Epitaxy of self-assembled $Al_{1-x}Sc_xN$ nanowires on metallic TiN: Towards vertical and flexible piezoelectric nanogenerators

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The incorporation of Sc into the hexagonal wurtzite lattice of AlN is an effective way to extend the functionalities of the group III-nitride semiconductor family. Ternary $Al_{1-x}Sc_xN$ exhibits giant piezoelectricity, ferroelectricity and exciting non-linear optical properties, which are already utilized in novel devices. New functionalities, such as flexibility and enhanced piezoelectric response may arise from the growth in the form of nanostructures.

In this work, we demonstrate the molecular beam epitaxy of ternary $Al_{1-x}Sc_xN$ nanowires. We start with the previously established, self-assembled growth of AlN nanowire stems on metallic TiN thin films [1], which are subsequently overgrown with ternary $Al_{1-x}Sc_xN$ varying both substrate temperature and metal flux ratio. At high substrate temperatures (> 800 °C), a phase separation of the ternary $Al_{1-x}Sc_xN$ is observed, accompanied by nanowire branching and Raman signals characteristic for cubic rock-salt ScN. In contrast, moderate substrate temperatures below 800 °C favor the formation of wurtzite $Al_{1-x}Sc_xN$ nanowires, with a morphology characterized by inverse nanowire tapering. Still, Sc is homogeneously incorporated with concentrations of $0 \leq x \leq 0.35$, as investigated by energy-dispersive x-ray spectroscopy (EDX) and scanning transmission electron microscopy (STEM). The E_2^{high} and A_1(TO) Raman modes of AlN are broadened upon Sc-incorporation, suggesting wire-to-wire inhomogeneities and/or disorder in the $Al_{1-x}Sc_xN$ alloy. Their consistent red-shift observed as a function of Sc concentration confirms its enhanced incorporation into the wurtzite lattice.

Pure wurtzite $Al_{1-x}Sc_xN$ nanowires are processed into vertical piezoelectric nanogenerators, for which the metallic TiN substrate serves as bottom electrode. The output response resulting from a sinusoidal force excitation indicates metal-polarity and is compared to that of AlN and GaN nanowire-based reference samples [2].

The growth of wurtzite $Al_{1-x}Sc_xN$ nanowires on conductive substrates and the demonstration of first nanogenerators paves the way towards the development of flexible piezoelectric energy harvesters with improved device performance.

[1] P. John *et al.*, Nanotechnology **34**, 465605 (2023).

[2] N. Buatip *et al.*, ACS Appl. Nano Mater. **7**, 15798 (2024).

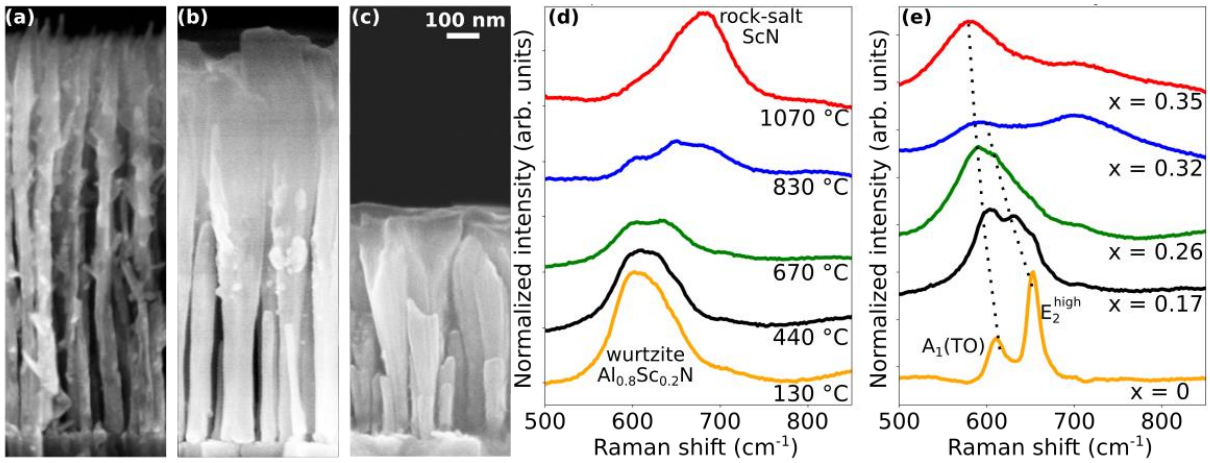

Fig. 1: Cross-section secondary electron micrographs of $Al_{0.8}Sc_{0.2}N$/AlN nanowires grown at (a) 1150 °C, (b) 830 °C and (c) 440 °C. The scale bar is identical for all micrographs. Raman spectra of (d) $Al_{0.8}Sc_{0.2}N$/AlN nanowires grown at different temperatures and (e) $Al_{1-x}Sc_xN$/AlN nanowires with different Sc concentrations grown at 440 °C. The spectra are taken at room temperature with a 473 nm excitation laser.

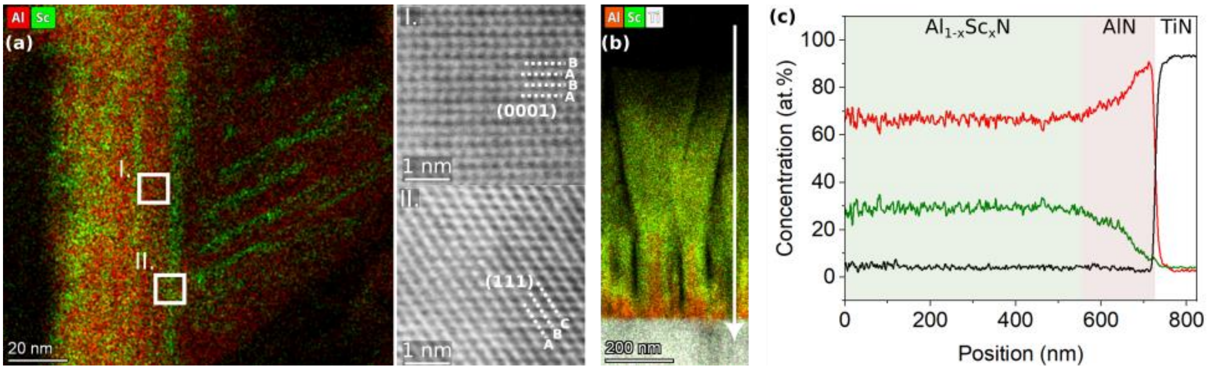

Fig. 2: (a) STEM-EDX map of a branched $Al_{0.8}Sc_{0.2}N$/AlN nanowire grown at 1150 °C, indicating regions of Al-rich wurtzite (inset I) and Sc-rich rock-salt phases (inset II). (b) STEM-EDX map of a inversely tapered $Al_{0.74}Sc_{0.26}N$/AlN nanowires, indicating homogeneous Sc incorporation. (c) STEM-EDX profile along the direction indicated by the white arrow in (b) and confirming the nominal Sc concentration.

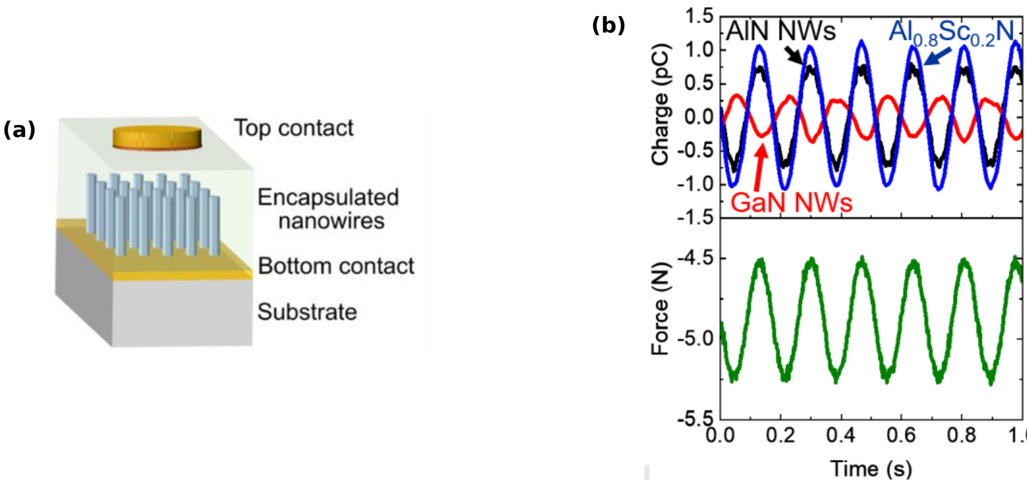

Fig. 3: (a) Schematic of a vertical nanowire-based piezoelectric generator. (b) Charge output of an $Al_{0.8}Sc_{0.2}N$/AlN nanowire generator in response to a sinusoidal force excitation, compared to GaN and AlN reference devices.