Phase Change Nanowires: Extremely Low Resistance Drift and Direct Observation of Field-Induced Nucleation and Switching

Ritesh Agarwal*, Mukut Mitra, Yeonwoong Jung, Sungwook Nam and Hee-Suk Chung

Department of Materials Science and Engineering
University of Pennsylvania, Philadelphia, PA 19104
*riteshag@seas.upenn.edu

ABSTRACT

Time dependent drift of parameters such as threshold voltage and amorphous state resistance have important implications because they lead to spontaneous changes in the measurable device parameters used for recording and reading information in PCM devices. Our study on PCM devices based on Ge$_2$Sb$_2$Te$_5$ nanowires show much lower temporal drift of device parameters such as threshold voltage, and amorphous state resistance compared to conventional thin-film PCM devices. It has been observed that PCM nanowires exhibit at least one order of magnitude lower drift coefficients in comparison to thin-film devices. We show that the lower temporal drift observed in nanowire devices is due to their unique geometry which has a large surface area leading to efficient stress relaxation during the formation of the amorphized “dome”. We will present results from experiments where stress in reintroduced into nanowire devices, upon which they display much higher temporal drift. These measurements strongly suggest that temporal drift observed in PCM devices is dominated by stress-relaxation and not due to relaxations involving dynamics of the intrinsic traps. We also utilized Ge$_2$Sb$_2$Te$_5$ nanowires to study the role of electric-field during PCM operation via insitu TEM microscopy. Most of all, we obtained direct evidence of electric-field assisted nucleation process which guides the crystalline nuclei formation in a correlated manner with the applied electric-field, unlike the random nucleation and percolation behavior typically observed in thermally-induced recrystallization. Our observations suggest that the electric-field plays a unique role in fast switching behavior, combined with the thermal and mechanical processes caused by joule-heating.

Key words: nanowire, phase change memory, drift, stress, insitu microscopy.

1. INTRODUCTION

Electric-field induced structural phase transformations in chalcogenides have attracted significant interest due to their potential use in non-volatile phase change memory (PCM) devices [1]. Chalcogenide materials (e.g., Ge-Sb-Te alloys) are particularly important for PCM owing to their fast and reversible crystalline to amorphous phase change properties via Joule heating to produce electrically distinct states. However, various challenges need to be addressed before PCM can become a viable alternative to flash technology. These challenges include understanding their structural, electronic, thermal and mechanical properties especially in the amorphous state, the effect of field on electrical switching, and device scalability.

Chalcogenide glasses are affected by relaxation processes that occur on a large distribution of timescales resulting in time dependent electrical [2-5], optical [6], mechanical [7], and thermal [8] behavior. For PCM device operation, the amorphous state resistance and the field strength at which it switches to a higher conducting state (threshold voltage, $V_{th}$) are fundamental parameters that determine the device reliability. Any phenomenon that affects these critical parameters leading to temporal drift is an important issue that needs to be investigated. Time dependent drift [2-4] of these parameters have important implications because they lead to changes in the measurable device parameters used for recording and reading the information in phase change materials. Particularly, the issue of drift becomes very important for designing multilevel memory devices, as drifts in resistance would lead to states being overwritten causing serious errors [9,10]. Therefore, it becomes important to understand the physical origin of phenomena that lead to drift in material properties to eventually minimize such effects.

The drift of amorphous phase resistance in PCM devices has been described by a power law (typical of activated processes in chalcogenide glasses)
\[ R(t) = R(t_0)(t / t_0)^\alpha, \]

where \( \alpha \) is reported in the range of 0.03 to 0.1 depending on the device type and initial amorphous state resistance [2-4]. However, the drift in \( V_{th} \) has been fitted either with a power law [2, 3], or to a logarithmic dependence [4],

\[ \frac{\Delta V_{th}(t)}{V_{th}(t_0)} = \frac{V_{th}(t) - V_{th}(t_0)}{V_{th}(t_0)} = \nu \ln \frac{t}{t_0}, \]

where \( \nu \) has been reported in the range of −0.02-0.04 [4].

The fundamental understanding and the origin of drift in phase change materials is still being debated and has been explained by a variety of effects including stress relaxations in the amorphous material [2, 4], relaxation processes which anneal the electronic defects [2,3], and the formation of valence alternation pairs (VAPs) [11-13], all of which can increase the mobility gap causing an increase in material’s resistivity and \( V_{th} \). Within the electronic structural relaxation model, the annealing of traps occurs due to atomic motions resulting in an increase in the intertrap distance causing a change from modified Poole to Poole-Frenkel (P-F) mechanism of conduction. The stress relaxation model is based on the large internal hydrostatic pressure that is built in the amorphous dome due to the melt-quench process owing to the large difference between the densities of the crystalline and amorphous phase (several percent). The slow relaxation of internal stress (volume dilation), consistent with the stress relaxation data [14], is due to atomic motions within the completely embedded amorphous dome which increases the Fermi level from the valence band edge causing time-dependent increase in resistance and \( V_{th} \).

One way to distinguish between these proposed mechanisms is to design experiments on un-embedded nanoscale systems in which the stress upon amorphization can relax efficiently. The stress relaxation efficiency can also be engineered by changing the surface to volume ratio or by embedding the nanostructured device without altering the material’s electronic properties. If the stress relaxation mechanism dominates the drift dynamics, then any change in the system’s ability for efficient stress relaxation should significantly influence its drift characteristics.

Phase change nanowires (NWs) are an important class of materials in this regard as they represent the minimum dimension that can be reliably connected into devices, their sizes can be controlled down to 10 nm to tune the surface to volume ratio, and unlike thin-films, NW devices can be configured with their surfaces exposed or completely embedded [15-17]. Experiments on NWs have shown efficient electrical switching due to material confinement and current localization, scalability [15], multi-bit operation [16], and evidence of strong heterogeneous nucleation from its surfaces [17]. Here, we utilize the unique geometry of phase change NWs to understand the mechanism of resistance and \( V_{th} \) drift in PCM. It is shown that NW devices have extremely small values of drift coefficients in comparison to thin-films. By systematically varying the stress relaxation parameters such as the surface to volume ratio of the NWs and comparing un-embedded and embedded devices, it is demonstrated that the release of the built-in stress upon amorphization is primarily responsible for drift in phase change materials.

One of the biggest advantages for performing electric-biasing experiments on lateral NW devices in a TEM is to be able to monitor the initiation, the spatial location and the extent of structural and chemical changes in the device upon the application of electrical pulses with controlled amplitudes and durations as the device is cycled along the programming curve through intermediate and complete SET and RESET states. In comparison, thin-film and embedded devices need to be mechanically cross-sectioned for determining their structural state in \textit{ex situ} TEM/SEM after electrical switching, which also implies that the device cannot be used anymore thereby severely limiting the ability to study the evolution of structural/chemical changes over a period of time. In addition, the threshold process can be directly observed (not the electronic switching part as it may not involve any structural change but the events immediately following the electronic switching), which contains fundamental information of the process in many more ways than what has been theorized or observed before.

2. EXPERIMENTS

Phase change Ge$_2$Sb$_2$Te$_5$ NWs were synthesized using the bottom-up approach of catalyst mediated vapor–liquid–solid process [15]. All NW devices were fabricated with Pt electrodes with a separation of 4 \( \mu \)m [15] and their resistances were measured at 0.2V (d.c.). The NW devices were amorphized by 200 ns electrical pulses to a resistance value of 1–4 M\( \Omega \), and then were allowed to relax over 5 decades of time during which the resistance was measured at different intervals. For \( V_{th} \) drift measurements, d.c. \( I-V \) sweeps were measured beyond the \( V_{th} \) and the devices were amorphized back to the original resistance for time-dependent measurements. The amorphized region in a NW device
mostly occurs near the center of the device and sometimes next to the contacts, but never totally embedded under the contacts.

In order to enable *in situ* TEM analysis of nanowire devices, we used commercially available SiN TEM membranes (300 nm thick for mechanical stability) and cut 2 µm wide trenches by FIB to allow HRTEM analysis of the nanowire devices. The Ge$_2$Sb$_2$Te$_5$ NWs were then aligned across the trenches by either direct dry transfer or microfluidic alignment. In order to localize the active phase change part at the center of the trench region to enable HRTEM analysis, we carefully sculptured a notch structure, which due to the smaller cross-section eventually serves as “hot spot” during electric-driven switching operations (Fig. 10c) and undergoes phase switching. This structure serves as a convenient starting point to confirm and investigate the structural phase change and other properties. Combining with the real-time imaging system, in situ TEM allowed us to operate the PCM device in the TEM column, at the same time while observing the structural and chemical changes between amorphous and crystalline states.

3. RESULTS & DISCUSSION

The time evolution of amorphous state resistance (normalized at t=1s, first measurement) of a 100 nm thick NW device from the initial value of 2.1 MΩ (Fig. 1a) clearly shows that the resistance drift is very small with the resistance increasing to just 2.3 MΩ over five decades in time. The data are fit to a power law (Eqn. 1) and the power exponent, α is found to be 0.005, which is very small in comparison to thin-film devices where α typically ranges from 0.03-0.1 [4]. The corresponding data for drift in $V_{th}$ (normalized at 2s, first measurement) can be fit to Eqn. 2 (Fig. 1b), which also reveals a lower value of drift exponent (υ = 0.009) in comparison to typical values ranging from 0.01-0.04 in thin-film devices [4]. These experiments demonstrate that drift coefficients are lower in NW devices in comparison to thin-film devices.

In order to study if there is any correlation of drift coefficients with NW size, we measured the drift of device resistance on three different NW thicknesses, 140, 90 and 45 nm, all amorphized to resistance values that were at least 100 times more than their crystalline state resistance. The NW devices show a systematic size-dependent drift of amorphous state resistance (Fig. 2); the drift coefficients increase with increasing NW thickness. The thinnest NW (45 nm) with the highest surface to volume ratio shows the lowest value of drift (α=0.002), while the thickest NW device (140 nm) with the lowest surface to volume ratio shows a much higher drift coefficient (α=0.009), but still much smaller than the reported values for thin-film devices. The drift coefficients of $V_{th}$ for different NW thicknesses did not reveal any clear size-dependence, mostly because the $V_{th}$ changes typically from ~1.5 V (t=2s) to ~1.7 V (t=10’s) for all the measured devices, a small increase to reliably extract their size-dependence.

The above described data suggests that the unique geometry of NW devices with exposed surfaces may be responsible for the observed low but size-dependent drift coefficients. In order to explore the effect of exposed surfaces on the drift behavior of NW devices, we performed the drift experiments on the same NW devices by depositing thick (~300 nm) dielectric films such as SiO$_2$ or Si$_3$N$_4$ on them. The devices were imaged with SEM to ensure that they were completely embedded. The same 100 nm NW device as discussed in Fig. 1, but embedded under SiO$_2$ film was amorphized again to a resistance value of 2.1 MΩ.
and its drift behavior was measured. The NW device now showed a much higher resistance ($\alpha=0.086$, compared to 0.005 for un-embedded), and $V_{th}$ drift coefficients ($\nu = 0.031$, compared to 0.009 for un-embedded), which are similar to values reported for embedded thin-film PCM devices (Fig. 1). Similar values of increase of drift coefficients for NWs embedded under $Si_3N_4$ film in comparison to un-embedded devices were obtained (data not shown). These data suggest that the drift characteristics of the devices can be engineered by both altering the materials surface to volume ratio and exposing/embedding the surfaces.

Our measurements on NW devices clearly demonstrate the difference in drift behavior as a function of surface to volume ratio and exposed surfaces. These observations suggest that the efficient relaxation of the built-in stress upon amorphization is primarily responsible for drift in PCM devices in comparison to annealing of electronic defects or VAP generation mechanisms. In a conventional thin-film PCM device, a polycrystalline film is sandwiched between two electrodes; upon amorphization, an embedded amorphous dome results, that is encapsulated from all sides and is compressed under large stresses from the surrounding materials. In the course of time, the metastable amorphous region relaxes with a large distribution of timescales, which has been mapped with stress relaxation experiments [14], resulting in a time-dependent increase of resistance and $V_{th}$ due to volume dilation. These relaxations have been extensively studied in glasses and have been attributed to atomic structural relaxations [18,19], where unsaturated, stretched and distorted bonds characteristic of the metastable state relax to more stable states leading to time-dependent mechanical, electrical and optical properties.

Unlike thin-film devices, NW devices do not have a completely embedded amorphized dome, which will enable them to efficiently relax their stress rapidly from the large available surface (Fig 3), leading to very different drift behavior as observed. Typically, phase change NWs have a ~1-2 nm coaxial surface oxide shell and the amorphized region will terminate at this interface. This extremely thin oxide shell can easily expand when the NW device is locally amorphized thereby releasing the stress that builds up due to the material expansion. Smaller diameter NWs have large surface to volume ratio and can relax their stress more easily. It is known that NWs can be epitaxially grown on highly mismatched substrates and their heterostructures can be created that can withstand large strains due to the presence of free surfaces allowing for lateral strain relaxation [20,21]. Recent theoretical efforts on mechanical properties of NWs have also revealed that at the nanoscale, strain relaxation becomes more efficient with decreasing surface to volume ratio [22]. For the case of NW devices which are completely buried under a uniform dielectric layer, the situation becomes similar to convention thin-film devices and the amorphous volume cannot relax the built-in pressure and hence relaxes slowly on multiple timescales leading to higher drift coefficients. This is in agreement with measurements of crystallization-induced stress in $Ge_2Sb_2Te_5$ thin films where the stress was reported to be much higher for capped films [23]. It is unlikely that the deposition of the dielectric film significantly alters the electronic properties of the NWs as the presence of the thin coaxial oxide layer minimizes

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**Fig. 2.** Size-dependent drift of normalized resistance for $Ge_2Sb_2Te_5$ NW devices. Smaller diameter devices show less drift compared to larger diameter devices. Solid lines are fit to Eqn. 1 and all devices were amorphized to resistance ratios of at least 100 in comparison to their crystalline state.

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**Fig. 3.** (a) SEM image of an un-embedded NW device. (b-d) finite element analysis of the elastic first principal stresses that develop in a $Ge_2Sb_2Te_5$ NW cross-section (100 nm x 100 nm) upon incurring a volume change of 5%. An un-embedded NW (b) develops small stresses due to adhesion at the substrate interface, but large compressive stresses develop in devices confined with $SiO_2$ (c) and $Si_3N_4$ (d). These stresses are likely accommodated by relaxation mechanisms in the amorphous material, which influences the drift behavior [14]. Note that stresses in the substrate and capping layers...
direct interaction of the deposited material with the active region of the NW. In addition, the drift properties of the embedded NW devices do not appear to be strongly dependent on the chemical composition of the dielectric film, although the drift dependence on the film thickness and mechanical properties would require further investigation.

We have estimated the elastic stresses associated with the amorphization of the NW geometry for both the embedded and un-embedded devices using finite element analysis to provide insight on the relationship between drift and structural confinement. Plane strain 2D calculations were performed on a Ge$_2$Sb$_2$Te$_5$ NW cross-section (100 nm x 100 nm) on a SiO$_2$ substrate, where the bottom surface of the NW was constrained while the other surfaces were modeled as free (Fig. 3b). A volume change of $\Delta V/V = tr(\epsilon_\nu) = 0.05$ where $\epsilon_\nu$ is the strain tensor, representing the decrease in density upon amorphization, Young’s modulus of 35 GPa and Poisson’s ratio of 0.3 were used for the Ge$_2$Sb$_2$Te$_5$ NW [24]. The first principal stress $\sigma_1$ for the un-embedded NW (Fig. 3b), reveals that a very small but finite stress develops due to the constraint from the substrate. In contrast, large compressive stresses develop when SiO$_2$ and Si$_3$N$_4$ capping layers are applied (Figs. 3c, 3d) due to confinement effects upon amorphization, which are on average ~20 times more than the un-embedded case. The low and size-dependent drift coefficients are consistent with the notion of the high surface to volume ratio of the NW serving to effectively accommodate the stresses, although a detailed understanding of the atomic relaxation mechanisms in Ge$_2$Sb$_2$Te$_5$ NWs requires future investigation.

**The Role of Electric Bias on the Phase-Change Mechanism**

The data on a 160 nm thick Ge$_2$Sb$_2$Te$_5$ NW with a notch structure (still largely single-crystalline) with ~60 nm narrow width is shown in TEM image (Fig. 4). The electric resistance of the as-prepared notch ed nanowire device was ~90 kΩ, and the corresponding programming curve of the device resistance as a function of applied voltage pulses as it is cycled from crystalline to amorphous (4.9 MΩ; complete RESET) states is shown in Fig. 4e, followed by switching back to the SET state. We then imaged the microstructure of the notched region by TEM and characterized the complete RESET and SET states. Figure 4f compares the representative TEM images of the notch at electrically RESET (top) and SET (bottom) states. The structure of the notch at RESET state clearly displays brighter bright-field imaging contrast in comparison to that at the SET state. The bright region is due to the amorphous structure, whereas the dark region represents the crystalline state. HRTEM data of complete SET and RESET states clearly shows the formation of amorphous and polycrystalline regions in the notch area, where the heat is localized due to the high current density, thereby confirming that phase change is responsible for the observed electrical characteristics. These data establish that the correlation of structure with electrical properties is possible for nanowire phase change devices during their switching.

A subject of particular interest is to study the electronically intermediate states signified by a resistance value falling in between two extremities of high (RESET) and low (SET) resistances, as these structural phases are not well characterized in studies based on thin-film PCMs. Such intermediate states can be realized by applying precisely controlled voltage pulses to the nanowire devices to reach different states along the programming curve (Fig. 5). Our initial attempts to study the intermediate state have produced very interesting results: We started from a complete RESET state and applied a small amplitude pulse to change the resistance of the nanowire device from ~4.9 MΩ to

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**Figure 4.** Fabrication of a free-standing phase-change NW device for the electronics in TEM (a) Suspended 300 nm-thick SiNx membrane with a fabricated trench structure. (b) Phase change NW (Ge$_2$Sb$_2$Te$_5$) device crossing the trench. (c,d) SEM and TEM image of free standing NW which is sculpted by FIB to create a notch. The sculpted localized region serves as a hot spot which undergoes switching process. (e) Programming data of the notched nanowire device. (f) TEM images of the notch region showing the corresponding RESET (lighter contrast, top) and SET (dark contrast, bottom) states, confirming phase change process.
~0.6 $\Omega$ and then imaged the device in TEM. (Fig. 5). The structures obtained from electric-field-induced recrystallization process shows a different behavior from the thermally heated recrystallization process as discussed before (Fig. 4). The field-induced recrystallization behavior shows that crystallized nuclei are not randomly generated all over the amorphized region of the device but have directionality along the applied electric field (Fig. 5). The field-induced directional nuclei/grain formation in the recrystallized region differs from the random percolation-type nuclei formation which has been observed in a normal annealing process. The recrystallized region was generated with a localized “pyramidal” shape (maybe due to non uniform field or some grain growth in the direction of the applied field. Based on this observation, it seems that the formation of the sharp and correlated crystalline region stems from the electric-field-induced behavior rather than random percolation-type behavior. More detailed experiments are required to study the events that lead to complete switching, which is an important issue. Although, we realize that TEM measurements may not provide direct evidence for the “electronic filament” formation which have been hypothesized earlier, however, these measurements will provide direct observation whether the field-induced crystallization is a random process or proceeds along the electric field direction in a correlated manner.

These experiments will be very important in demonstrating the effect of electric field in nucleation/crystallization process in contrast to the thermal crystallization process which leads a random percolation nucleation process. These observations can then be directly fed into different electrical conduction models to refine them and precisely account for the different events that take place during the switching process. According to the percolation theory, the random nuclei generation is followed by the connection of low resistance spots which serves as the current path. In the case of phase change materials, the percolation of crystalline clusters has been studied, in which Joule heating leads to random generation of crystalline clusters and the connection of the crystalline clusters is responsible for the increase in electrical conduction. However, recently the electric-field-induced nucleation model offers a possibility of the important role of electric field in the course of the formation of crystalline filament [25]. Electric-field-induced filament formation can lead the alignment of crystalline nuclei according to the electric field, which offers a new perspective on the switching mechanism. Future work will involve investigation of the electric-polarity dependant behavior such as directional mass-transport and polarity-involved switching behavior in these materials.

4. CONCLUSION

In conclusion, we have shown that stress relaxation mechanisms are primarily responsible for the observed drift behavior in PCM devices by using un-embedded NWs as a model system. The NW devices have extremely low values of drift coefficients due to efficient stress relaxation from the exposed free surfaces in comparison to thin-film devices. These results help understand the effect of stress relaxation on electrical properties of phase change chalcogenides and will be useful for the development of new device geometries that can efficiently relax stress upon amorphization to minimize drift for practical memory applications.

By monitoring the structural changes in GST nanowires via insitu microscopy, we obtained direct evidence of electric-field assisted nucleation process which guides the crystalline nuclei formation in a correlated manner with the applied electric-field, unlike the random nucleation and percolation behavior typically observed in thermally-induced recrystallization. The electric-field lowers the thermodynamic energy barrier for amorphous-to-crystalline phase transformation due to field assisted filament generation. In addition, we will also observed the effect of electrical stress on the built-in mechanical stress and relaxation during the field driven phase change process. High current density (> MA/cm$^2$) required for joule-heating process induces significant electrical stress which is converted to
mechanical stress and possibly influences the reversible switching process. Our observations suggest that the electric-field plays a unique role in fast switching behavior, combined with the thermal and mechanical processes caused by joule-heating.

REFERENCES


Biography

Ritesh Agarwal earned his undergraduate degree from the Indian Institute of Technology, Kanpur in 1996, and a master’s degree in chemistry from the University of Chicago. He received his PhD in physical chemistry from the University of California at Berkeley in 2001. After completing his PhD., Ritesh was a postdoctoral fellow at Harvard where he studied the optical and photonic properties of semiconductor nanowires. His work led to the development of electrically-driven single nanowire lasers and avalanche photodiodes. Ritesh is currently an assistant professor in the Department of Materials Science and Engineering at the University of Pennsylvania. His research interests include quantum confined optics and electronics in nanowire heterostructures, manipulating light-matter interaction in nanostructures, and studying phase transitions and electronic memory switching at the nanoscale. Ritesh is the recipient of the NSF CAREER award in 2007.