Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

Influence of Inhomogeneous Porosity on Silicon Nanowire Raman Enhancement and Leaky Mode Modulated Photoluminescence

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Plan-view Raman:

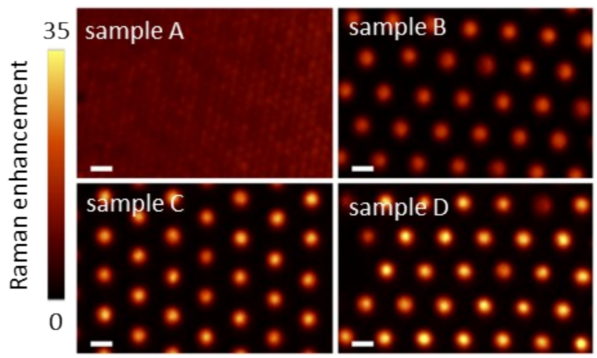

Figure S1. Raman enhancement over that of bulk silicon for samples A to D. All scale bars are 1 μm.

Figure S1 shows increasing Raman enhancement over that of bulk silicon from individual SiNWs in samples A to D, as measured in the plan-view configuration. The average Raman enhancement per SiNW from samples A, B, C, and D was 10.6, 19.6, 28.8, and 33, respectively. It is important to note that the SiNWs are microns long, and as such, longer than the focal depth of the objective (< 1 μm). The objective focal position in all cases was chosen by maximizing the optical signal.

The Raman enhancement from the base of the SiNWs imaged from the side in Figure 3 was relatively constant for all samples, while here, the Raman enhancements increase from samples A to D. In addition, the enhancements are larger in the plan-view of Figure S1, which likely stems from the higher efficiency of excitation and collection of light due to the geometric configuration. Light couples into a waveguide (in this case a SiNW) more efficiently when excited directly from the end of the waveguide vs. the side. Furthermore, more light couples out of the waveguide end as well. The increase in the Raman signal from sample A to D may result from the decrease in the refractive index as porosity increases. A decrease in the refractive index will reduce the Fresnel reflection coefficient at the SiNW tip/air interface, thereby, allowing more light to couple into the SiNW.

Correlation of structural inhomogeneities with Raman intensity:

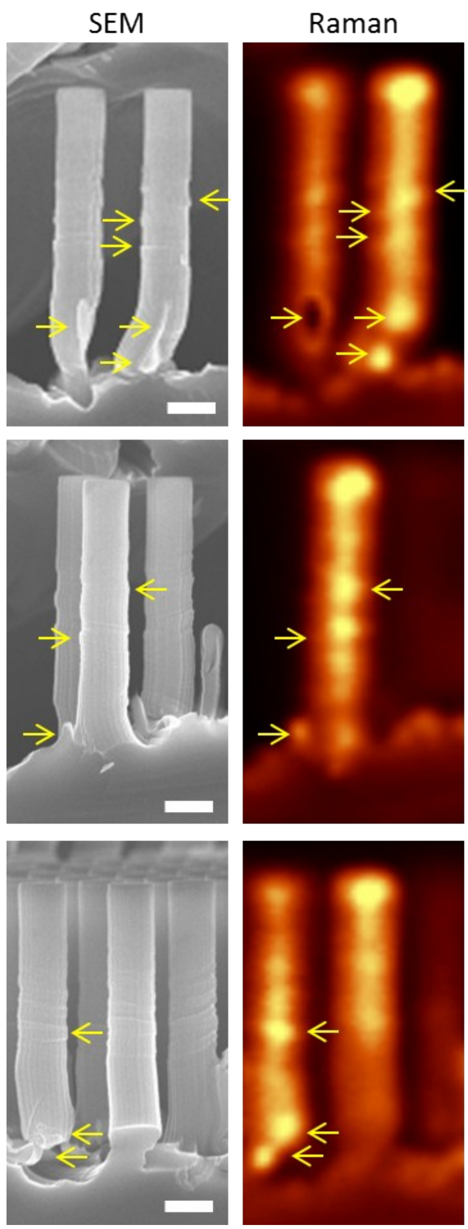

Figure S2. SEM images and corresponding Raman intensity from SiNWs with structural defects. All scale bars are 1 µm.

Figure S2 correlates Raman images with SEM images of a SiNW sample that has many structural defects. A close inspection of the images shows that many of the small structural features of the SiNWs are correlated with larger Raman intensities along the SiNWs. The yellow arrows help the eye correlate structural roughness and discontinuities with higher Raman intensities.

PL lifetime measurements:

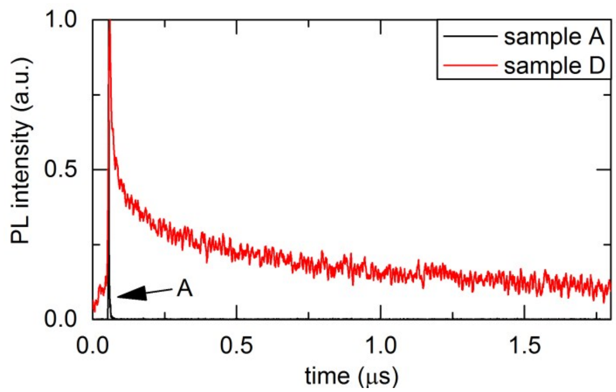

Figure S3. Comparison of PL decay from sample A and D.

PL decay measurements were acquired from sample A and D to help determine the origin of the PL from the different samples. Data was taken using a time-correlated single photon counting module (Becker-Hickl SPC-630). The samples were excited with a pulsed laser (λ = 400 nm). The PL collected from the samples was filtered through a 480 nm long pass filter and detected with a PMT. The data, shown in Figure S3, clearly shows large differences in the PL decay from sample A and D. The PL decay from sample A (black line) is on the ns time scale, while the sample D PL decay (red line) is multi-exponential with a much longer μs decay component. The time-correlated single photon counting module has a maximum detection window of 2 μs. During the measurement, the samples were excited every 2 μs, therefore, sample D didn't have time to fully decay before it was re-excited. While this hardware limitation prevented us from extracting a quantitatively accurate decay time for sample D, it is clear that the PL decay time of sample A is much shorter than sample D. The slower PL decay of sample D is consistent with "S-band" emission generally attributed to originating from quantum confinement.[1] The fast decay of sample A is more consistent "F-band" luminescence, typically attributed to oxide defects.[2]

1. Cullis, A. G.; Canham, L. T.; Calcott, P. D. J., The Structural and Luminescence Properties of Porous Silicon. *Journal of Applied Physics* 1997, 82, 909-965.
2. Tsybeskov, L.; Vandyshev, J. V.; Fauchet, P. M., Blue Emission in Porous Silicon - Oxygen-Related Photoluminescence. *Physical Review B* 1994, 49, 7821-7824.