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Tailoring the crystal structure of individual silicon nanowires by polarized laser annealing

Chia-Chi Chang¹, Haitian Chen², Chun-Chung Chen², Wei-Hsuan Hung¹, I-Kai Hsu³, Jesse Theiss², Chongwu Zhou¹,² and Stephen B Cronin¹,²,⁴

¹ Department of Physics, University of Southern California, Los Angeles, CA 90089, USA
² Department of Electrical Engineering, University of Southern California, Los Angeles, CA 90089, USA
³ Department of Materials Science, University of Southern California, Los Angeles, CA 90089, USA

E-mail: scronin@usc.edu

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Abstract
We study the effect of polarized laser annealing on the crystalline structure of individual crystalline–amorphous core–shell silicon nanowires (NWs) using Raman spectroscopy. The crystalline fraction of the annealed spot increases dramatically from 0 to 0.93 with increasing incident laser power. We observe Raman lineshape narrowing and frequency hardening upon laser annealing due to the growth of the crystalline core, which is confirmed by high resolution transmission electron microscopy (HRTEM). The anti-Stokes:Stokes Raman intensity ratio is used to determine the local heating temperature caused by the intense focused laser, which exhibits a strong polarization dependence in Si NWs. The most efficient annealing occurs when the laser polarization is aligned along the axis of the NWs, which results in an amorphous–crystalline interface less than 0.5 μm in length. This paper demonstrates a new approach to control the crystal structure of NWs on the sub-micron length scale.

(Some figures in this article are in colour only in the electronic version)
study the crystallization process of core–shell Si NWs under laser irradiation in an argon environment. A continuous (CW) 532 nm wavelength laser is focused through a 100× objective lens (0.9 NA) and used as a local heat source to modify the crystallinity of core–shell Si NWs. In our Raman spectrometer, a holographic notch filter is used, which enables us to take both Stokes and anti-Stokes Raman spectra. A half-wavelength polarizer is placed before the notch filter to rotate the laser polarization. In situ Raman spectra are taken during the annealing process with the same incident laser, which give information about the heating temperature based on the anti-Stokes:Stokes Raman intensity ratio [16] and the temperature-induced Raman lineshape broadening and frequency downshifting [17–19]. Low laser power (0.5 mW) Raman spectra with an integration time of 60 s are taken before and after annealing to reveal changes in the crystallinity due to the local annealing process. The laser annealing process is carried out in an argon environment to prevent oxidation during annealing.

Figures 1(a) and (b) show electron microscope images of Si NWs grown in this study. Metal strips with grid markers were deposited on top of one of the NWs, as shown in figure 1(c). AFM was used to determine the diameter of this NW to be 78 nm, as shown in figure 1(d). Figure 1(e) shows the Raman spectra of an individual Si NW before and after laser annealing at 50 mW, while the laser polarization is aligned along the NW axis. In the following, we align the laser polarization along the axis of the NWs, unless stated otherwise. The laser annealing process is carried out in an argon environment at 1 atmosphere to prevent oxidation during annealing. Figure 2(a) shows the evolution of the Raman spectra taken after 30 s irradiations with different laser powers at the same focused laser spot. Before annealing, a broad peak centered at 480 cm$^{-1}$, the Raman signature of amorphous silicon, is observed in this NW. As the incident laser power is increased, this peak can be seen to upshift and become narrower due to the reduction in phonon confinement effects [1–4, 20, 21]. The raw spectra in figure 2(a) were fitted with two Lorentzian peaks, as shown in the inset of figure 2(b). The crystalline fraction can be obtained from the relative peak intensities by following the equation:

$$X_c = I_c/(I_c + \gamma I_a)$$

where $I_c$ and $I_a$ are the integrated Raman intensities of the crystalline and amorphous components, respectively. $\gamma$ is the scattering ratio of crystalline and amorphous silicon, which ranges from 0.8 to 1 [22–25]. We use $\gamma = 1$ here. In figure 2(b), the crystallinity increases with increasing annealing power during
the crystallization process. Also, the lineshape and frequency of the crystalline component becomes narrower and upshifts as the annealing power is increased. These observations indicate that the crystalline core of the NW grows, while the amorphous shell becomes thinner due to the crystallization process. Note that the crystalline Raman peak becomes visible after laser annealing at 20 mW but is downshifted from the single crystal value to 513 cm\(^{-1}\) and significantly broadened to 20 cm\(^{-1}\). We attribute this to the effect of phonon quantum confinement because of the small crystalline core. As the crystalline core increases due to successive annealing, the crystalline peak blue shifts to 520 cm\(^{-1}\), while the linewidth narrows to 7 cm\(^{-1}\), which is closer to the values of single crystal bulk Si. The linewidth and Raman shift \(\Delta \omega\) of the crystalline peak are plotted as a function of annealing power in figures 2(c) and (d), where the peak downshift is from 520.5 cm\(^{-1}\). The crystalline size \(D\) can be calculated from the bond polarization model: 
\[
\Delta \omega = B (a/D)^{\gamma},
\]
where \(B = 2.0\) cm\(^{-1}\), \(\gamma = 1.44\), and \(a\) is the silicon lattice constant \((a = 0.543\) nm\) [26]. Various models [1–4, 20, 21] have been developed to obtain the mean crystal grain size from these Raman features. However, they are all in agreement when the crystal size is above 3 nm [20].

The mechanism of CW laser-induced crystallization is different from that of a pulsed laser. The crystallization takes place in the solid phase under CW laser irradiation. The annealing temperature depends on the laser power and the heat loss to the substrate. The crystalline core acts as a seed for crystallization and the growth of the crystalline core is expected to depend on the annealing time at a given temperature. However, the crystalline fraction of the annealed NWs does not show any time dependence, as shown in the inset of figure 2(c). This is because the irradiated nanowire reaches thermal equilibrium on a time scale of microseconds, and the resulting changes in crystallinity take place far below our minimum time resolution.

Figure 3(a) shows the Raman spectra of a core–shell Si NW before and after annealing with 50 mW. A Raman spatial map scan is used to resolve the crystallinity changes along the NW after the single spot laser annealing. The integrated crystalline peak intensity \(I_c\) plotted as a function of position gives a full width at half maximum of 680 nm by fitting with a Lorentzian function. We believe that the slightly wider profile of the crystalline peak intensity is due to the finite thermal gradient produced while annealing, which results in different levels of crystallization that have occurred near the annealing spot. The integrated amorphous peak intensity \(I_a\) follows the opposite trend of the crystalline peak, as expected in the crystallization process. Further spatial mapping of the Raman intensity is plotted in figure 3(c), which shows the modulations of both a-Si and c-Si peaks along the length of the NW.

Nanowires were also deposited on 100 nm thick silicon nitride (Si\(_x\)N\(_y\)) membranes (SPI, Inc.), enabling HRTEM imaging to be taken after laser annealing. Figure 4(a) shows a TEM image of a locally annealed NW. Although the same laser conditions (50 mW with polarization along NW axis) were used, the annealed region is twice as large as that of the NW deposited on the glass substrate. This is because the heat conduction through the Si\(_x\)N\(_y\) membrane is far less than that
of the glass substrate, which also increases the amorphous–crystalline interface to 0.5 μm in length. The drawing in figure 4(b) illustrates the cross section at the boundary between the unannealed and annealed regions. The unannealed region remains as a core–shell structure, as seen in figure 4(c). Here, the crystalline structure can only been seen near the core of the NW. However, in the annealed region (figure 4(d)), the crystalline core fills nearly the entire NW cross section, with a thin silicon oxide layer. The same uniform crystalline structure as in figure 4(d) is observed within 1 μm of the annealed region, indicated by a gray box in figure 4(a). The axial modulation in crystal structure is also reflected in the spatial Raman mapping (intensity, Raman shift, and linewidth), as shown in figures 4(f) and (g). The uniformity of Raman shift and linewidth within the annealed region agrees with the TEM inspection and further corroborates the high crystal quality. The Raman Stokes (S) and anti-Stokes (AS) spectra shown in figure 4(e) were taken during the laser annealing process. These Raman modes downshift and broaden to 496.6 and 18 cm$^{-1}$ due to the high temperature reached [17–19]. The annealing temperature is estimated to be 1103 K, based on the AS/S intensity ratio, $I_{AS}/I_{S} = Ce^{-\hbar \omega_{0}/k_BT}$, where $C$ is a calibrated coefficient from room temperature data, $\hbar \omega_{0} = 64.6$ meV is the phonon energy, and $k_B$ is Boltzmann’s constant.

We also observe a strong polarization dependence of the laser-induced heating. The Raman intensity follows the expression $I(\phi) = c \cos^2(\phi)$, where $\phi$ is the angle between laser polarization and NW axis as shown in figure 5(a). The temperature profile obtained from the Raman AS/S intensity ratio over a wide range of polarization angles, in figure 5(b), shows a strong preferential heating effect when the laser polarization is aligned at $\phi = 0^\circ$ and $180^\circ$. There is a maximum temperature difference of 200 K under 40 mW irradiation. In figure 5(c), the Raman linewidth oscillates between 5 and 8 cm$^{-1}$ and the Raman shift varies from 520 to 517 cm$^{-1}$, which can also be understood by the preferential heating. The polarization dependence of the Raman intensity has been reported in crystalline silicon films [27, 25]. The intensity of Raman scattering depends on the orientation of the incident laser polarization relative to the crystal axes followed by the simplified expression $I(\theta) = c \cos^2(2\theta)$, where $\theta$ is the angle between laser polarization and crystal axes. However, we do not observe other oscillation patterns of Raman intensity rather than the one in figure 5(c), which implies that the former effect dominates in the NW system. The polarization dependence of laser heating is attributed to the different degrees of absorption of the polarized laser. A recent finite-difference time-domain (FDTD) study on light absorption in a 50 nm Si NW shows that the absorption per unit volume of transverse magnetic (TM) light is almost 20-fold larger than that of transverse electric (TE) light at a wavelength of 532 nm [28].

In figure 6, we demonstrate the effect of polarization-dependent annealing on a 12 μm-long core–shell NW with a fixed laser power of 50 mW at various laser polarization angles specified on the top of figure 6(a). Each annealing spot is separated by 1 μm along the wire axis to avoid proximity heating from the Gaussian laser beam. Prior to annealing, spatial Raman mapping was performed and correlated with the polarization angles to reveal the uniformity of crystallinity over the length of the NW. After preferential annealing, the same spatial Raman mapping was performed again to determine the crystallinity modulation along the NW, as plotted in figure 6(c).
Figure 4. (a) TEM image of a locally annealed Si NW in which the annealed area is 1 μm indicated by the box. (b) Schematic diagram of the NW boundary between annealed and unannealed regions. Corresponding HRTEM images in (c) and (d) are indicated by the dashed boxes. (c) HRTEM image of the unannealed area near the core of the NW. (d) HRTEM image of the annealed segment near the NW surface. (e) Stokes and anti-Stokes Raman spectra taken during the laser annealing process. (f) Crystalline peak intensity, (g) Raman shift and linewidth plotted as a function of position along the NW.

Figure 5. (a) Experimental setup of polarization-dependent laser heating on crystalline NWs. (b) AS/S intensity ratio and corresponding temperature as a function of polarization angle. (c) Raman intensity, linewidth, and Raman shift plotted as a function of polarization angle with respect to the NW axis.
In figure 6(b), visible a-Si peaks are observed at integer position numbers, which are unannealed spots. The intensity modulation of a-Si peaks is merely due to the polarization angle effect described in the previous paragraph. At the annealed spots (half-integer position numbers), the a-Si peaks either diminish or become very weak. For these c-Si peaks, there are two factors responsible for the intensity modulation. Besides the polarization angle effect, the crystalline fractions after annealing are different, as depicted in figure 6(a). The drawing illustrates the crystal structure modulations in both axial and radial directions. Figure 6(c) also shows the corresponding annealing temperatures as a function of polarization angle. The improvement of crystallinity shows strong polarization dependence due to preferential heating.

In conclusion, Raman spectroscopy was used to study the effect of laser annealing on crystalline–amorphous core–shell Si NWs grown by the CVD method. The crystalline fraction was found to increase gradually with increasing laser power based on the local Raman spectra. The Raman shift and linewidth show upshifting and sharpening, respectively, due to the reduction of phonon confinement effects, as the crystalline core of the NW increases. Strong preferential heating due to the laser polarization was utilized to control the crystallinity of individual NWs. Using the focused laser annealing, we are able to create an amorphous–crystalline interface less than 0.5 μm in length.

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