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Electrical Switching and Phase Transformation in Silver Selenide Nanowires

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Resistance switching in solid-state electrolyte materials has been receiving a growing amount of interest for memory device applications. In these memory devices, a polycrystalline or amorphous Ag^+ or Cu^+ ion conductor film is sandwiched between two electrodes.[1−4] Electrical switching is believed to be realized by growing or dissolving a nanoscale metallic Ag or Cu filament when a voltage is applied between the two electrodes, although insufficient work has been done to characterize the nature and formation mechanism of the filament. In addition, the nanoscale conductive pathway is thought to be much smaller than the total device area, and the active device regions are polycrystalline or amorphous, sometimes even having complicated nanostructures.[2] The presence of a large number of random interfaces complicates interpretation of experiments done in these systems.

Single-crystal nanowire (NW) devices offer a system with a small number of well-defined interfaces, and their cross section is on a scale similar to that of the proposed conductive pathways. For these reasons, they may offer the potential to study in depth the fundamental processes involved in resistance switching in these devices. Here we report for the first time electrical transport measurements in NW structures of a solid-state electrolyte. By single NW electrical transport and in situ transmission electron microscopy (TEM) studies, we discover two types of electrical behavior linked to Ag_2Se NW phase transformations.

Ag_2Se is a mixed ionic conductor with a transition from a low-temperature orthorhombic phase (β) to a high-temperature superionic conducting cubic phase (α) at 135 °C.[5] Ag_2Se NWs were produced by solution-phase synthesis following the procedure published by the Xia group.[6,7] Briefly, crystalline Se NWs are grown from amorphous selenium colloid. These Se NWs are reacted with $AgNO_3$(aq) to form Ag_2Se NWs (Supporting Information). NWs were characterized in a 200 kV Phillips CM20 transmission electron microscope (TEM). Compositional analysis was by energy dispersive X-ray spectrometry (EDX). Electrical contacts to single NWs were fabricated by electron beam lithography (EBL). The EBL process requires baking the resist. A range of temperatures were used (95−180 °C). The metals used for contact were Au, Ag, and Ni.

The Ag_2Se NWs as synthesized varied in diameter from 40 to 200 nm (Figure 1a). The tetragonal phase observed by Xia for wires smaller than 40 nm was not observed here.[6] The EDX data indicate that NWs consist of Ag and Se with an atomic ratio of 2:1 (Figure S1 in Supporting Information). They were single crystalline orthorhombic Ag_2Se as determined by TEM and selected area electron diffraction (SAED) (Figure 1b and inset). The growth direction is along [001] direction, different from the [100] direction in Xia's study.[7] The reason is not yet understood.

Ag_2Se NW electrical devices consist of single NWs contacted by two or more electrodes (Figure 1c and d). The transport measurement was done by applying a voltage (V) across the two metal electrodes and recording the resulting current (I). A resistor (2−3 MΩ) is connected in series with the whole circuit to protect the NWs from Joule overheating when they are switched into a highly conducting state. The two-terminal electrical transport shows two different behaviors. The first type of behavior exists in devices fabricated with an electron-beam resist curing temperature below 140 °C. The devices exhibit a linear dependence of I versus V, suggesting ohmic conduction (Figure 1e). Scanning the voltage upward and downward does not change the $I-V$ curve. The resistance of the NW is 4.7 kΩ without a serial resistor (Figure S2). The resistivity is 1.2×10^{-3} Ω·cm, consistent with the literature value.[10] Devices baked at 140 °C or above predominately displayed a second type of behavior (Figure 1f). These devices would maintain a very high resistance (off-state) of >GΩ (resistivity >10^3 Ω·cm), until some threshold voltage, where the resistance would drop precipitously to a value of several 100 Ω (on-state, resistivity ~10^{-4} Ω cm, Figure S3). The resulting on−off ratio approaches a very high value, near 10^7. The on-state generally persists no more than a few seconds after the voltage is scanned back to a small value or zero, but occasionally on-state persistence times on the order of minutes were observed, so the switching was volatile. Voltage thresholds for switching varied from device to device and from scan to scan on the same device, with values ranging from 0.5 to 3 V. Devices were fabricated both with single

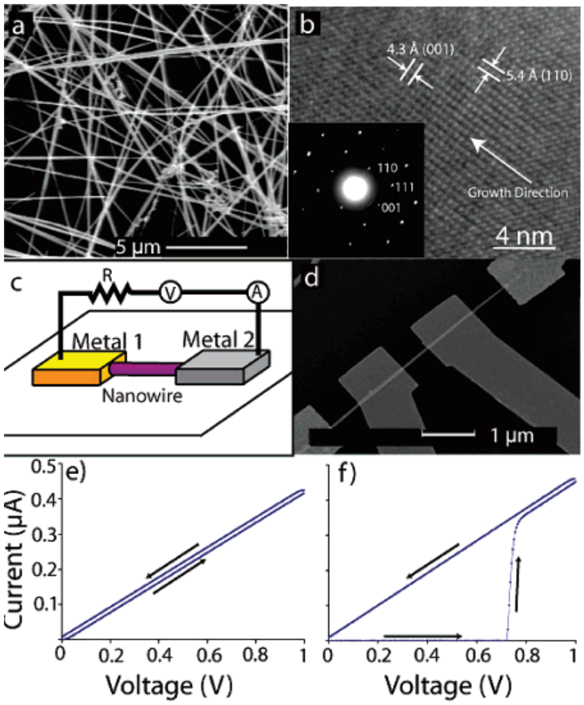

Figure 1. (a) SEM image of Se NWs before $AgNO_3$ reaction. Ag_2Se NWs are morphologically similar. (b) HRTEM image of Ag_2Se NW (SAED inset). (c) Device schematic. (d) SEM of a fabricated device. Contacts are Ag−Ni−Ni−Ag. (e) Electrical behavior of devices baked at 95 °C, in series with a 2.34 MΩ resistor. (f) Electrical behavior of devices baked at 140 °C, in series with a 2.15 MΩ resistor.

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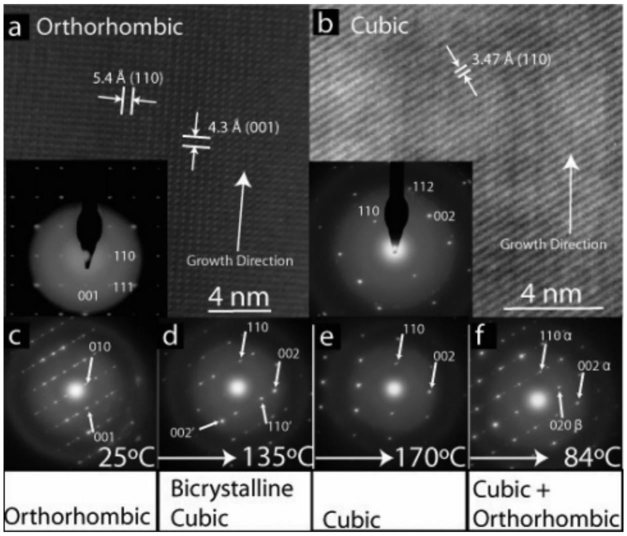

Figure 2. (a, b) HRTEM image of Ag_2Se NWs baked under resist at 120 and 160 °C, respectively (SAED inset). (c−f) SAED of an Ag_2Se NW at different temperatures during an in situ TEM heating experiment.

metal contacts of Au, Ag, and Ni and also with two metal contacts of Ag−Au and Ag−Ni. Gaps varied from device to device but were in the range of 75 nm to several micrometers. Threshold switching was observed for all contact types and was independent of bias direction with respect to the silver electrode in the Ag−Au and Ag−Ni devices. These observations are different from the metal filament forming device in previous studies,[1−4] which requires voltage polarity control to build or dissolve the metal filaments.

The temperature, drawing a line between the two different behaviors of the Ag_2Se NWs is 140 °C, which is approximately the superionic transition temperature of 135 °C. In the superionic state, Ag ions can diffuse nearly freely.[8] Thus we propose that NWs had changed to a phase different from β-Ag_2Se after they had been baked above the superionic transition temperature and cooled to room temperature. To prove this conjecture, we used TEM to study Ag_2Se NWs with a baking history at 120 and 160 °C, respectively. To mimic the conditions of transport device fabrication, these NWs were baked under a cover of EBL resist and the lift-off process was performed before the TEM study. The high-resolution TEM and SAED patterns (Figure 2b and inset) show that the NWs baked at 160 °C are single crystalline although their crystal structure has been changed to a new one, which can be indexed as a cubic α-Ag_2Se with the NW long axis along the [111] direction. Excitingly, this is the first time that the α-Ag_2Se structure has been stabilized at room temperature. A possible reason might be small domain size and/or the large contribution of surface energy in NWs. Although a large number of NWs show a pure α-Ag_2Se phase, we also found that some NWs have a mixture of both α- and β-phase within the same NW. In comparison, NWs baked at 120 °C remain orthorhombic β-Ag_2Se (Figure 2a).

To understand how the phase transformation takes place, we have performed an in situ TEM heating and cooling study (Figure 2c−f). The rate of temperature ramping was slow (∼5 °C/min). NWs were kept at the desired temperature for ∼15 min for structural studies. NWs started in the orthorhombic structure at room temperature (Figure 2c). At 135 °C, the orthorhombic β-Ag_2Se NWs transformed to the superionic conducting α-phase but with a bicrystalline structure (Figure 2d). When the temperature was raised to 170 °C, the twinning was annihilated and only a single crystal of α-Ag_2Se remained (Figure 2e). On cooling, this high-temperature structure was maintained to 84 °C, where another transition was observed, not to the original orthorhombic structure but to a predominantly cubic structure with some orthorhombic phase (Figure 2f). The temperature hysteresis is common in Ag_2Se.[9]

The correlation of electrical and phase behavior suggests that Ag_2Se NWs in the room-temperature cubic α-phase have an initially high resistance and display threshold switching, while the orthorhombic β-Ag_2Se NWs have a low resistance and do not display threshold switching. Ag_2Se is generally cited in the literature as an n-type semiconductor with a resistivity of $10^{-3}-10^{-4}$ Ω·cm for the orthorhombic phase.[10] In the off-state cubic NWs, the Ag^+ cations are randomly arranged,[8] forming a amorphous sublattice, which might cause the formation of localized trap states close to the conduction band edge, resulting in high resistance.

The cubic NWs exhibit a "threshold switching" phenomenon. While it is tempting to explain the switching in terms of the observed phase transformation, we believe that this is not the case since our switching is volatile. Threshold switching has appeared in many chalcogenide glass systems lacking such phase behavior. A highly conductive transitory filament is usually conceived, which may be electronic in nature.[11] Such an explanation might be applicable here.

In summary, we have shown the correlation of electrical properties with phase transformation in mixed ionically conducting Ag_2Se NWs. The high and low conducting phases correspond to the orthorhombic β-Ag_2Se and cubic α-Ag_2Se, respectively.

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Supporting Information Available: Synthesis of Ag_2Se NWs, fabrication and electrical data of two terminal devices, and EDX of Ag_2Se NWs. This material is available free of charge via the Internet at http://pubs.acs.org.

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