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Investigation of electromigration in In$_2$Se$_3$ nanowire for phase change memory devices

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The decomposition of In$_2$Se$_3$ nanowire phase change memory devices during current-driving operation was investigated. The devices were subjected to thermal/electrical stress with current density and electric field during the reset operation at 0.24–0.38 MA/cm$^2$ and 5.3–6.4 kV/cm, respectively. After multiple operation cycles, a change in morphology and composition of the In$_2$Se$_3$ nanowire was observed and led to the device failure. The transmission electron microscopy and energy dispersive analysis indicate that electromigration causes the catastrophic failure by void formation where In atoms migrate toward the cathode and Se atoms migrate toward the anode depending on their electronegativities. © 2013 AIP Publishing LLC.

The concept of using the phase transition of certain chalcogenides for data storage was introduced by Ovshinsky in 1968. The information (“1” or “0”) is stored by crystalline cogenides for data storage was introduced by Ovshinsky in 1968. The information (“1” or “0”) is stored by crystalline amorphous (c to a) or amorphous to crystalline (a to c) transformation of a phase change material (PCM). This resistive switching is obtained as a function of a set/reset current (I$_S$/I$_R$) pulses, which induces joule heating in the PCM. The two states can easily be distinguished since the crystalline phase has substantially larger resistivity than that of the amorphous phase. Phase change random access memory (PRAM) is one of the most promising candidates for replacing conventional flash memory due to its excellent scalability, fast switching speed, low programable current, a large sensing margin, and non-volatility.

Nanowire (NW) based PRAM devices have been constructed using various materials such as Ge$_2$Sb$_2$Te$_5$, GeTe, GeSb, Bi$_2$Te$_3$, Sb$_2$Te$_3$, In$_2$SbTe$_6$, and In$_2$Se$_3$. In general, preliminary devices using PCM NWs in all of the above material systems have shown good switching characteristics while enabling scalability without resorting to complex lithography, special device structures, or etching of the PCM into nano-meter size. Despite these advantages of NW based PRAM devices, their device failure mechanisms remain unexplored; even in the case of thin films, device failure has been understood only for Ge$_2$Sb$_2$Te$_5$. The NWs are susceptible to damage during the current driving operation, and any decomposition can result in operation failure of the device.

As studies continue to emerge on utilizing NW structures for future memory devices, it is critical to understand the reliability and failure mechanism, and we undertake such a study here for indium selenide NW devices. Recently, Lee and Kang reported failure of In$_2$Se$_3$ thin film PRAM devices. However, their explanations for failure mechanism were unclear and the failure of their devices might be affected by the interface with a metal electrode. Here, we fabricate In$_2$Se$_3$ NW PRAM devices and analyze the failure mechanism during current driving operation. The decomposition due to phase change volume can be ruled out as a dominant failure mechanism since the active region is in the middle of the In$_2$Se$_3$ NWs through post-annealing for minimization of the contact resistance as well as the initial crystallization of the PCM.

In$_2$Se$_3$ NWs were synthesized in a 1 in. quartz-tube furnace system with two-temperature zones using a vapor-liquid-solid (VLS) mechanism. High purity In$_2$Se$_3$ powder (0.2 g, CERAC, 99.99%) was placed in the middle of the high-temperature zone (920 °C) and a 50 nm of thermal SiO$_2$-coated Si wafer with 1 nm thick gold film as catalyst was loaded in the middle of the low-temperature zone (690–740 °C). Argon (25 SCCM) mixed with hydrogen (5 SCCM) was introduced as carrier gas at 1 Torr for 60 min.

The morphology and composition of the NWs were analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) operated at 200 kV, with energy dispersive x-ray spectroscopy (EDS) for the chemical composition analysis of individual NWs. The as-synthesized NWs were separated from the substrate and suspended uniformly in isopropyl alcohol by sonication for 1 min. The NW suspension was dropped on a 50 nm thermal SiO$_2$-coated Si wafer (100) with pre-patterned Au pads prepared by optical lithography. Pt interconnect lines were deposited between the NW and Au pads using focused ion beam (FIB) for electrical contact. The electrical characteristics of the In$_2$Se$_3$ NW devices were measured using a Keithley 4200 semiconductor parameter analyzer with a probe station and an Agilent 81110A pulse generator.

Figure 1(a) shows an SEM image of a high density as-synthesized In$_2$Se$_3$ NW ensemble with diameters in the range of 50–300 nm and lengths up to 100 µm. Figure 1(b) shows a single In$_2$Se$_3$ NW with a tetragonal faceted structure. Figure 1(c) provides the EDS spectrum of a single NW with In and
Se composition in the approximate atomic ratio of 2:3. The Cu and C signals in the spectrum are from a carbon-coated copper TEM grid.

A two-terminal In$_2$Se$_3$ NW device was fabricated to investigate the resistive switching behaviour and analyze the morphology of the NW during device operation. Here, the diameter of the NW is 150 nm and the length between the pads is 6 μm (effective NW length: 11.7 μm). The devices were annealed at 400 °C under Ar ambient before measurement for the initial crystallization and the reduction of contact resistance between the NW and pads. This post-annealing step is important to discriminate the decomposition of In$_2$Se$_3$ NW from the interface with metal electrode since low contact resistance forms an active region apart from the metal electrode. The electrical characteristics of the device were measured with current pulses and the device resistance was measured at a small read voltage of 0.2 V (DC) after each pulse. The studies were repeated for a few devices and the results were found to be consistent.

Figure 2(a) shows the resistance change of the In$_2$Se$_3$ NW device as a function of IS/IR (set/reset) pulses. The NW was initially in a crystalline state after post-annealing. In order to accelerate the failure mechanism, harsh bias conditions were intentionally applied for the resistance change. A pulse of 200 ns fixed width and 2 ns sharp fall-down edge was applied for amorphization. A large increase in resistance (8.7 GΩ) was observed upon applying the pulse above a threshold value of 86 μA due to amorphization by joule heating and rapid quenching. A pulse of 100 μs fixed width and 20 μs fall-down edge was applied for crystallization. In contrast to amorphization, a significant decrease in resistance (85 kΩ) was observed upon applying the pulse above a threshold value of 0.51 nA for the crystallization. Once the NW is set to a specific resistive state, its resistance is stable and the storage of data is nonvolatile. The I-R curve clearly shows two identified memory states with a high resistance switching ratio of $10^5$. Figure 2(b) shows the endurance characteristics of the NW device with repeatable memory switching between the high and low resistance states. However, the device was stuck in the high resistance state after several cycles which is mainly caused by void formation.

An analysis of the morphology and composition change during the operation of the NW device is necessary to understand the NW decomposition. Figure 3(a) shows the SEM image of the In$_2$Se$_3$ NW device before the decomposition of

![Figure 1](image1.png)

**FIG. 1.** (a) SEM image of the as-synthesized In$_2$Se$_3$ NWs. (b) SEM image of a single In$_2$Se$_3$ NW. (c) EDS spectrum of a single In$_2$Se$_3$ NW.

![Figure 2](image2.png)

**FIG. 2.** (a) Resistance change of the PRAM device as a function of I$_S$/I$_R$ (set/reset) pulses. For crystallization/amorphization, 100 μs/200 ns of I$_S$/I$_R$ pulses were applied, respectively. (b) Endurance characteristics of the same device.
the NW and Figure 3(b) shows the image after the decomposition. At this stage, a void is clearly seen in the active region in the middle of the NW. During repeated switching, the joule heating due to \( I_s/I_R \) pulses is concentrated in the active region of the NW\(^1\) and this thermal/ electrical stress causes the decomposition in the PCM, seen as void which is responsible for the operation failure of the device.\(^{11-14}\) The decomposition of NWs of ZnTe and CdTe commonly used in thermoelectric power generation has been previously reported.\(^{17,18}\) Small NWs subjected to electrical and thermal stress face different forms of disintegration depending on the material, size, electric field, local heat load, etc.

The decomposition in In\(_2\)Se\(_3\) NW has been carefully analyzed here by using TEM and EDS data. Figures 4(a) and 4(b) show the cross-sectional TEM images of the NWs with a small void in devices A and B, respectively. Ti and Pt were deposited on the NWs for preparation of TEM samples and the devices were cut by FIB to include the NW with a small void at the edge. Figure 4(c) shows EDS line profiles along the line A-B and K-L. The ratios between In and Se is almost constant and the same as the EDS profile in Fig. 1(c).

Figure 4(d) shows the EDS line profile along the line C-J and M-W. Although the In and Se compositions remain at the atomic ratio of 2:3 in regions C-E and M-O, the In intensities show a hill in regions F and P, and Se intensities show a hill in regions G and Q in EDS profiles. As for the thermal mechanism, the hottest spot (active region) can be shifted from the middle of the NW by Thomson effect.\(^{20}\) However, asymmetric thermal gradient is irrelevant to directional preference of decomposition. The asymmetric thermal gradient plays a role in defining the active region and melting the NW at the hottest spot.\(^{11}\) The direction of migrating atoms can be explained by the mass movement of ionized atoms in the molten state. The electronegativities of In and Se are 1.5 and 2.4, respectively.\(^{21}\) The In atoms become anions, whereas Se atoms become cations in the molten state of In\(_2\)Se\(_3\). Therefore, the anionic Se ions diffuse to the anode and the cationic In ions diffuse to the cathode in molten state under electrostatic force. Far from the void (regions I-J and U-W), the intensity of each element and the ratio between In and Se are nearly restored to the composition of In\(_2\)Se\(_3\). These EDS results indicate that the device operation is seriously affected by the decomposition which can be explained by the combination of incongruent melting and electrostatic force.\(^{11,14}\)

The movement of atoms under the influence of electrostatic force is referred to as electromigration. The electric fields (current densities) of devices A and B during reset programming are 6.4 kV/cm (0.38 MA/cm\(^2\)) and 5.3 kV/cm (0.24 MA/cm\(^2\)), respectively. These values are large enough to cause electromigration in normal metals such as Ag, Cu, Au, In, TiN, Pb, and Mg.\(^{22}\) Figure 4(e) shows the endurance characteristics of the device B. An improved endurance characteristic for device B has been achieved due to reduced atomic flux by lower electric field.\(^{12}\) The temperature in the active region reaches above the melting point of \( \approx 680 ^\circ C \) by
joule heating during the reset programming. The mass movement of ionized In and Se atoms occurs in the molten state under the influence of electrostatic force. Therefore, decomposition of the PCM due to an electrostatic force-induced electromigration results in operation failure of the PRAM. The electromigration can be mitigated and the endurance characteristics can be improved by applying reverse polarity pulses. The reset voltage pulse can be lowered by decreasing the NW diameter which reduces the electric field. This indicates that the scaled NW devices can improve the endurance characteristics besides doping and device passivation.

In summary, we studied the decomposition of In$_2$Se$_3$ NW PRAM devices during their operation. The NWs were synthesized by a VLS method and two-terminal PRAM devices were fabricated. The phase change volume was well isolated from the metal electrode through post-annealing. Reversible switching operation was realized by applying 100 $\mu$s/200 ns of current pulses for the crystallization/amorphization. After repeated switching cycles, a void was formed in the active region of the NW, which led to catastrophic failure of the device. The endurance improved with a reduction in operating electric fields. The TEM and EDS results show that the atomic migration occurs in the molten state under the influence of electrostatic force-induced electromigration where the ionized In atoms migrate toward the cathode and ionized Se atoms migrate toward the anode depending on their electronegativities.

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