Elemental Analysis of Ge-Si_xGe_{1-x} Core-Shell Nanowire Heterostructures

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Abstract:

We investigate Ge-Si_xGe_{1-x} core-shell nanowire heterostructures, where the silicon germanium (Si_xGe_{1-x}) shell is grown *in situ* on the Ge nanowire core using ultra-high-vacuum chemical vapor deposition. Transmission electron microscopy shows that the Si_xGe_{1-x} shell is single crystal and grows epitaxially on the Ge cores. To determine the shell thickness and elemental composition of these nanowire heterostructures, we employ energy dispersive x-ray spectroscopy and electron energy-loss spectroscopy. We show that by tuning the growth conditions, the shell thickness and the relative content of the Si_xGe_{1-x} shell can be controlled, enabling radial band engineering in these nanowire heterostructures.

Introduction:

Semiconductor nanowires are of interest for electronic, photonic, and sensing applications. Nanowire heterostructures are attractive building blocks for low-power, high-speed electronics, due to their reduced dimensionality and the ability to engineer their electronic properties. Here we study Ge-Si_xGe_{1-x} core-shell nanowire heterostructures, and characterized their dimensions and content in order to enable radial strain and band engineering in this system. The valence band of the Si_xGe_{1-x} shell lies below the valence band of the Ge core, which allows for the engineering of one-dimensional hole gases confined to the Ge core [1,2]. We employ high-resolution transmission electron microscopy (TEM) to analyze the crystal structure of the Ge-Si_xGe_{1-x} core-shell heterostructure, and energy dispersive x-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS) to determine the elemental content [3,4].

Experimental Procedure:

The Ge-Si_xGe_{1-x} core-shell nanowires are grown using a combination of low pressure and ultra-high-vacuum (UHV) chemical vapor deposition (CVD). The Ge cores are grown via the vapor-liquid-solid (VLS) mechanism and using Au catalysts [5,6]. The Si_xGe_{1-x} shell is then grown epitaxially on the Ge core using UHVCVD techniques and with various molar ratios of SiH_4 and GeH_4 (Figure1) [5].

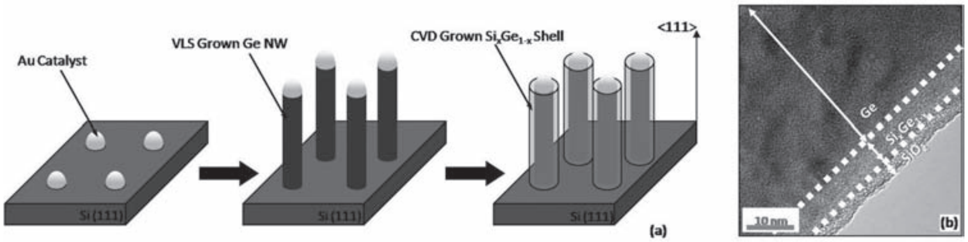


Figure 1: (a) Ge-Si_xGe_{1-x} nanowire core-shell growth. (b) Transmission electron micrograph of a Ge-Si_xGe_{1-x} core-shell heterostructure.

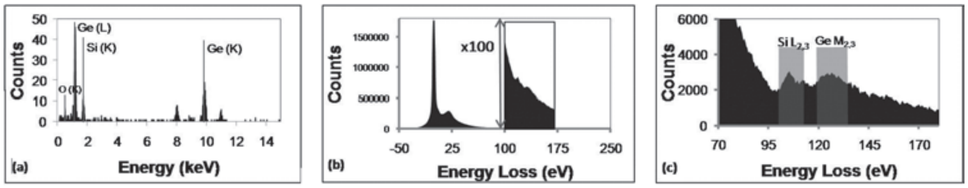
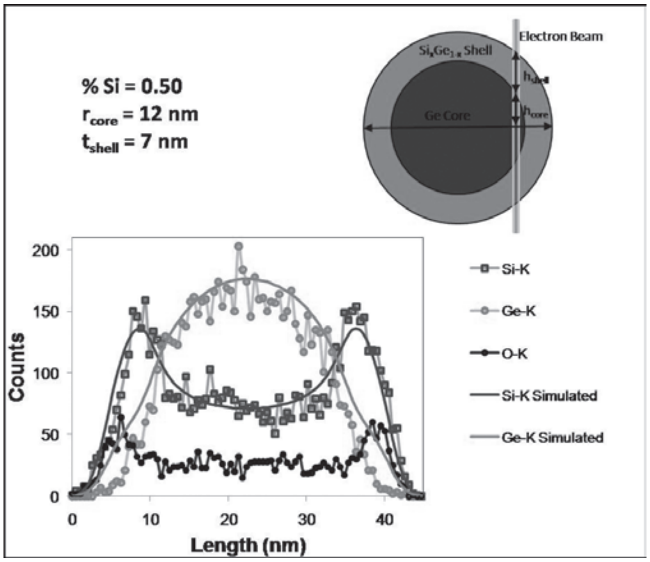


Figure 2: EDX/EELS point spectra (a) EDX spectrum showing the Si and Ge K-lines; (b) EEL-spectrum showing the zero-loss and plasmon peaks and the Si $L_{2,3}$/Ge $M_{2,3}$ edges; (c) The EEL-spectrum after background subtraction, showing the edges more clearly.

After growth the nanowires are harvested in an ethanol solution and deposited on a TEM copper grid. For analysis we use an FEI Tecnai TF20 microscope, equipped with high-angle annular dark field (HAADF) detectors and EDX and EELS spectrometers. The EDX and EELS data were collected using scanning TEM (STEM) linescans (Figure 2).



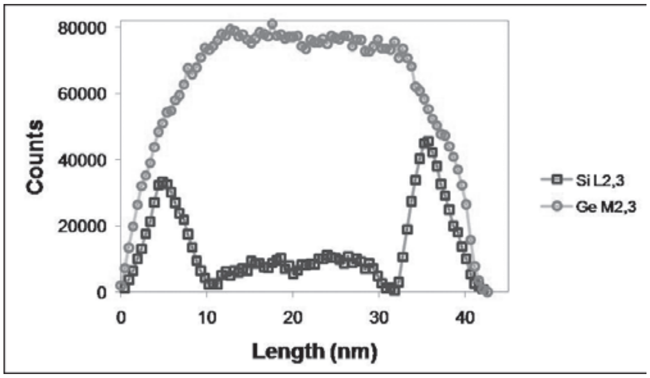


Figure 3, left: EDX linescan showing the Ge, Si, and O K-line counts as a function of beam position along nanowire cross-section. The inset diagram depicts the cross-section of the wire, and illustrates the electron beam's position along the linescan.

Figure 4, above: EELS linescan shows clear Si peaks in the shell, qualitatively consistent with the EDX data.

Results:

In order to analyze the EDX data, the Si and Ge concentrations are modeled as following: $\psi_{Si}(x) = 2X_{Si}\bullet h_{shell}(x)$ and $\psi_{Ge}(x) = 2X_{Ge}\bullet h_{shell}(x) + 2h_{core}(x)$. Here X_{Si} represents the percentage of Si in the shell, and $h_{shell}(x)$ the nanowire thickness spanned by the electron beam at position x. The concentrations are then convoluted with a Gaussian beam profile in order to compare with the measured EDX data [5].

The data of Figure 3 reveals the formation of a ~ 5 nm thick SiO_2 layer on the nanowire surface, which we associated with the O_2 plasma clean of the TEM sample. Interestingly, this causes the Ge atoms in the shell to move towards the core, a phenomenon known as Ge condensation [7]. This accumulation of Si atoms at the shell surface leads to larger and wider Si peaks than expected.

The EELS data shown in Figure 4 agrees qualitatively with the EDX data of Figure 3. However, we note the EELS analysis is sensitive to background subtraction, and the Ge $M_{2,3}$ edge is not suitable for core thickness measurements because of its weakness and proximity to the stronger Si $L_{2,3}$ edge [3].

Conclusions:

Transmission electron microscopy reveals single crystal Si_xGe_{1-x} shells epitaxially grown on the Ge cores. The EDX data allows a quantitative determination of the Si_xGe_{1-x} shell content and shell thickness. The EELS elemental analysis data is qualitatively consistent with EDX, and reveals the core-shell boundary more clearly.

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