

## Supplementary Information

# Superionic Phase Transition in Individual Silver Selenide Nanowires

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# 1. Experimental Methods

## Chemicals

Bismuth (Bi, ChemPur), cadmium oxide (CdO, ChemPur), gold (Au, 999.9 fineness, PIM), octanoic acid (C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>, Sigma Aldrich), selenium (Se, Acros Organics), silver nitrate (AgNO<sub>3</sub>, Sigma Aldrich), tetradecylphosphonic acid (C<sub>14</sub>H<sub>31</sub>O<sub>3</sub>P, ABCR), titanium (Ti, Alfa Aesar), tributylphosphine (C<sub>12</sub>H<sub>27</sub>P, Acros Organics), trioctylphosphine (C<sub>24</sub>H<sub>51</sub>P, ABCR), trioctylphosphine oxide (C<sub>24</sub>H<sub>51</sub>OP, Sigma Alrich). For pre-patterning of the samples AZ ECI 3012 photoresist (MicroChemicals) and AZ 726 MIF Developer (MicroChemicals) were used. Nanowires were contacted using LOR5A lift-off resist (MicroChem), as well as MICROPOSIT S1805 photoresist (DuPont), MICROPOSIT MF-319 developer (DuPont) and MICROPOSIT Remover 1165 (DuPont). All chemicals were used without further purification.

## Synthesis of CdSe Nanowires

The general procedure for growing nanowires (NW) directly on substrates is derived from Littig *et al.*<sup>1</sup> Briefly, the pre-patterned sample was mounted in a four-neck flask loaded with trioctylphosphine oxide. After degassing at elevated temperature, the solution was heated up to the reaction temperature of 255 °C. The substrate was then submersed at minimized stirring. First, the cadmium precursor (Cd(OCA)<sub>2</sub>, 0.5 M) was added followed by the selenium precursor (TOP:Se, 2 M) over the course of 60 s (molar ratio of 1:1). After a reaction time of 10 min the substrate was withdrawn from the solution, allowed to cool to room temperature and was thoroughly cleaned using toluene, hexane and iso-propanol.

For the synthesis of nanowires derived from Ouyang *et al.*,<sup>2</sup> the pre-patterned sample was mounted in a four-neck flask loaded with cadmium oxide, tetradecylphosphonic acid and trioctylphosphine oxide, which were degassed at elevated temperatures and heated up to 350 °C under nitrogen atmosphere over the course of one hour to form a clear solution. The solution was then cooled down to 255 °C, the substrate was submersed in the solution and the reaction was started by adding TBP:Se (3.46 M) in a molar ratio of 1:2.3 (Cd:Se). After a reaction time of 15 min the substrate was withdrawn from solution and processed as described above. **CAUTION!** Cd- and Se-containing compounds are highly toxic. Special care needs to be taken when handling and disposing the chemicals.

## Device Fabrication

A double-layer photoresist approach utilizing a lift-off resist together with a photoresist was chosen in order to provide an undercut for better lift off. Using a spin-coater, the lift-off resist *LOR5A* was applied at 50 rps for 60 s and pre-baked on a hot-plate at 180 °C for 300 s. Next, photoresist *S1805* was applied at 67 rps for 60 s and pre-baked at 120 °C for 60 s. The sample was then placed in a microwriter (*ML3* by Durham Magneto Optics) and the contact patterns were transferred onto the resist at an intensity of typically 130 mJ/cm<sup>2</sup>. The process was completed by submersing the substrate in developer (*MF-319*) for 90 s and thoroughly rinsing with DI water. Prior to the deposition of metal layers for the leads, samples were exposed to a mild O<sub>2</sub> plasma using ambient air for 30 s. Typically, a 75 nm titanium layer was deposited *via* physical vapor deposition, before placing the sample in remover (*Remover 1165*) for three hours. Substrates were then rinsed with acetone, followed by iso-propanol and subsequent drying with nitrogen. Finally,

samples were annealed in vacuum at 150 °C and 300 °C for 30 min each and exposed to UV irradiation for 20 min.

## **Cation Exchange**

For cation exchange from cadmium selenide to silver selenide, a stock solution (5 mM) of silver ions was freshly prepared by dissolving 8.5 mg of silver nitrate ( $\text{AgNO}_3$ ) in 10 mL methanol. The samples were submerged into a solution of methanol and toluene with a ratio of 4:1 and the reaction was then started by adding 80  $\mu\text{L}$  of  $\text{AgNO}_3$  ( $\text{MeOH}$ ), with reaction times of up to 24 hours. To block light during the reaction, the vessel was wrapped in aluminum foil. The reaction was terminated by removing the substrate from solution and thorough rinsing with methanol and iso-propanol.

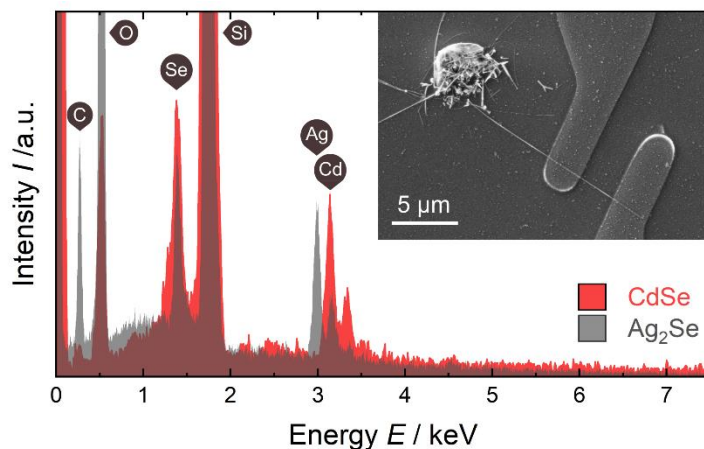
## **Characterization of CdSe/Ag<sub>2</sub>Se NWs**

**Atomic Force Microscopy** was performed using a JPK *Nanowizard II* without any additional sample preparation. Image processing and profile extraction for determining the NW diameters was done with the software package *Gwyddion*. **X-Ray Diffraction** was carried out in a Philips X'pert Pro MPD in a range of 5 to 60 ° with a Cu K- $\alpha$  source ( $\lambda = 1.54 \text{ \AA}$ ). The software *X'pert HighScore Plus* was used for data evaluation. A background subtraction according to the Sonneveld & Visser method was applied to each measurement. **Scanning Electron Microscopy** was performed on a LEO 1550 using a beam energy of 10 keV for imaging and 5-20 keV for energy-dispersive X-ray spectroscopy for single Ag<sub>2</sub>Se nanowires as well as a Zeiss EVO MA 10 using a beam energy of 22 keV for energy-dispersive X-ray spectroscopy on ensembles of CdSe nanowires.

## Transport Measurements

Electrical characterization of the devices was carried out in a self-built probe station. All measurements were performed in the dark. The sample was placed inside a grounded metal container and contacted with tungsten tips. Yokogawa *GS200* voltage source units were used to apply voltages to the *drain* and *gate* electrodes. A series resistance of 10 k $\Omega$  was connected to the *gate* electrode to protect the sample and the equipment in case of a failure of the dielectric layer. Currents were measured with a Femto *Current Amplifier DLPCA-200* in conjunction with a Keysight *34465A* multimeter. Measurements were automated using a *LabView* program. Some measurements were also performed using a Keithley *K4200 SCS*. For temperature dependent measurements, the samples were mounted in a Linkam *LTS420E-P* probe stage. Prior to experiments the stage was purged with nitrogen for ten minutes. Throughout experiments, samples were continuously flushed with nitrogen. Heating rates ranged from 0.5  $^{\circ}\text{C}/\text{min}$  to 10  $^{\circ}\text{C}/\text{min}$ . Voltage pulses of 1-10 mV were applied every 0.5-10 s to measure the current as a function of the temperature. The transition temperature  $T_c$  was determined from the maximum of a Lorentzian fit applied to the derivative of the current and averaged over 1-15 measurements. For the temperature dependent transistor measurements, the temperature was raised by 5  $^{\circ}\text{C}/\text{min}$  and allowed to settle for 2 min, to ensure thermal equilibrium.

## 2. EDX spectra of nanowires

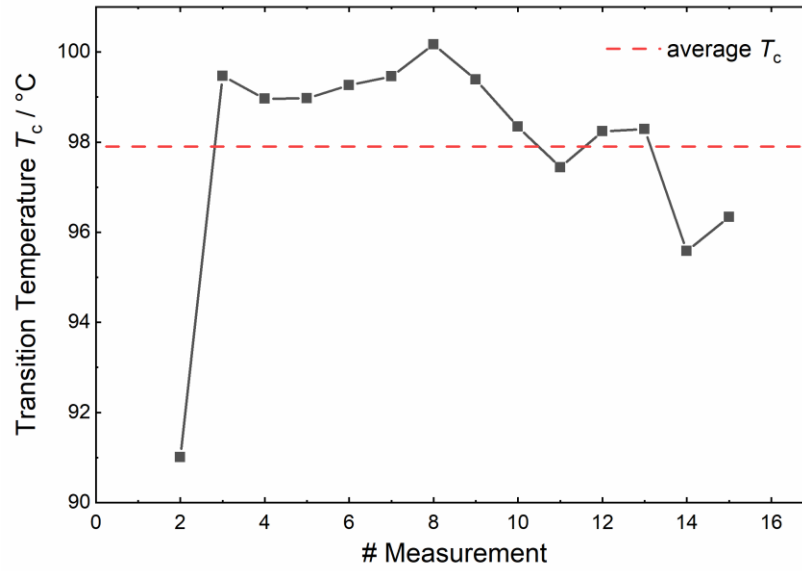


**Figure S1.** EDX spectra obtained from nanowires with a composition of CdSe (ensemble, red) and Ag<sub>2</sub>Se (single nanowire, grey), revealing the complete removal of cadmium. Spectra are normalized to the dominant Cd and Ag peak, respectively. The inset shows a scanning electron microscope image of the investigated Ag<sub>2</sub>Se device. Electron microscopy was performed after all transport measurements had been carried out, in order to not damage the devices.

Energy-dispersive X-ray spectroscopy (EDX) was used to obtain the elemental composition of individual nanowires once all electronic measurements were performed. After complete cation exchange, no traces of cadmium were found, though large amounts of silver were present. To within the resolution limit of our EDX measurements, on the order of 3%, cation exchange to Ag<sub>2</sub>Se is complete. From previous reports in the literature it is known, that cation exchange from CdSe to Ag<sub>2</sub>Se is typically very efficient and only trace amounts of cadmium ions remain, if at all.<sup>3-5</sup> In order to ensure maximum removal of cadmium from the nanowires, we performed cation exchange reactions typically over the course of 24 hours. However, the presence of trace amounts of cadmium remaining in the nanowires after cation exchange cannot be ruled out. The selenium deficiency observed prior to cation exchange is likely an artefact caused by the background signal

from the silicon substrate. When correcting for the initial deficiency in selenium, the ratio of silver to selenium after complete cation exchange is close to 2:1, to within experimental accuracy.

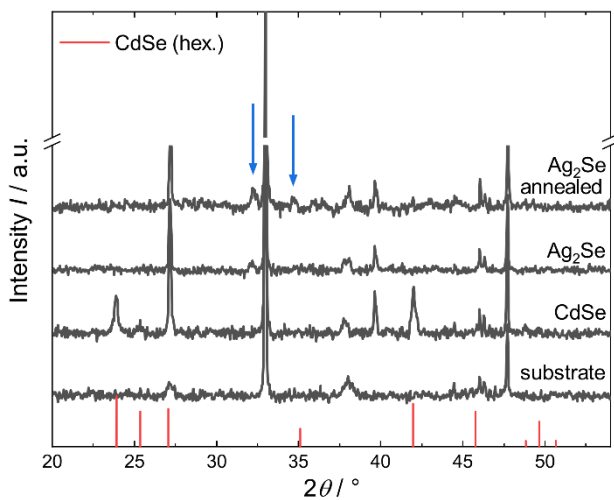
### 3. Evolution of $T_c$ during temperature cycling



**Figure S2.** Evolution of the transition temperature  $T_c$  for a single  $\text{Ag}_2\text{Se}$  nanowire with a diameter of  $44 \pm 7$  nm, obtained from different temperature cycles.  $T_c$  was determined from the maximum of a Lorentzian fit to the derivative of the current for every cycle.



## 4. XRD of nanowire ensembles



**Figure S3.** X-ray diffraction (XRD) patterns of a bare substrate, after synthesis of an ensemble of CdSe nanowires, after cation exchange to Ag<sub>2</sub>Se, as well as after heating the Ag<sub>2</sub>Se nanowires to 150 °C. The red lines represent the expected peaks for hexagonal CdSe (JCPDS 08-0459). Blue arrows indicate the peaks obtained from Ag<sub>2</sub>Se (JCPDS 24-1041) after annealing at 150 °C.

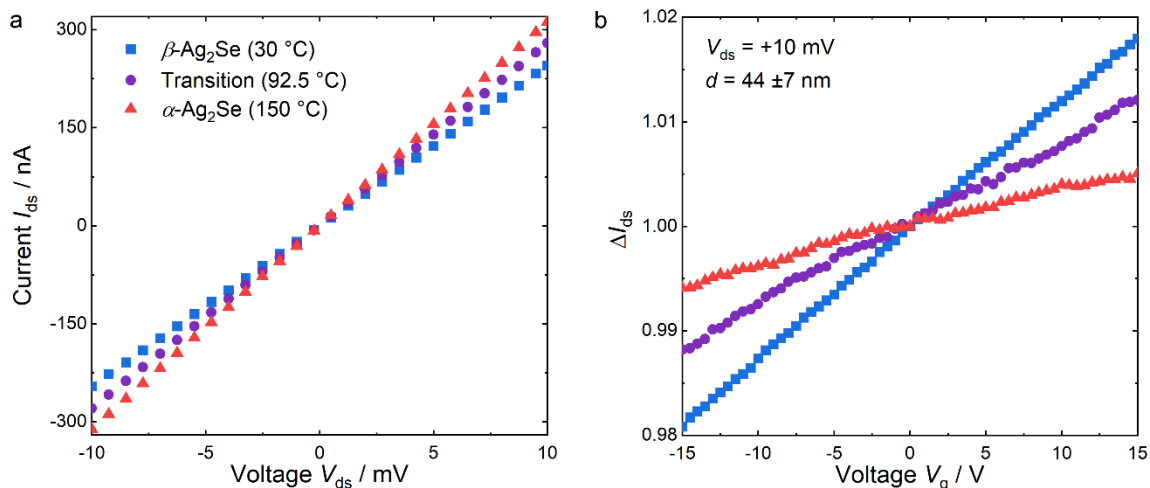
Cation exchange from CdSe to Ag<sub>2</sub>Se was additionally confirmed *via* X-ray diffraction (XRD) using large-scale ensembles of nanowires (Figure S3), as the signal from individual nanowires is too weak. After CdSe nanowire synthesis peaks at 23.8° and 42.0° can be identified, corresponding to (100) and (110) of hexagonal cadmium selenide, respectively. The additional peaks around 27° and 39.5° can potentially be attributed to the (012) and (110) peaks of bismuth, which was present as patches of thin film on the substrate to form catalyst particles upon melting during synthesis. Subsequent to cation exchange, the peaks corresponding to CdSe vanished completely, indicating the removal of cadmium, though no additional peaks were observed that could be attributed to Ag<sub>2</sub>Se. Reduced crystallinity due to the exchange reaction, formation of multiple crystal phases and the strong background signal from the substrate could potentially mask

other peaks, especially as peaks corresponding to the (112) and (121) plane are expected around 34 ° (JCPDS 24-1041), which coincides with the peak originating from the silicon substrate. Furthermore, Jang *et al.*<sup>6</sup> reported that for as-deposited Ag<sub>2</sub>Se nanoparticles no distinct peaks were obtained from XRD patterns, but that sintering the sample above the transition temperature increases the crystallinity of the sample, allowing to obtain peaks of a mixture of the  $\beta$ - and  $\alpha$ -phase as a result of the nano-sized particles. In our samples, heating the substrate to 150 °C in a nitrogen atmosphere did result in a slightly more defined signal, where two peaks were obtained at 32.2 ° and 34.7 °, as indicated by the blue arrows. Those peaks may correspond to the (120) and (121) peaks of orthorhombic silver selenide, however the first peak appears to be slightly shifted from 32.7 ° according to the reference (JCPDS 24-1041).

Different crystal structures have been reported for the low-temperature phase of silver selenide, mostly in terms of tetragonal<sup>7</sup>, monoclinic<sup>8</sup> or orthorhombic<sup>9,10</sup> structures, where the latter is known to be the most common at room temperature<sup>11</sup>. The monoclinic phase has been observed as a distorted orthorhombic structure after multiple heating cycles<sup>12</sup>, while the tetragonal phase has been found in nanosized particles<sup>13</sup>. However, this phase has been reported to be stable only prior to the initial phase transition ( $\gamma \rightarrow \alpha$ )<sup>14</sup>.

This indicates that the crystal structure of pristine Ag<sub>2</sub>Se nanowires directly after cation exchange differs from the typical low-temperature phase. After annealing this is believed to have no effect on subsequent measurements, which is concurring with previous reports<sup>14,15</sup>. Given the consistent behavior of nanowires investigated here with diameters from 17 nm to 52 nm and the lack of peaks indicating the presence of the tetragonal phase in XRD (Figure S3), the room-temperature phase is assumed to correspond to the orthorhombic phase.

## 5. $I$ - $V$ curves and transistor characterization at different temperatures



**Figure S4.** Electronic characterization of a single  $\text{Ag}_2\text{Se}$  nanowire at 30 °C, 92.5 °C and 150 °C. The superionic phase transition was at 91.7 °C. (a)  $I$ - $V$  characteristics. Ohmic behavior is observed at all three temperatures. (b) Change in *source-drain* current at constant bias as a function of *gate*-voltage. The majority charge carriers are seen to be n-type above, below and at the superionic phase transition.

### References

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