statistically possible, especially for larger diameter fibers. Defects may "come and go" during growth, but the twin in Model 4 grows indefinitely, providing constant kink sites to enhance growth. A $\langle\bar{1}10\rangle$ orientation develops, whereas either twin alone would grow $\langle\bar{1}11\rangle$. Several growth orientations have been reported, and fiber diameter related to growth direction [4]. However, the growth orientation can be controlled by defects, which in turn are dependent on the statistics of nucleation. Although the twin is easy to interpret in this 2D model, it is not readily visible by TEM normal to a 3D fiber; and analysis requires a difficult 30° tilt of small fibers.

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Ref. 2. G. Seryogin, et al, "Catalytic hydride vapor phase epitaxy growth of GaN nanowires, submit. to APL.
Ref. 3. J. Jasinshi, et al, "Characterization of hydride vapor phase epitaxy GaN, APL 78:2297-99, 2001.
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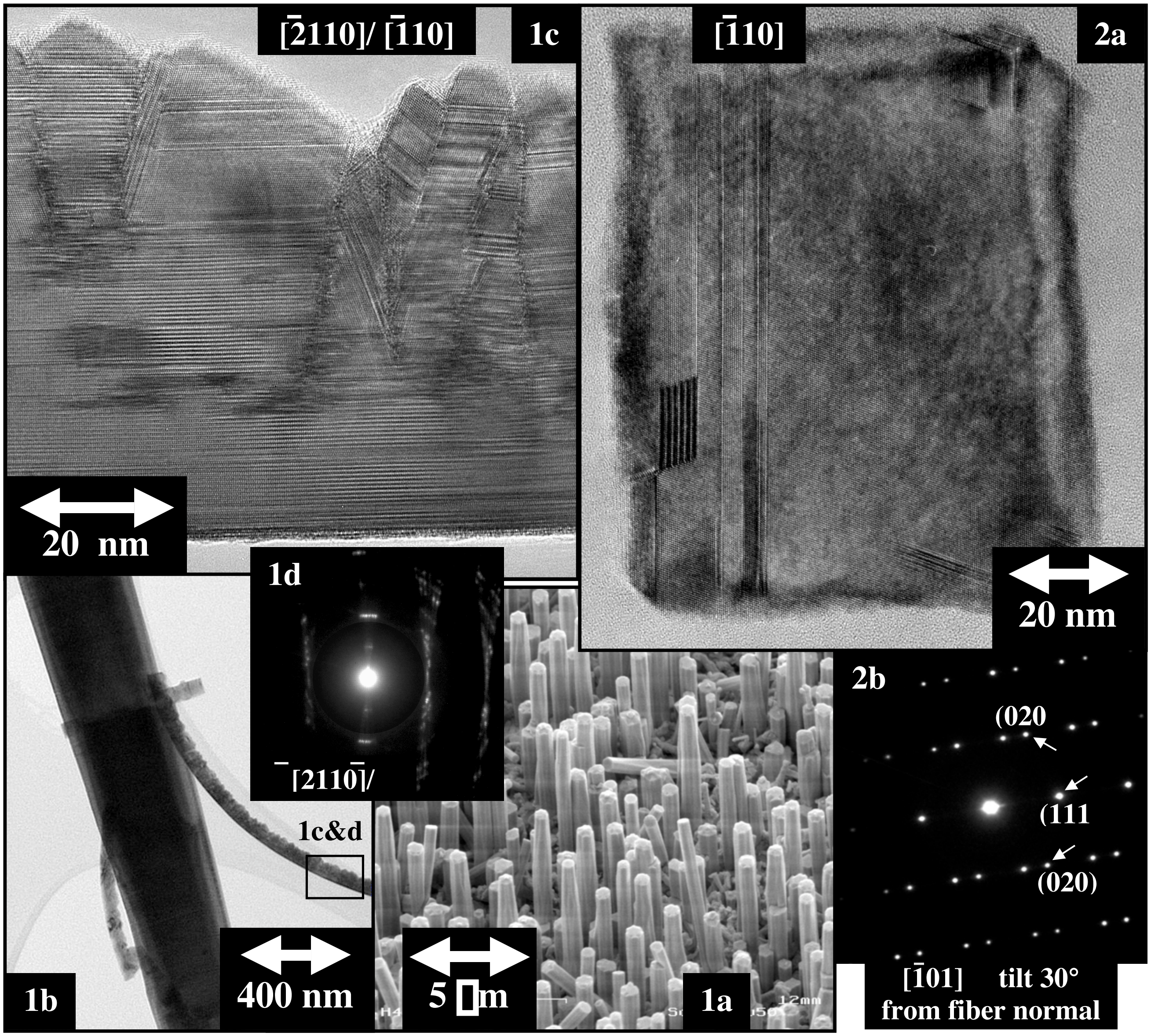

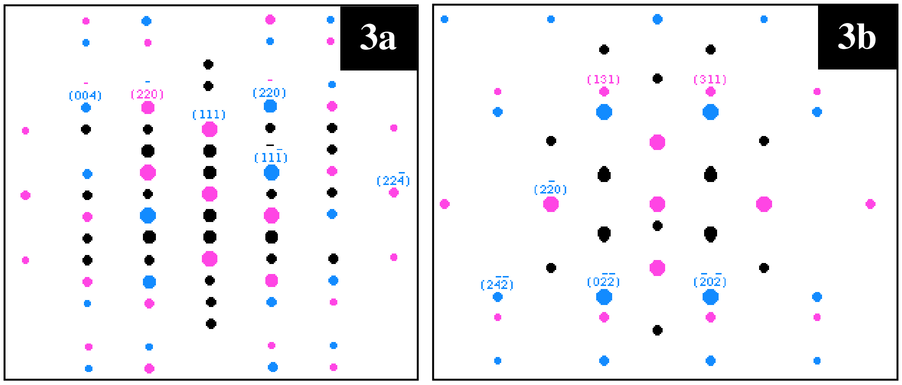

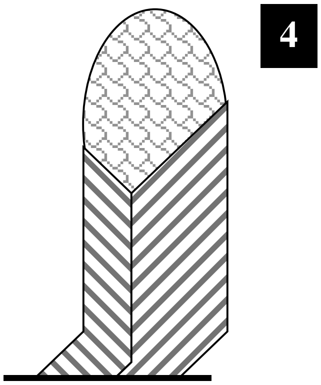

FIG. 1. SEM & TEM of GaN fibers. 2H-GaN grows straight, but multiple defects can lead to cubic-GaN. FIG. 2. TEM of Si fibers: faults visible either in X-TEM (S.Hu, X.Guo) or non-normal to fiber. FIG. 3. Calculated SADPs with 1/3<2224> double diffraction due to inclined defect planes. FIG. 4. Multiple nucleation model with defect plane enhancing growth and controlling orientation.