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A little ribbing: Flux starvation engineering for rippled indium tin oxide nanotree branches

Ryan T. Tucker,1 Allan L. Beaudry,1 Joshua M. LaForge,1 Michael T. Taschuk,1 and Michael J. Brett1,2

1Department of Electrical & Computer Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada
2National Institute for Nanotechnology, Edmonton, Alberta T6G 2M9, Canada

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Combining vapour-liquid-solid growth with glancing angle deposition (VLS-GLAD) facilitates fabrication of branched nanowires not possible with either technique alone. Indium tin oxide (ITO) nanostructures grown by VLS-GLAD produce extremely porous nanotree structures, where periodic branch diameter oscillations are sometimes observed. We explain this rippled branch growth with a simple model linking the physics governing branch growth to the process variables controlled in VLS-GLAD. The model is verified by inducing specific, aperiodic ripples onto growing ITO branches through macroscopic vapour flux control and manipulation of local shadowing. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4764508]

The vapour-liquid-solid (VLS) mechanism, whereby growth proceeds by precipitation from a liquid catalyst that concentrates the surrounding vapour, has been used to grow crystalline whiskers.1 Branched nanowires (or nanotrees) can be formed by placing catalytic droplets on the sides of nanowires during growth via a stochastic or engineered process, enabling bottom-up fabrication of complex three-dimensional architectures.2,3 Control over intra-wire morphology has also been investigated, with several groups reporting variations in nanowire diameters.4–15 Givargizov and others suggest an unstable model of self-oscillations based on droplet contact angle and surface roughness driven by droplet supersaturation.4–6,13 Most of these reports attribute rippled (or bamboo) nanowire structures to this self-oscillatory growth mode.5–8,13,14 However, others have demonstrated discontinuous diameter changes through annealing-driven catalyst migration,12 switching between different crystal cross-sections during growth,15 and segmented nanowire morphologies controlled by carrier gas pulsing.9

Recently, a geometrical modification of VLS growth through glancing angle deposition (GLAD) was developed.16–18 For the self-catalyzed indium tin oxide (ITO) system,19–22 this technique (VLS-GLAD) provides additional control over nanowhisker diameter, spacing, and branching behavior.18 Two key features distinguish VLS-GLAD: (i) a collimated (low divergence) flux which breaks flux symmetry at the growth surface, enabling geometrical shadowing effects to mediate the nanowhisker growth and (ii) three-dimensional substrate motion to orient the flux during growth. Continuous rotation about substrate normal modulates the incident flux on the branches as they pass through the trunk’s shadow. In response, the branch diameter oscillates during growth producing a rippled surface. Figure 1 shows ITO nanowhiskers grown by VLS-GLAD exhibiting branch ripples. The ripple period shown in Figure 1(b) is consistent between branches ($\sigma_{\text{RSD}} = 15\%$), as expected in the trunk-dominated shadowing model. Unlike the self-oscillatory mechanism, surface ripples produced by flux shadowing are controllable through engineering of substrate motion during growth. Here, we present our observations of branch surface rippling, derive a model linking branch growth physics to experimentally accessible variables in the VLS-GLAD technique, and verify the explanation by inducing aperiodic ripples into growing branches. As changes in incident flux drive change in the diameter, this model captures diameter control modulated by both motion-controlled shadowing and flux rate. The VLS-GLAD technique provides an opportunity to study VLS growth kinetics, and produces nanostructures that have been previously unachievable.

We describe VLS-GLAD ITO nanowhisker growth in our previous work.18 Briefly, samples were grown in a high vacuum system (<0.1 mPa) with dynamic control of the angle between vapour flux source and substrate normal ($\alpha$) and rotation about substrate normal ($\phi$) (see Figs. 2(a) and 2(b)). Si substrates were heated by two 150 W halogen lamps

![Fig. 1. SEM images of VLS-GLAD ITO nanotrees exhibiting rippled branch features deposited with the parameters (a) $\alpha = 87^{\circ}$, $T = 240\, ^{\circ}\text{C}$, $R = 2\, \text{Å/s}$, $\tau_{\text{ex}} = 50\, \text{s}$; (b) magnified edge and (c) plan view of $\alpha = 85^{\circ}$, $T = 240\, ^{\circ}\text{C}$, $R = 10\, \text{Å/s}$, $\tau_{\text{ex}} = 10\, \text{s}$. All scale bars are 200 nm.](image-url)
and shrinking of the droplet. The growing branch’s diameter follows droplet diameter, as long as the droplet does not become completely depleted. Figure 2(b) shows this rotational effect on flux arriving at a droplet and its periodic nature in an ideal case. The correct conditions produce periodic ripples along the branch growth direction. However, the GLAD process is tunable, and can produce complex shadowing environments, providing a route to enhancing control of VLS growth.

The schematic in Figure 2(c) shows the parameters used in a model relating volume change to both flux rate and rotation rate. Using MATLAB, a single droplet of hemispherical shape was simulated in a finite time domain for varying incoming flux volume. For simplicity, only single branch growth was considered. One type of particle was used, with properties calculated for an average atom in a cubic 91% In2O3-9% SnO2 lattice: \( \rho = 7.18 \text{ g/cm}^3 \), 55.0 g/mol, and monolayer thickness \( d = 233 \text{ pm} \). All vapour phase atoms within a certain projected area, \( A \), were assumed to condense into the liquid droplet (we expect a high probability of atom diffusion to the liquid droplet within a certain distance\(^2\)). The rate of incoming volume to the droplet (\( V_{in} \)) was calculated

\[
V_{in}(t) = RA \gamma(t),
\]

where \( R \) is the material flux rate as measured at the QCM in nm/s and \( \gamma \) parameterizes the flux modulation due to rotation-induced shadowing or flux shuttering \( (0 \leq \gamma \leq 1) \). For continuous rotation, \( \gamma(t) = (\sin(2\pi t / \tau_{rot}) + 1)/2 \), where \( \tau_{rot} \) is the rotation period in seconds. As neighbouring trunks increase in height, a branch will eventually become completely occluded from the flux. This effect is incorporated as an envelope on \( V_{in} \). For this work, we approximate the envelope as an exponential of the form \( 1 - e^{a(t-t_{max})} \), where \( a \) is a constant and \( t_{max} \) is the time for a certain branch to grow. Detailed studies will be required to elucidate the envelope’s functional form.

We assume the branch crystallizes in a layer-by-layer, or birth and spread growth mode,\(^{25,26} \) with each layer having a circular cross-section of the same radius as the droplet and monolayer thickness of \( d \). We further assume nucleation time dominates layer crystallization time, such that liquid-solid crystallization time \( (\tau_{LS}) \) is independent of droplet size and constant for growth of an entire branch. In reality, the growth rate is likely dependent on droplet diameter,\(^{27,28} \) however, this assumption is tolerable for small changes in droplet diameter. The rate of outgoing volume from the droplet is then

\[
V_{out}(t) = d \pi r(t)^2 / \tau_{LS},
\]

where \( r \) is the instantaneous radius of the both the droplet and the branch at the liquid-solid crystallization interface. For growth of a branch of length \( L \) in time \( t_{max} \), \( \tau_{LS} = t_{max} d / L \). Note that this is not valid at extremely slow rotation rates where the droplet becomes extinct. At each time step \( t_i \) of length \( \Delta t \), the instantaneous droplet volume and droplet/branch radius were then calculated

\[
V(t_i) = V(t_{i-1}) + \dot{V}_{in}(t_i)\Delta t - \dot{V}_{out}(t_i)\Delta t,
\]

FIG. 2. Schematic of VLS-GLAD rippling phenomenon. Side view (a) shows glancing angle (\( \alpha \)) and flux shadowing region. Darker droplets are receiving incoming flux and lighter droplets are occluded; (b) plan view shows rotation of substrate by the angle \( \varphi \), and flux modulation (\( \gamma \)) at a droplet from shadowing by the attached trunk; (c) droplet radius (\( r \)) and volume (\( V \)), branch length (\( L \)) and monolayer thickness (\( d \)), flux rate (\( R \)) and capture area (\( A \)), and incoming/outgoing volume rates (\( V_{in}/V_{out} \)), as used in the model.

From mass conservation, droplet diameter is controlled by the vapour flux capture rate and the liquid-solid crystallization rate. Vapour flux capture rate is a function of evaporation conditions, adatom diffusivity, and most importantly for the work presented here, the local shadowing environment a growing nanowire experiences. Unlike typical isobaric VLS growth systems, the collimated vapour approach used here allows for dynamic control over local vapour pressure. For a growing nanowire array, high deposition angles (\( \alpha \)) produce shadows between adjacent nanowires, as shown in Figure 2(a). When deposition flux is occluded by “upstream” nanowire trunks or branches, the liquid Sn-In-O droplet is starved of growth material. Vapour undersupply can lead to droplet decay and subsequently, branch tapering.\(^{23} \) In some cases, the liquid-solid crystallization process can continue until the droplet is exhausted, resulting in a blunt-ended nanowire.\(^{20} \)

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V(t_i) = V(t_{i-1}) + \dot{V}_{in}(t_i)\Delta t - \dot{V}_{out}(t_i)\Delta t,
\]
The calculated input and output volume rates ($\dot{V}_\text{in}$ and $\dot{V}_\text{out}$, respectively) are shown in Figure 3(a) in the case of constant rotation with $R = 1 \text{ nm/s}$ and $\tau_{\text{rot}} = 10 \text{ s}$. From the magnified image of the branch (Fig. 3(b)), we measure $L = 225 \text{ nm}$ and 13 rippling nodes. Based on the number of nodes and rotation speed, we calculate $t_{\text{max}} = 125 \text{ s}$, with $\tau_{\text{LS}} = 0.13 \text{ s}$. We achieved a fit of the extracted branch profile by varying the envelope parameter ($a$) and capture area ($A$). A good match is shown in Figure 3(c) between the observed and simulated rippling behavior for parameters of $a = 0.025$ and $A = 4900 \text{ nm}^2$ (equivalent to a circle with $\sim 39.5 \text{ nm}$ radius). Several other rippled branches were simulated (not shown) and all showed good fit with the model.

To explore the conditions for which these rippling effects can be observed, the same simulation was run with different rotation speeds. Figure 3(d) shows a simulation of the same parameters, but with $\tau_{\text{rot}} = 1 \text{ s}$, $\tau_{\text{rot}} = 100 \text{ s}$, and $\tau_{\text{rot}} = 1000 \text{ s}$. In the case of $\tau_{\text{rot}} = 1 \text{ s}$, the rippling effect is still present, however, the amplitude of the rippling is so small that it is only visible in the magnified inset. For the case of one and two orders of magnitude increase in rotation time, the length of the rippling events is on the order of the branch length. The rippling is effectively lost as a result of the slower rotation times.

To further validate the hypothesis that rippling is a result of flux starvation, more complex structures were grown by two different methods of controlling the incoming flux to the liquid droplet. This was achieved by controlling the local shadowing function (e.g., changing the rotation rate) and by attenuating the vapour flux directly (e.g., rate control or shuttering). The model indicates that both methods should have a similar effect. We have previously shown that rate modulation dynamically controls ITO nanowhisker diameter; here we have demonstrated the effect of shuttered flux and the local shadowing environment. ITO nanowhiskers grown with shuttered flux are shown in Figure 4.

We use the flux shutter profile shown in Figure 4(a), with constant rotation, to produce the ITO nanowhisker shown in Figure 4(b). The branch’s features follow the shuttering events, controlling ripple amplitude and frequency. Figure 4(c) is a magnified image of a characteristic branch. Figures 4(d) and 4(e) show the approximate shuttering ($\gamma_{\text{shutter}}$) and rotational shadowing ($\gamma_{\text{rotation}}$) functions, respectively, resulting in the total flux modulation function ($\gamma$). Figure 4(f) contributes to the growth of the magnified branch. In both the shuttering and variable rotation cases, we demonstrate control over the rippling features according to the flux profile. Faster rotation rates result in smaller ripple spacing, and shuttered flux can result in long nodes between ripples. Both the variable rotation and shuttering methods demonstrate (through local shadowing and macroscopically modulated vapour pressure, respectively) direct control over supersaturation in the branch droplets.

\[ r(t_i) = \sqrt{3V(t_i)/2\pi}. \]  

FIG. 3. Branch simulation (a) input volume rate ($\dot{V}_\text{in}$) to droplet for $\tau_{\text{rot}} = 10 \text{ s}$ and volume rate out ($\dot{V}_\text{out}$) of the droplet as calculated in each time-step; (b) enlarged SEM image of a branch deposited at $t_{\text{rot}} = 10 \text{ s}$; (c) branch edge profile (open circles) and simulated branch morphology (red line) for $t_{\text{rot}} = 10 \text{ s}$; (d) simulated branch profile for $t_{\text{rot}} = 1 \text{ s}$ (blue), $t_{\text{rot}} = 100 \text{ s}$ (green), and $t_{\text{rot}} = 1000 \text{ s}$ (magenta); y-axis of inset is 1 nm range.

FIG. 4. Complex VLS-GLAD ITO branch growth by shutter-modulated flux according to the pattern shown in (a), where 1 is shutter open and 0 is shutter closed; (b) SEM image of resulting nanowhisker with unique branching morphology; (c) magnified key branch region, with (d), (e), and (f) displaying the flux modulation due to shuttering, due to rotation-induced shadowing, and the combined shutter-rotation effect on the flux profile, respectively, for the magnified branch.
We have demonstrated that flux starvation in VLS-GLAD enables controlled branch diameter modulation during ITO nanotree growth, consistent with a simple volume in/out model. Flux starvation can be induced through shading or by adjusting the flux rate directly, both general features of VLS-GLAD. The nanostructures made possible by the VLS-GLAD technique should be available to any material system compatible with branched VLS growth.

Droplet diameter is coupled to nanowire properties such as composition,\textsuperscript{9,36} phase,\textsuperscript{31} and crystallographic growth direction.\textsuperscript{32,33} Thus, modulation of growth diameter with VLS-GLAD may provide a mechanism to modulate these properties during growth as well. Surface rippling may prove to be a valuable technique to enhance active surface area, create high energy surface defects, or induce phase changes in the material during growth. This technique also allows for the placement of “time stamps” during growth which may allow for improved investigation of time-related growth kinetics.

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See supplementary material at http://dx.doi.org/10.1063/1.4765438 for a demonstration of similar rippling control with varying rotation rates.