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Strain and Sn distribution in $Ge/Ge_{1-x}Sn_x$ Core-Shell Nanowires

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Studies have shown that core-shell $Ge/Ge_{1-x}Sn_x$ nanowires are promising candidates to achieve direct band-gap engineering for silicon-compatible optoelectronic device applications by controlling the inter-related characteristics of Sn content, strain state and defects in the nanowires [1,2]. Both the incorporation of Sn into the diamond cubic Ge structure and tensile strain of Ge are expected to shift the bandgap toward a direct transition [3]. Because the mismatch between α-Sn and Ge is 14% and the solubility of Sn in Ge is less than 1%, nanowire synthesis offers an alternative to thin film growth for increasing Sn content. Here we report on strain measurements and Sn distribution in vapor-liquid-solid (VLS)-grown core-shell $Ge/Ge_{1-x}Sn_x$ nanowires with increasing Sn content up to an estimated 8 at%.

The VLS nanowires are synthesized using 40 nm Au colloids and GeH_4 and $SnCl_4$ precursors in hydrogen carrier gas. Fig. 1a shows an ADF STEM cross section of a nanowire containing about 4 at% Sn in the shell. As reported by several groups, a typical cross-section is a hexagon with {112} facets and with the shell exhibiting a Sn-deficient spoke structure intersecting the corners of the hexagons [1,2]. We carried out 4D STEM measurements on the cross-sections but saw no measurable lattice difference between the core and the shell, consistent with x-ray measurements showing that the Ge core is compliant and under tensile strain by the shell [4]. We therefore made a longitudinal TEM cross-section, as shown in Fig. 2a, where the inclusion of the unstrained Ge substrate in the sample provides a suitable reference for a 4D STEM measurement of the nanowire. The results (Fig. 2, b-d) show a 0.5% out-of-plane strain, consistent with 4 at% Sn in the shell, and a Ge core under tensile strain.

We increased the $SnCl_4$ partial pressure in order to increase the amount of Sn in the shell. Fig. 2a shows an SEM image of these nanowires, many of which are slightly bent. An EDS line scan showed the Sn content was higher on the outside of the bend, measuring approximately 8 at%, decreasing to approximately 4 at% on the inside. Fig. 2, b and c are a HAADF image and EDS Sn mapping of a cross-section of one of these wires, showing a Sn deficient pattern in one half of the nanowire shell. This unusual shape was observed in three out of four nanowires examined; it appears to combine a Sn deficient crescent-shaped area that forms as the shell grows, and that overlaps and interacts with the Sn-deficient spoke pattern. We are currently investigating the nanowire bending and the formation of this Sn-deficient pattern; preliminary results suggest a correlation between asymmetric thicknesses (growth rates) of the shell facets, nanowire bending, and the resulting Sn distribution pattern, with the nanowire growth density [5].

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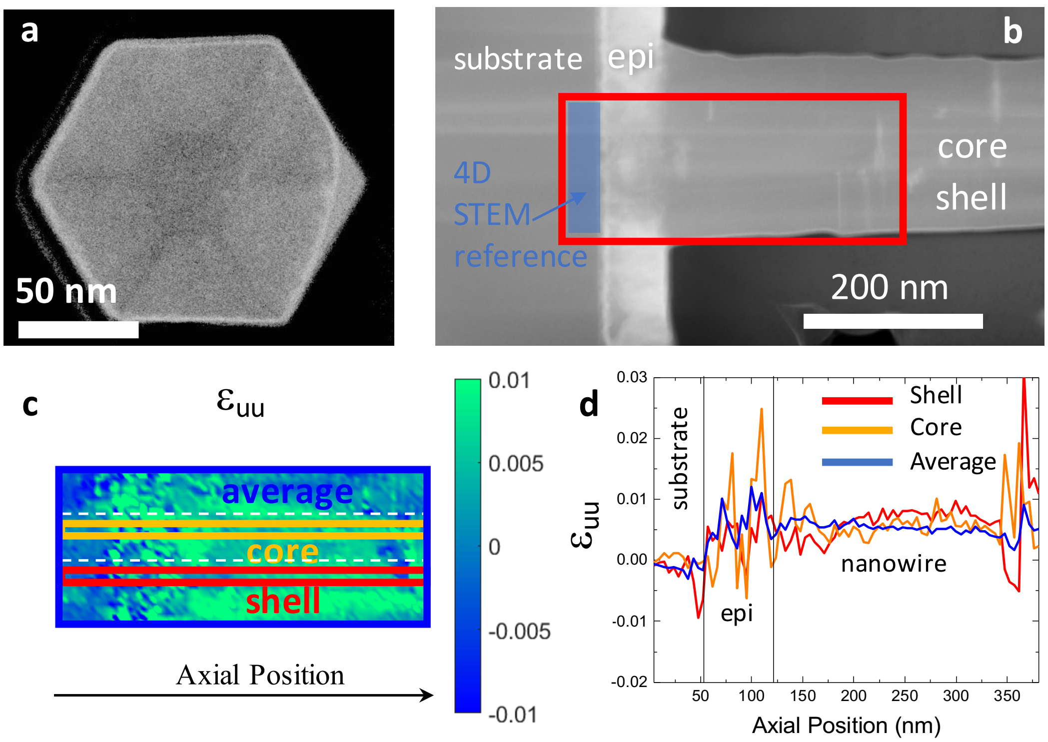

Figure 1. a. ADF STEM cross-section of a core-shell nanowire. b. longitudinal cross-section showing regions for 4D STEM analysis. c,d. measured out-of-plane strain along the NW axis.

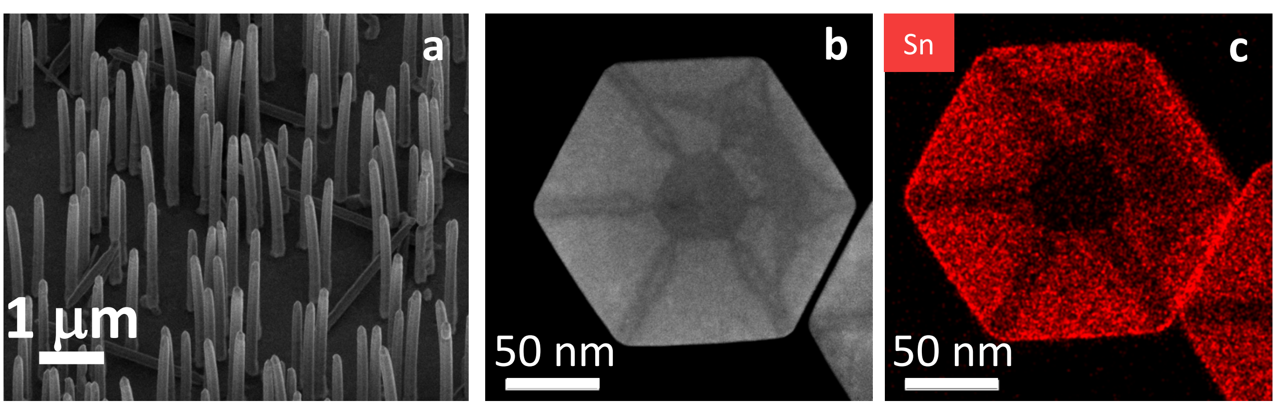

Figure 2. a. SEM image of bent NWs. b. HAADF image of bent NW cross-section showing spokes plus an intersecting crescent pattern in one half of shell. c. EDS map showing Sn-deficiency in the pattern.