Sn Alloying Impact on Structural and Electronic Properties of Core-Shell Ge-GeSn Nanowires: A TEM Study

Milenka Andelic[1], Dr. Alexandre Pofelski[1,4], Dr. Isobel Bicket[1,2,3], Dr. Simone Assali[5], Dr. Sebastian Koelling[5], Dr Lo Luo[5], Dr. Oussama Moutanabbir[5], Dr. Gianluigi Botton[1,6]
[1]McMaster University, Hamilton, Canada, [2]Atominstitut, TU Wien, Vienna, Austria, [3]University Service Centre for Transmission Electron Microscopy, TU Wien, Vienna, Austria, [4]Brookhaven National Laboratory, Upton, USA, [5]Ecole Polytechnique Montreal, Montreal, Canada, [6]Diamond Light Source, Oxfordshire, UK

Background incl. aims

Alloying group IV elements in out-of-equilibrium conditions when there is a significantly different atomic size between the atoms of the host lattice (Ge) and the alloying element (Sn) results in peculiar modifications of the structure and electronic properties of the parent phases. Growing alloys in the form of core-shell Ge-GeSn heterostructures adds an additional degree of freedom for strain accommodation. Moreover, such core-shell configuration induces changes in their morphological, chemical, electronic, and optical properties. Investigating these heterostructures, where Ge acts as the core and GeSn as the shell in hexagonally faceted nanowires with a diameter in a range of 80-100 nm and length exceeding tens of µm, poses significant challenges. While there are challenges, these heterostructures offer numerous opportunities for developing silicon-compatible devices with enhanced capabilities in the mid-infrared wavelength range (5-20µm). These capabilities include, among others, CMOS and MOSFET devices, night-vision devices, and lasers [1], owing to their advanced band-to-band transitions and enhanced carrier mobility. Consequently, a thorough investigation and precise characterization, at the atomic level, are crucial for these heterostructures, requiring a high degree of sensitivity and high-spatial resolution. The introduction of Sn to Ge, a high carrier mobility element, will undoubtedly have a profound impact on its bandgap characteristics, influencing transitions within the bandgap [2]. We observe and extract information locally and detect features using the Scanning Transmission Electron Microscopy (STEM) technique, employing an extremely narrow electron probe directed at the sample to obtain detailed insights into the structure and chemical composition of these intriguing core-shell structures. The initial Sn content ranges from below 8 at. % to above 14 at. % representing a substantial amount of Sn. It has been predicted that the transition from an indirect to a direct bandgap will occur at approximately 8 at. % Sn [3], a hypothesis we aim to experimentally confirm and deepen further.

Methods

To study such core-shell heterostructures, we utilize a High-Resolution (HR) STEM with the High-Angle Annular Dark Field (HAADF) detector and Energy-Dispersive X-Ray Spectrometer (EDS). For such purpose we employ the ThermoFisher Scientific Spectra Ultra double-corrected TEM operated at 300 kV with a segmented Ultra-X EDS detector enabling atomic-resolved EDS maps. Additionally, we implement electron energy-loss spectroscopy (EELS) in STEM mode using the Nion HERMES 100 instrument operated at 60 kV, with optimal energy resolution of 4.8 meV for detailed examination of electronic and optical properties.

Results

The results of this investigation unveil a substantial impact of increased Sn content in the core-shell Ge-GeSn nanowires on their structural, electronic, and optical characteristics. The performed EDS analysis validates the distinctive core-shell configuration, highlighting a region depleted of Sn in the core, alongside a discernible degree of its uniformity in the shell (Figure 1a). Additionally, findings show that the notable segregation of Sn adatoms along the hexagonal facets promotes the generation of complex defects and that their complexity is more prominent with the elevated Sn content and incorporated strain. The presence of twinning may contribute to the growth of supplementary structures such as nanobelts (NB) with unique non-hexagonal cross-sectional shapes. Moreover, the coexistence of both diamond cubic (DC) and hexagonal-wurtzite (WZ) structures (Figure 1b) or polytypism, results in notable changes in the polarity of these initially presumed non-polar elements (i.e. we alloy within the same group IV elements), enhancing the complexity and interest in the ordered nature of these structures. The investigation of electronic transitions at a high level of locality with high-energy resolution EELS confirms that the increase of the Sn content from 8 at.% up to 18 at.% leads to a transition from an indirect bandgap of Ge (measured 0.67 eV) to a direct bandgap of GeSn, and a shift from 0.56 eV for 8 at.% Sn to approximately 0.3 eV for 18 at.% Sn (Figure 1c).

Conclusion

In summary, our findings demonstrate that core-shell Ge-GeSn nanowires exhibit a unique morphology and crystalline structure ascribed to the Sn content within the GeSn shell. Furthermore, an in-depth investigation of high-spatial resolution HAADF data unveils that the presence of Sn segregation, occurring with higher Sn concentrations in the shell, significantly impacts the occurrence of intricate defects like twinning. As evidenced by the EELS data, the transition of the bandgap from indirect to direct concomitant with a reduced value (measuring below 0.67 eV for Ge), was confirmed with higher Sn concentrations surpassing approximately 8 at.%.

Graphic:

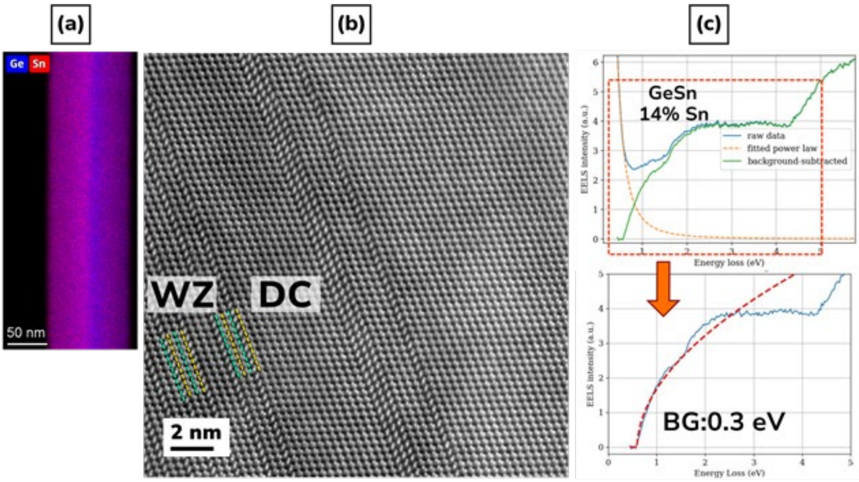

Figure 1: (a) EDS map illustrating the dominant core-shell structure with the Ge-rich area (blue region) in the core, and uniform Sn distribution in the GeSn shell (b) Atomically resolved HAADF image revealing the presence of the polytype crystal structures consisting of transitions between diamond cubic (DC) and wurtzite (WZ) through the emergence of stacking faults and twins; (c) EELS data extraction showing the bandgap energy onset of approximately 0.3 eV for 14 at. % of Sn.

Keywords:

GeSn core-shell nanowires, bandgap, STEM/EELS

Reference:

[1] Du, Wei, and Shui-Qing Yu. Mid-infrared Optoelectronics. Woodhead Publishing, 2020. 493-538.
[2] Fadaly, Elham MT, et al. Nature 580.7802 (2020): 205-209.
[3] Gupta, Suyog, et al. Journal of Applied Physics 113.7 (2013).