Electronic Supplementary Information for

Silicon Oxide Nanowire Growth Mechanisms Revealed by Real-Time Electron Microscopy

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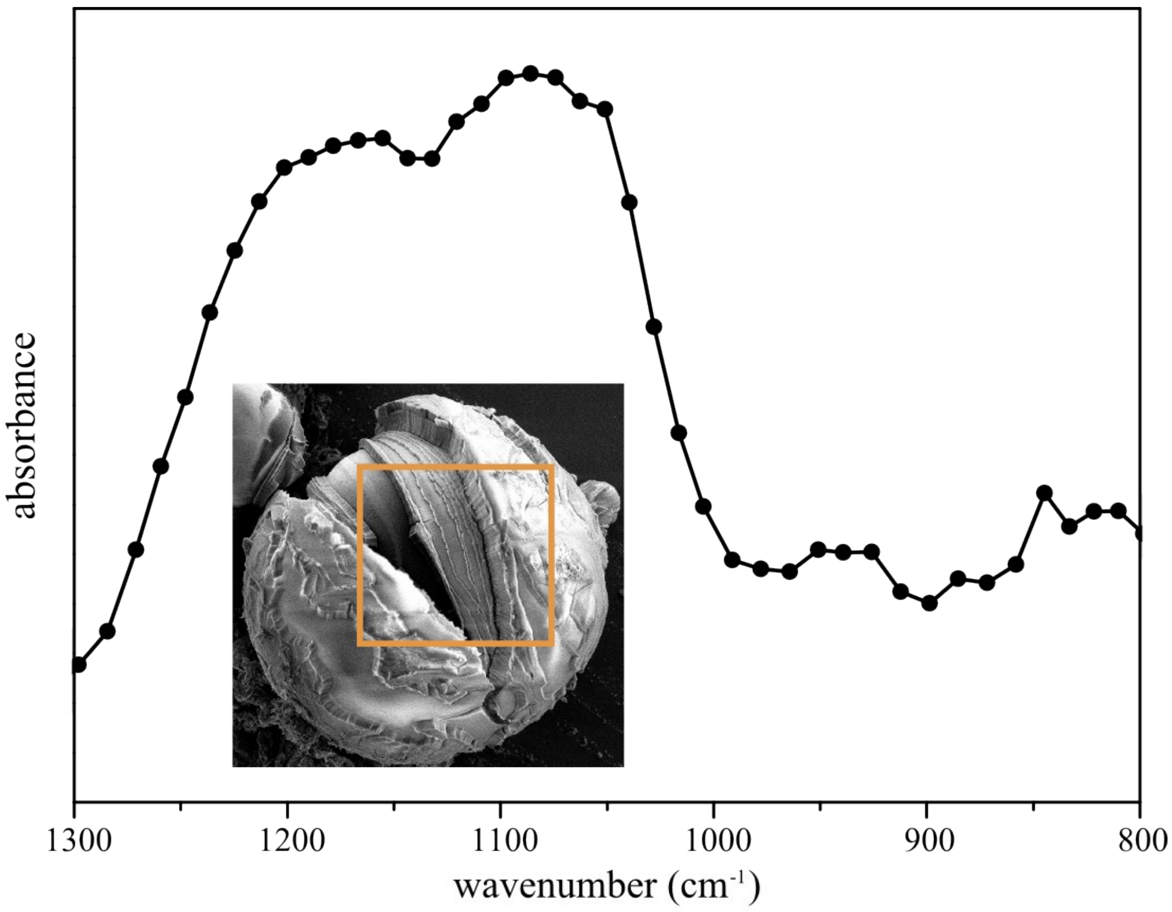

Fig S1. **FTIR spectrum** taken from a large Ga ball (100 μm diameter) after growth (930 °C, 250 Pa nitrogen, 10 minutes). The analyzed area (50×50 μm^2) covers the catalyst sphere exclusively, not the umderlying substrate, thus giving chemical information about silica nanowires in the shell. The presence of SiO_x is proven by the large peak structure near 1150 cm^{-1}. The component at 1107 cm^{-1} is indicative of an interstitial oxygen band (Si-O-Si). The occurrence of a broad feature around 1170 cm^{-1} is caused by the presence of substochiometric oxides (downshifted transverse optical phonon peak originally located at 1075 cm^{-1}, as well as longitudinal optical phonon at 1250 cm^{-1}) [SR1].

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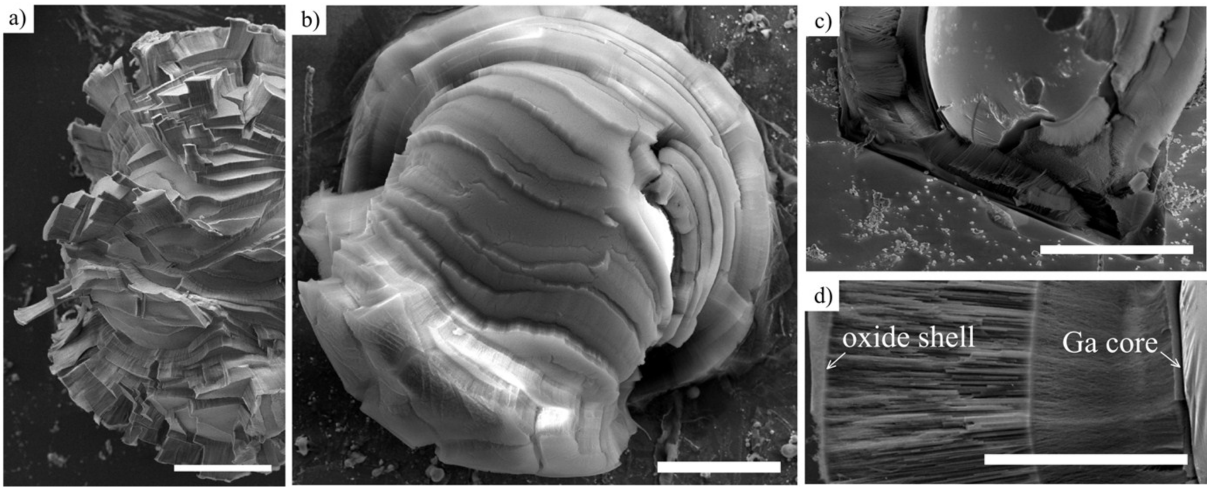

Fig. S2: **Distinct catalyst morphologies after growth in dry oxidizing atmosphere** observed ex-situ using a high resolution SEM. a) Ga catalyst ball exhibiting multiple shells with extensive cracking. As observed in real-time experiments, most of the cracks were formed during fast cooling or heating, supporting the hypothesis of large thermal stresses in the catalyst and oxide shell; scale bar, 20 μm, b) "Onion-like" structure with multiple nanowire shells. The evolution of such a structure is documented in Fig. S6; scale bar, 5 μm, c) Tilted SEM image (52°) taken close to the catalyst base, showing an etch pit below the catalyst. The shape of the pit reflects the crystallographic orientation of the underlying silicon wafer, in this case with the (111) orientation; scale bar, 2 μm. d) Two distinct nanowire morphologies grown from a Ga catalyst in an imprecisely-controlled oxidizing atmosphere. Bunches of small-diameter nanowires (right, resulting from growth assisted by residual water) are always located below the nanowire shell (left) and are in direct contact with the liquid Ga core; scale bar, 10 μm.

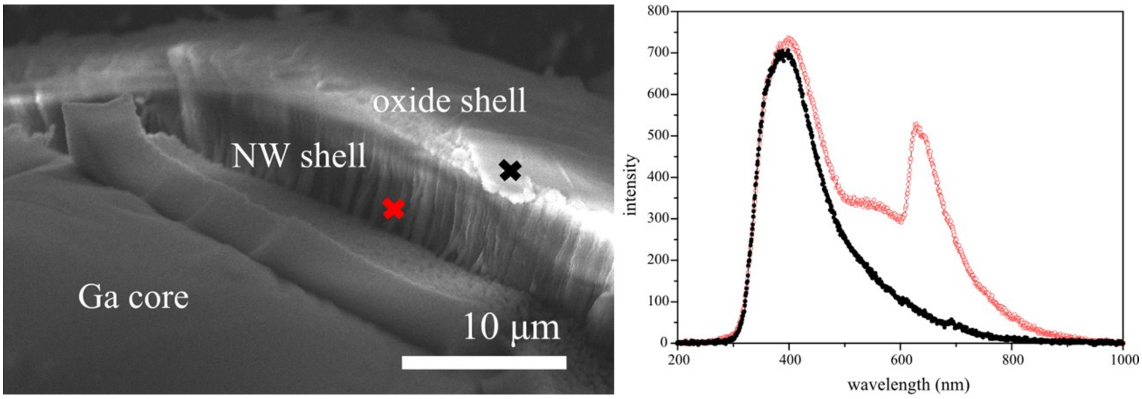

Fig. S3: **Cathodoluminescence inspection of the NWs**. Cathodoluminescence spectra were collected using a parabolic mirror and an OceanOptics CCD using a 10 keV electron beam. We have used both low and high beam currents to ensure that spectral features do not result from a beam-induced damage. The SEM image on the left (taken with the CL mirror retracted) shows a Ga ball with a nanowire shell formed by annealing in dry oxygen. The outer regions (black cross) emit light only around 400 nm, which is attributed to an emission from the Ga_2O_3 [SR2,SR3] layer that encapsulates the catalyst. Nanowire-containing regions (red cross) emit at around 650 nm in addition to the Ga_2O_3-related peak, which is always present to some extent. An additional emission is present at 480 nm and is likely related to the emission at 650 nm. Both emissions can be attributed to different oxygen-based defects in silicon oxide [SR4]. The emission at 480 nm was previously observed at a SiO_2/Si interface (oxygen vacancy centers) and confirms the non-stochiometric silicon oxide nature of the nanowires [SR5].

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[SR4] M. Dovrat, N. Arad, X.-H. Zhang, S.-T. Lee, A. Sa'ar, Phys. Rev. B 2007, 75, 205343.

[SR5] M. Yoshikawa, K. Matsuda, Y. Yamaguchi, T. Matsunobe, Y. Nagasawa, H. Fujino, T. Yamane, J. Appl. Phys. 2002, 92, 7153.

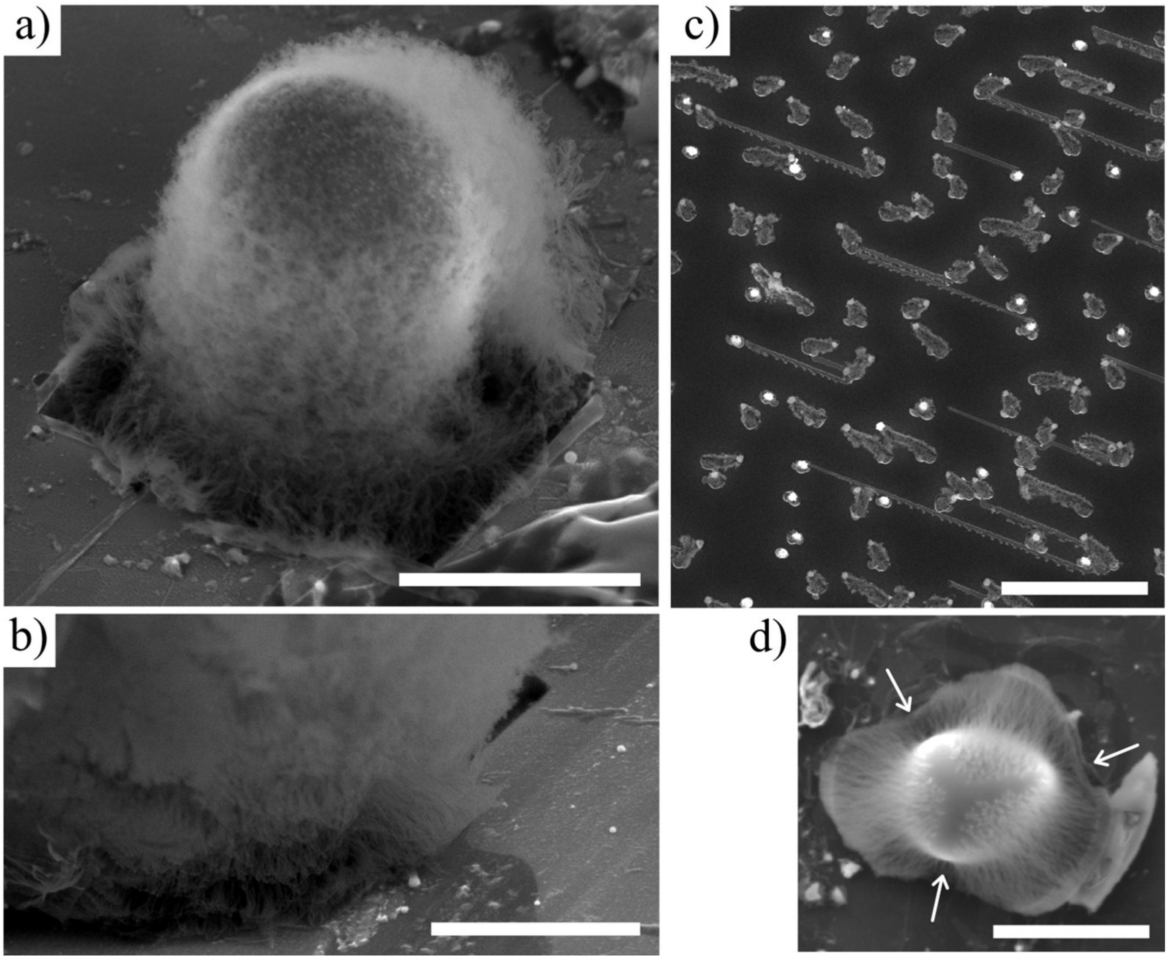

Fig. S4: **Distinct catalyst morphologies after growth in a wet oxidizing atmosphere** observed ex-situ in a high resolution SEM. a) Tilted SEM image (52°) showing an etch pit below the Ga catalyst droplet, which is covered by dense batches of silica nanowires. The etch pit has a rectangular shape, reflecting the substrate crystallographic orientation (100). The droplet is suspended above the etch pit, which suggests that silica nanowire growth had terminated before the growth experiment was finished; scale bar, 1 μm. b) Most often, the etch pits below catalyst droplets after wet oxidation are barely visible, as shown here. Image tilt 58°; scale bar 1 µm. c) The droplet mobility increases with decreasing catalyst droplet size. In this case the catalyst was evaporated under UHV conditions to prepare very small droplets (<500 nm). Most droplets of this size are mobile, as can be deduced from tracks behind the catalyst droplets. Image tilt 30°; scale bar 2 µm. d) SEM image showing a catalyst droplet with an oxide shell that probably cracked into three parts during the early stages of growth, before it was being etched away by hydrogen (the original position of the crack is marked by arrows). This structure (commonly observed in experiments) supports the hypothesis that the Ga oxide shell is necessary for nucleation, since no new nanowires nucleated on a free Ga catalyst surface after crack formation; scale bar, 3 µm.

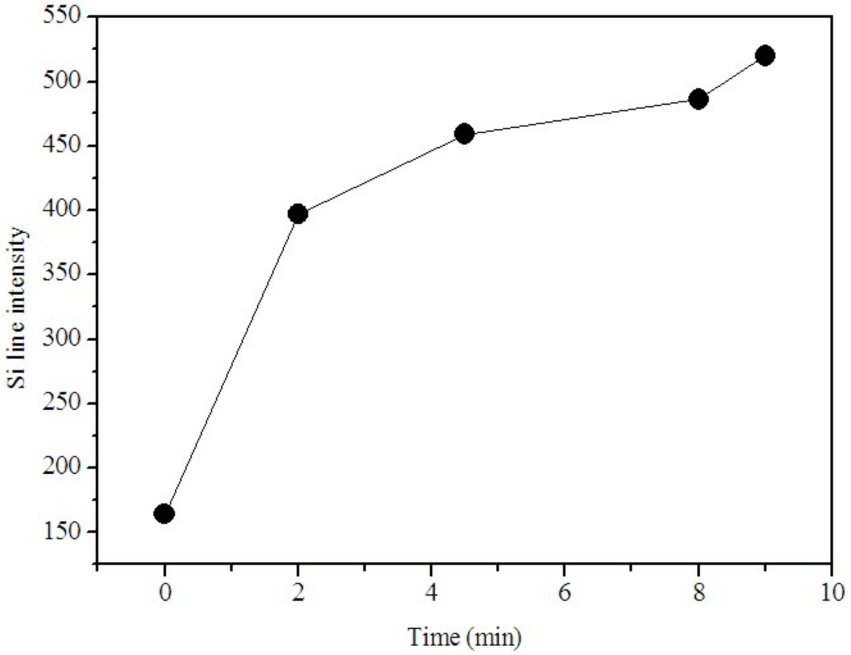

Fig. S5. **Si line intensity from the EDX measurement during annealing of the Ga catalyst in high vacuum at 550 °C.** The experiment proves that the silicon atoms are not transported via the vapor phase because the temperature is too low for Si sublimation from the substrate surface. The experimental details are given in Methods.

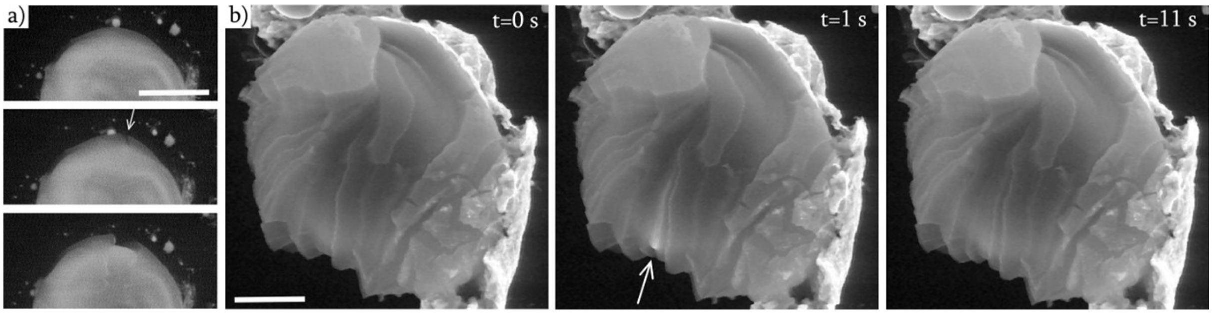

Fig. S6: **Shell cracking and formation of an "onion-like" multiple shell** documented by real-time SEM imaging. a) Ga ball imaged at 600 °C under 780 Pa of nitrogen. Images are taken in 2.5 s steps. After a crack is formed (white arrow in the middle image), the Ga core forces the crack to open, but it is quickly oxidized and the process terminates; scale bar, 10 μm. b) The sample was held at 770 °C under 350 Pa of nitrogen. The multiple shell structure is the result of extensive cracking of the stressed nanowire shell. The first image shows a Ga ball overgrown with several cracked nanowire shells. Crack formation is fast (marked by the white arrow in the second image), the Ga core is exposed to the gas (the bright area visible when the crack opens is indicative of liquid metallic Ga), it immediately oxidizes (documented by a change in contrast as the crack area gets darker) and a new nanowire shell is quickly formed. The subsequent cracking occurs at exactly the same location, the cracked shells are pushed away from the crack origin, thus forming the "onion-like" structure; scale bar, 10 μm.

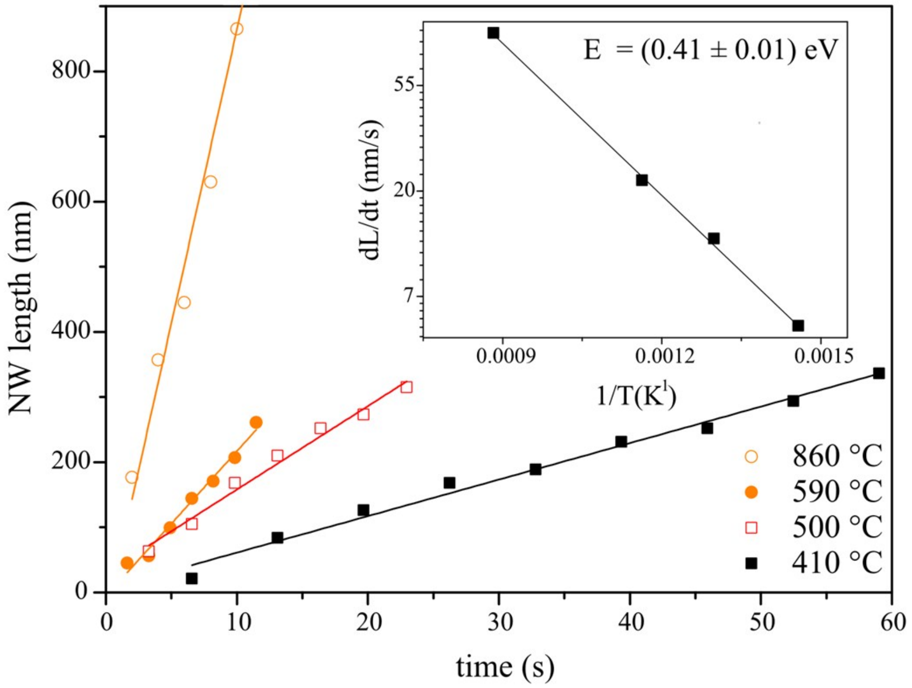

Fig. S7: **Activation energy determination.** Dependence of nanowire growth rate (determined from the nanowire shell thickness, similar to Fig. 2b) on time at different temperatures indicates that the process is thermally activated. The analyzed data represent the initial NW growth rates, hence the occasional increase in the growth rate due to gallium oxide shell etching by residual water vapor (Fig. 2b) is not visible. Assuming Arrhenius behavior (inset), a linear least-square analysis yields the activation energy of 0.41 ± 0.01 eV for Ga-catalyzed growth of silica nanowires in a dry oxidizing atmosphere.

S8. **Catalyst droplet movement.** Most of the large gallium balls appear to be immobile during growth, but smaller balls were move rapidly across the substrate surface during wet growth. Such a behavior is documented in Fig. S8. The droplet moves in one direction with a constant velocity, leaving a track behind. The movement eventually stops and the nanowires start to grow around the Ga ball. Similar to the immobile gallium balls, at a certain point in time the Ga ball contrast in the image changes (gets darker) and the growth ceases. Ex-situ high resolution images of the sample (Fig. S8b) show that the Ga ball is elevated from the substrate by underlying nanowire bunches that had grown from its surface. Importantly, the track behind the Ga ball is etched down to the substrate and decorated with nanowire bunches. Note that droplet movement was not observed during growth in a dry atmosphere, where the oxide-encapsulated Ga balls are pinned to the substrate. The movement of liquid metal droplets across the surface has been observed before [SR6-SR10], and attributed to the consumption of material at the leading edge of the droplets [SR11,SR12], which is probably also the case here.

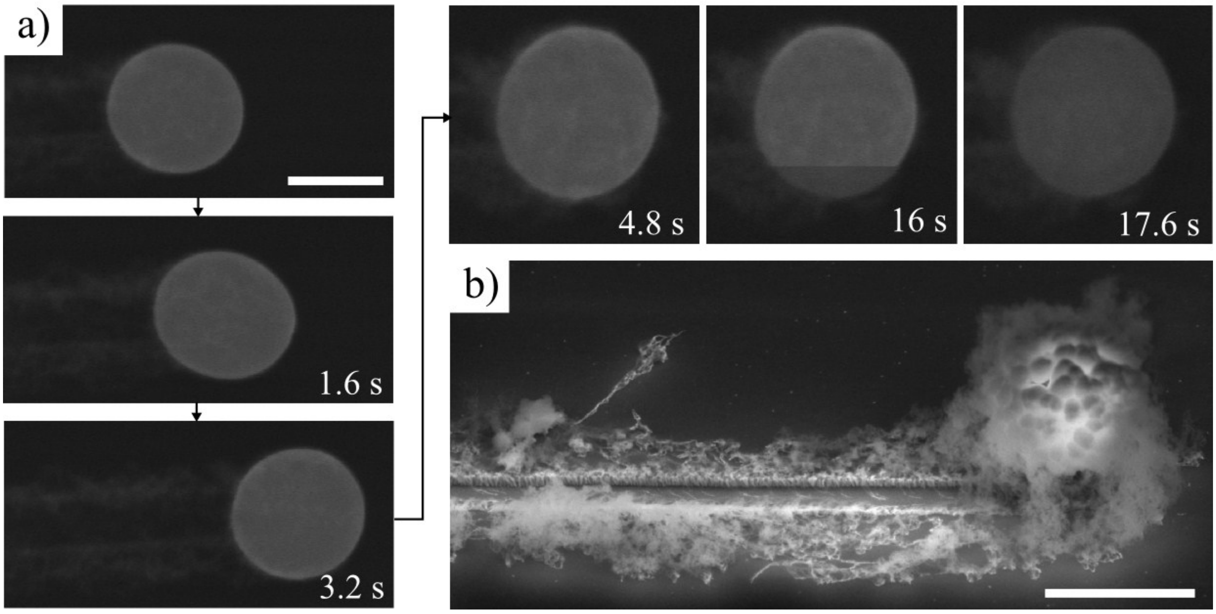

Fig. S8. a) Image sequence showing a rolling Ga ball on the surface. The track behind the ball is clearly visible. Once the ball stops (3.2 s after the start of observation), nanowire bunches grow away from the ball until the growth terminates (17.6 s). Growth termination is again accompanied by a rapid change in Ga ball contrast (linescan time is 1.6 ms); scale bar, 500 nm. b) Ex-situ image of the Ga ball after growth in a). The image is tilted (58° relative to the horizontal plane) to increase the visibility of the etched track, and of nanowire bunches that decorate the track; scale bar, 500 nm.

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