Phase Change Materials

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Phase change memory (PCM) is an emerging technology that combines the unique properties of phase change materials with the potential for novel memory devices, which can potentially realize new computer architectures. Phase change materials store information in their amorphous and crystalline phases, which can be reversibly switched by the application of external voltages. This article describes PCM with its advantages and challenges. The physical properties of phase change materials that enable the data storage are described and our current knowledge of the phase change processes is summarized. Various designs of PCM devices with their respective advantages and integration challenges are

presented. The scaling limits of PCM are addressed and its performance is compared to competing existing and emerging memory technologies. Finally, an outlook is given to new potential applications of phase change devices such as neuromorphic computing and phase change logic.

Taxonomy: phase transformation, electrical properties, crystallographic structure

Introduction

It has occurred many times during evolution of mankind and technology that novel storage concepts were developed, from cave paintings over printing, to phonographs, magnetic tape, dynamic random access memory (DRAM), compact disks (CDs), flash memory, just to name a few. Over the last four decades, silicon technology has enabled data storage by storing charge on metal-oxide-silicon (MOS) capacitive structures. However, as silicon devices are scaled to (sub-)10 nm dimensions, such minute capacitors become leaky by simple quantum mechanical considerations, and the memory storage density appears to plateau. Novel data storage concepts are under development that include storing data in the direction of the magnetic orientation (magnetic RAM [1], spin torque transfer RAM [2], racetrack RAM [3]), in the electric polarization of a ferroelectric material (ferroelectric RAM, [4]), in the resistance of a memory device (resistive RAM [5], memristor [6], conducting bridge RAM [7], carbon nanotube memory [8]), or in the resistance of the storage media itself (phase change RAM [9]). In

this article we describe the properties of phase change materials and their application to phase change memory (PCM).

Properties of Phase Change Materials

Phase change materials exist in an amorphous and one or sometimes several crystalline phases, and can be rapidly and repeatedly switched between these phases. The optical and electronic properties can vary significantly between the amorphous and crystalline phases, and this combination of optical and electrical contrast and repeated switchability allows data storage. This effect was discovered already in 1968 [10] but it took the breakthrough discovery [11] of fast switching materials along the pseudo-binary line between GeTe and Sb_2Te_3, notably the most studied and utilized $Ge_2Sb_2Te_5$, to enable phase change storage technology [12].

Many technologically useful phase change materials are chalcogenides and owe their success to a unique combination of properties, which include strong optical and electrical contrast, fast crystallization, and high crystallization temperature. Figure 1 shows the tertiary phase diagram of the Ge-Sb-Te material system. As mentioned above, alloys along the pseudo-binary line between Sb_2Te_3 and GeTe with compositions $(GeTe)_m(Sb_2Te_3)_n$ have been intensely studied [13] and are still used in state-of-the-art PCM devices [14]. In search of faster materials, undoped [15] and slightly Ge-doped Sb devices with a composition of $Ge_{15}Sb_{85}$ [16] have been fabricated. The term "doping" is used in the phase change materials community to describe adding amounts of another element in

the several per cent range, and alloying would be a more accurate term. Another set of materials along the pseudo-binary line between GeTe and Sb was studied as well [17], and starting from $Ge_2Sb_1Te_2$ on this line and adding further Ge (red arrow in Fig. 1) led to the design of phase change materials with very high thermal stability of the amorphous phase suitable for high temperature PCM applications [18]. All of these materials utilize a remarkable bonding mechanism in the crystalline phase, which has been termed resonance bonding by Linus Pauling [19, 20]. This bonding mechanism only prevails for a small subgroup of group V and group VI compounds, which helps to identify and optimize possible phase change materials [21] as illustrated in Fig. 2. Since resonance bonding requires long range order, amorphous materials only employ ordinary covalent bonding. Crystallization is hence accompanied by a change of bonding mechanism. Understanding the microscopic mechanisms employed in crystallization is crucial to optimize the performance of phase change memories. In recent years it has become clear that phase change materials are bad glass formers [22] that exhibit the characteristic behavior of fragile liquids [23, 24], i.e. a pronounced temperature dependence of the activation barrier for crystal growth. This ensures that the amorphous phase is stable for 10 years at about 100 ºC, while this state recrystallizes into the crystalline phase in less than 10 ns at elevated temperatures around 500 ºC [25, 26]. The fastest switching speeds reported are even less than 1 ns [27].

Principles of Phase Change Memory

Phase change memory (PCM) is based on the repeated switching of a phase change material between the amorphous and the crystalline state connected with a large change in resistance. The information is stored in the phase of the material and is read by measuring the resistance of the PCM cell, and the cell is programmed and read using electrical pulses. Figure 3 illustrates the principle. Switching from the high resistance or reset state, where part or all of the phase change material is amorphous, occurs when a current pulse is applied that heats the amorphous material above the crystallization temperature for a time long enough for the material to crystallize. Switching from the low resistance or set state, where the material is crystalline, is achieved by a high current pulse with a very short trailing edge. The current pulse heats the material by Joule heating, melts it, and enables very fast cooling (melt-quenching) so that the material solidifies in the amorphous state. This is only possible because of the threshold switching effect that leads to a drastic reduction of the resistance of the amorphous phase when a certain threshold field is surpassed. Otherwise, it would be impossible to heat the crystalline material using Joule heating with reasonably low voltages. The state of the memory cell is read with a small current pulse, which does not alter the state of the memory cell.

The current pulses are provided by an access device, which in addition also isolates the memory cell during programming and read operations. Field-effect transistors [28], bipolar junction transistors [29] and diodes [30] have been used as access devices, and in most cases the size of the access device is much larger than the PCM cell and determines the storage density. Considerable

development efforts are devoted to an optimization of the cell design that leads to reduced reset current, thus to reduced size of the access device, and increased storage density.

Phase change materials are at the heart of PCM technology and their properties to a large extent determine its functionality and success. Optimization of phase change materials is not only application specific but also technology node specific, for example the threshold voltage in current typical PCM cell is on the order of 1 V, but if devices are scaled to much smaller dimensions the threshold voltage scales with the size of the amorphous region, and for very small cells can become comparable to the reading voltage so that every read operation could alter the cell state. In the following section, we discuss various possible PCM applications with their material challenges and possible class of materials that could meet these challenges.

The first application, which in fact is on the market available already, is stand-alone memory to replace flash memory [31]. Here the requirements are moderate in terms of operation temperature (80 ºC), cycle number (10^5), switching speed (ms range), and $Ge_2Sb_2Te_5$-based alloys can provide the required materials properties and switch at much faster times in the tens of ns range. For storage class memory applications [32] the requirements are higher in particular for the cycle numbers (10^8-10^9). New materials such as reactively sputtered and doped $Ge_2Sb_2Te_5$ material was developed to increase the cycle numbers to 10^9 while maintaining fast switching (20 ns) [33]. Due to the highly competitive

nature of the materials development for PCM exact material compositions often are not published.

The requirements regarding data retention at high temperatures are much more stringent for automotive applications (150 ºC for 10 years) or precoded chips that need to pass a solder bonding process (250-260 ºC for tens of seconds). In these cases phase change materials with much higher crystallization temperature compared to $Ge_2Sb_2Te_5$-based alloys are required. Highly Ge-rich Ge-Sb-Te materials, sometimes doped additionally with N and C, and GaSb have been shown to be promising candidates for these applications [18, 34, 35].

Using PCM to replace DRAM (dynamic random access memory) is a formidable challenge because very fast switching time in the nanosecond range and extremely high cycle numbers of 10^{16} present a combination of requirements that have not been achieved by phase change materials so far. DRAM replacement is a special case since DRAM is a volatile memory whereas PCM is a non-volatile memory. If PCM were able to achieve DRAM-like performance, it would open up the possibilities to realize completely new computer architectures. Very fast switching time have been achieved for several phase change materials including $Ge_2Sb_2Te_5$ [26, 27] and GeTe [25] in actual PCM devices. The high cycle number remains the enormous challenge, but it appears that scaling to smaller dimension of the phase change material is beneficial for cycling. Data measured on highly scaled PCM cells using an Sb-rich Ge-Sb-Te phase change material demonstrated 10^{11} cycles under accelerated testing conditions using a switching power of $4.5x10^{-11}$ J, which leads to an extrapolated cycle number of

6.5×10^{15} cycles under normal switching conditions using 3.6×10^{-12} J [36], see Figure 4. Elemental segregation upon repeated cycling is one failure mechanism for PCM cells and the ultra-scaled volume (7.5×17 nm^2), which is probably completely melted in every reset operation, probably "remixes" the elements at every switching and also leaves very little room for the elements to spatially segregate.

Phase Change Memory Devices and Integration

Phase change memory will be successful in the market when it is possible to develop a manufacturing process that can achieve low cost, reliable production of large arrays of PCM cells and is compatible and easily incorporated in existing CMOS (complementary metal-oxide-semiconductor) processes. Device design and integration determine the PCM functionality and production costs, and what is particularly important for PCM technology, determine the size of the access device, which in turn determines the storage density.

The functionality of the PCM cell is strongly influenced by the choice of the phase change material and large research efforts are devoted to optimize phase change materials for specific applications with variable requirements for memory functionality such as switching speed, data retention, cyclability, and switching power. A second important aspect is the cell design, which needs to consider many aspects such as number of required process steps, parameter window for each process step, availability of the required deposition methods, e.g. atomic layer deposition of phase change materials, and other aspects of

manufacturability. Among the greatest challenges in PCM integration remains the reduction of the reset current. More details can be found in Chapt. 17 of [12].

Scaling Properties of Phase Change Materials and Phase Change Memory

For PCM (or any new memory technology) to be viewed as a useful technology, it must demonstrate scalability for at least several generations to justify the heavy investment the industry needs to commit. Many efforts have been directed to investigate PCMs' scalability at both the material and device level.

Table 1 shows a list of important parameters in phase change materials, their influence on PCM device performance and how they behave when the material is scaled down to smaller dimensions. The crystallization temperature T_x of phase change materials varies significantly as a function of the material dimensions [37-40]. Experiments performed on thin films [41, 42] and nanoparticles [43, 44] suggest that T_x of phase change material might increase with decreased dimensions. This means that unintentional crystallization is less likely and thus a longer data retention time prevails. Measurements on $Ge_2Sb_2Te_5$ nanowire devices by Lee *et al.* [45] found nanowire devices with smaller diameters have smaller activation energy, indicating a shorter data retention time. However, Yu *et al.* [46] did not observe any dependence of T_x on wire diameter. It has also been demonstrated that ultrathin films (1.3 nm) [47] and tiny nanoparticles (2 nm diameter) [37] could still transform to the crystalline phase. This suggests PCMs' high scalability and is promising for future generations. Melting temperature T_m

of phase change materials has been observed to decrease with reduced dimensions in thin film [48], nanowires [49] and nanoparticles [50]. This is also favorable since lower T_m means less power is needed in the power-limiting reset step.

The crystallization speed of the phase change materials either increases (desirable) or decreases (detrimental) at reduced dimensions, depending on the material's composition and species [9, 51]. Thermal conductivity of phase change material in both amorphous and crystalline phases is important because it determines how energy efficient the PCM device is during programming. Reifenberg *et al.* [52] studied the thermal conductivity of $Ge_2Sb_2Te_5$ thin film (60 nm and 350 nm) in the amorphous, face-center cubic and hexagonal states. They found that the thermal conductivity decreases as the film thickness decreases in all three phases. This suggests a favorable scaling trend since it helps reduce thermal power loss during operations. The threshold voltage is found to show a linear relationship with the device dimension, suggesting an underlying threshold electric field [15]. This is beneficial for voltage/power scaling. The resistivity ratio of phase change material does not seem to vary much on device scaling [53]. This means there would be large enough window for multi-level cell programming in PCM even at diminished dimensions [54]. Overall, phase change materials demonstrate a highly desirable scaling behavior, which can still be extended to several generations of technology nodes.

One of the major considerations of prototype PCM device is its large programming current, especially during the power intensive reset step [16]. To

reduce *Ireset*, one way is to reduce the volume of the phase change region. This can be done by reducing the contact area between phase change material and the electrodes. Figure 5 shows the reset current as a function of the effective contact area for different cell structures [22, 55, 56]. It is evident that the reset current scales with the effective contact area, indicating an average reset current density ~ 40 MA/cm^2. And by using sublithographic electrodes such as carbon nanotubes that have diameters of a few nanometers the reset current could be brought to as low as a few μA [53, 56, 57] . At the same time, innovative device design by optimizing the thermal control could reduce the current density even further. These promising results provide directions on how to overcome arguably the biggest obstacle in PCM technology.

New Applications of Phase Change Memory

PCM cells can not only be programmed in the on or off state, it is also possible to reach intermediate resistance states. Up to 16 levels have been demonstrated using a write-and-verify scheme [54]. Utilizing acontinuous transition between resistance levels in PCM devices in an analog manner, this effect can be used to program PCM devices to mimic the behavior of a synapse in an attempt to design a neuromorphic computer with electronic hardware that resembles the functions of elements of a brain, such as the neurons and synapses. The phenomenon of Spike Timing Dependent Plasticity (STDP), a form of Hebbian learning that is observed biologically, could be demonstrated in PCM devices using specific programming schemes [58, 59]. Image recognition using a

neural network of PCM devices was also demonstrated [60, 61]. These could potentially lead to a compact and low power neuromorphic computing system that is capable to process information through learning, adaptation and probabilistic association like the brain.

Thermoelectric (TE) effect, the conversion of heat energy into electrical energy, has also been actively studied in PCM devices [62, 63]. TE efficiency is characterized by the figure of merit $ZT = \sigma S^2 T/k$, where σ is the electrical conductivity, k is the thermal conductivity, T is the temperature, and S is the Seebeck coefficient. Phase change materials are promising p-type TE materials because they have similar chemical compositions compared to traditional telluride based TE materials and they have low thermal conductivity and relatively high electrical conductivity, which improves ZT. Chalcogenide based phase change materials have shown to exhibit Seebeck coefficients as high as ~350 – 380 μVK^{-1} [64, 65] and $ZT \sim 0.7$ at elevated temperature [66] (commercial TE materials have $ZT \sim 1$). This opens up opportunity for applications like Peltier cooler or thermogenerators based on phase change materials. Studies have also suggested that Thomson heating in PCM cells and the Peltier effect at the electrode contact area could increase the temperature rise in the device and thus reduce the reset current [65, 67]. This effect is more prominent at smaller dimensions due to better thermal insulation. Thus, understanding and optimizing the thermoelectric phenomena has significant impact on PCM device performance.

Summary

In short, phase change memory is a promising novel data storage concept because of its unique combination of features such as fast access time, large optical/electrical contrast, non-volatility and high scalability. This article summarizes the properties and working principles of phase change materials, their applications to PCM devices and how scaling affects these properties.

Ever since the breakthrough discovery of fast switching materials along the pseudo-binary line between GeTe and Sb_2Te_3, people have been constantly working to optimize materials' properties to improve the performance of PCM devices. Depending on the specific application, the requirements for important properties such as crystallization speed, thermal stability and endurance are different. Material composition and preparation method are carefully optimized to meet the prerequisite of the specific application.

We also examined the scaling properties of phase change materials. Crystallization temperature (T_x), melting temperature (T_m), crystallization speed, thermal and electrical resistivity all demonstrate favorable scaling behavior when the device dimension goes down. PCM's endurance is shown to improve to 6.5×10^{15} cycles at ultra-scaled dimension since complete melting and "remixes" of the bit eliminates elemental segregation, which is a major failure mechanism for PCM cells. Recent results also suggest that reset current in PCM device scales down with the device's electrode contact area, which would reduce the volume of the access device and enhances storage density.

Acknowledgments

One of us (MW) gratefully acknowledges funding within SFB 917 ('Nanoswitches') and by the ERC ('Disorder Control').

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Figure Captions

Figure 1. Tertiary Ge-Sb-Te phase diagram with some popular phase change alloys highlighted.

Figure 2. Empiric map for materials with about three p-electrons per atomic site and even numbers of anions and cations. The axes that span the map are the tendency towards hybridization, r_{π}^{-1}, and the ionicity, r_{σ}'. The coordinates of a large number of materials have been calculated (see the supplement to ref. [21] for an index of materials). Phase-change materials are located within a small region of the map that is prone to the occurrence of resonant bonding. The graphs on the outside illustrate the weakening of resonance effects as one leaves this region due to the formation of less, more saturated covalent bonds via distortions or due to charge localization at the ions due to increasing ionicity. Reproduced with permission from ref. [21].

Figure 3. Principle of phase change memory. Starting from the amorphous phase with large resistance R a current pulse is applied which heats the material above the crystallization temperature T_x for a time long enough to crystallize (set operation). In the crystalline state the resistance is low. A large, short current pulse is applied to heat the material above the melting temperature T_m. The material is melt-quenched and returns to the amorphous, high resistance state (reset operation).

Figure 4. (a) Cross sectional view transmission electron microscopy (TEM) micrograph of 7.5nm (width) ·17nm (length) dash confined cell: (a) length direction cutting image (b) enlargement image of unit cell of perfectly filled phase change (PC) film deposited by atomic layer deposition in contact with the bottom electrode (BE) and (c) top view scanning electron microscope (SEM) image. (d) Endurance characteristic of dash confined cell at 4.5×10^{-11} J reset program energy, which is marked in red in (e) where cycles to failure as a function of program energy at acceleration condition are shown. Reprinted with permission from [29], copyright IEEE (2010).

Figure 5. RESET current scaling vs. electrode contact area in PCM device. Reprinted with permission from [56], copyright American Chemical Society (2013).

Tables

Table I: Scaling of PCM properties.

Material Property	Influence on PCM Device	Scaling Behavior
Crystallization temperature T_c	SET power	Good
Melting temperature T_m	RESET power	Good
Crystallization speed	Data rate and SET power	Depends
Thermal conductivity (amorphous and crystalline)	SET and RESET power	Good
Threshold voltage	SET voltage/power	Good

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Pop is an Associate Professor of Electrical Engineering (EE) with Stanford University. Previously, he was with the University of Illinois Urbana-Champaign, first as an Assistant Professor (2007-12) and then as an Associate Professor with tenure (2012-13). His research interests are in energy efficient electronics, novel 2-D and 1-D devices and materials, nanoscale energy conversion and harvesting. He received his Ph.D. in EE from Stanford (2005), M.Eng./B.S. in EE and B.S. in Physics from MIT (1999). Between 2005-2007, he did post-doctoral work at Stanford, then worked at Intel on non-volatile memory. He received many awards for his work including the 2010 Presidential (PECASE) award from the White House.

Figure 1

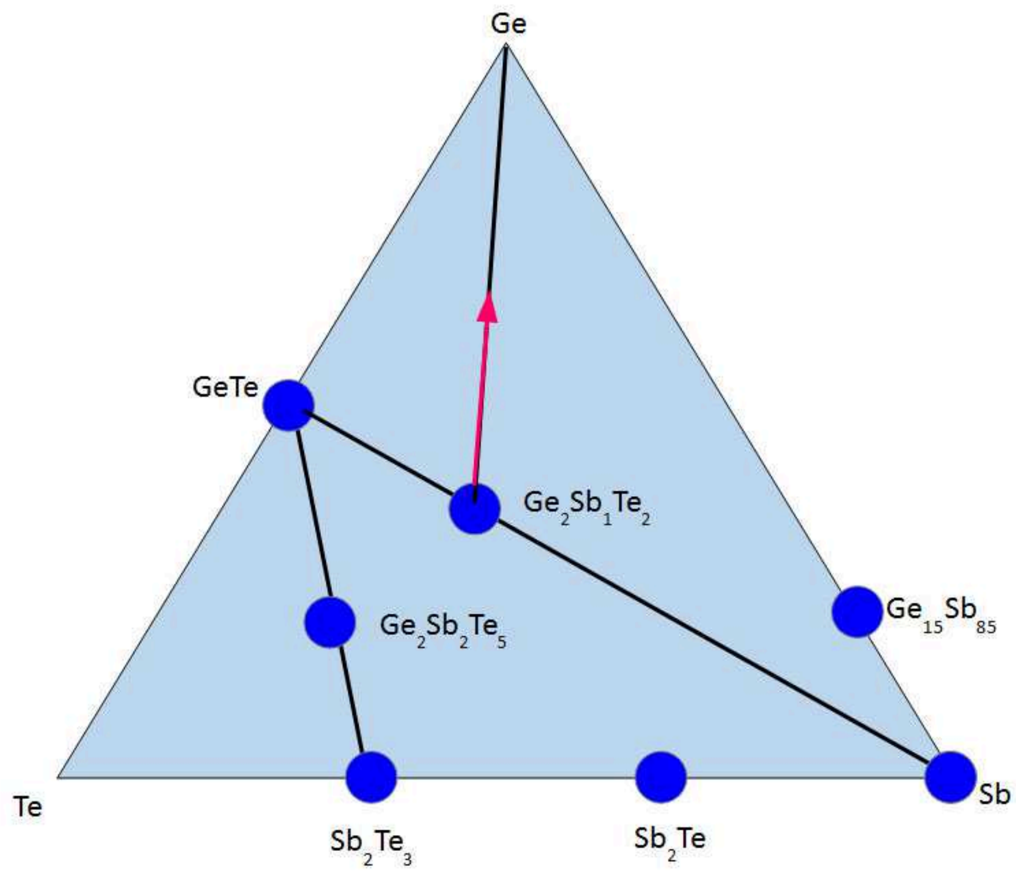

Figure 2

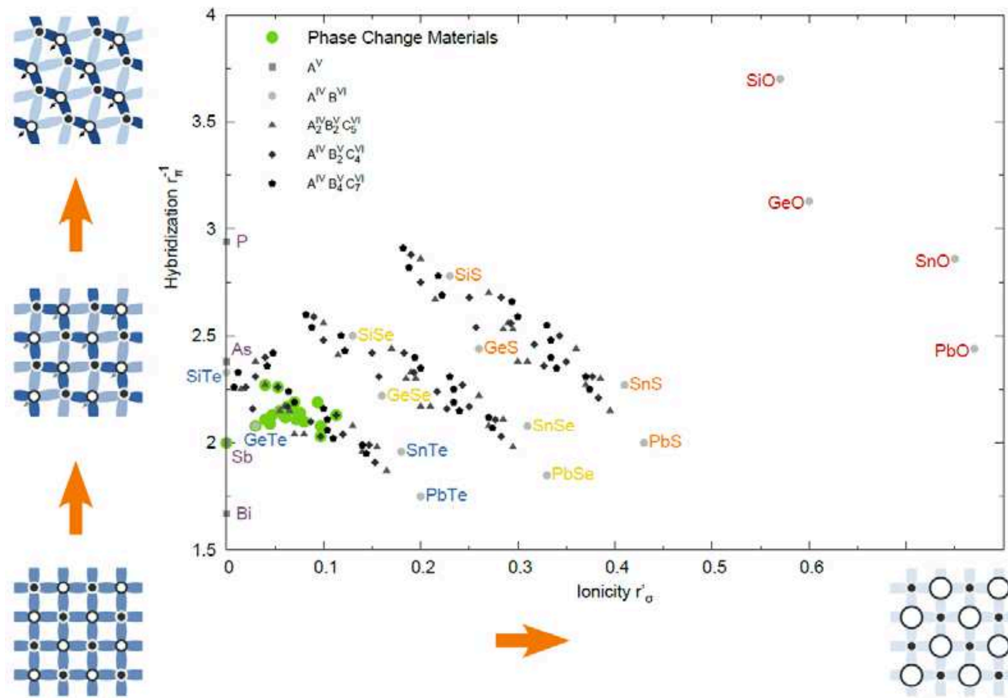

Figure 3

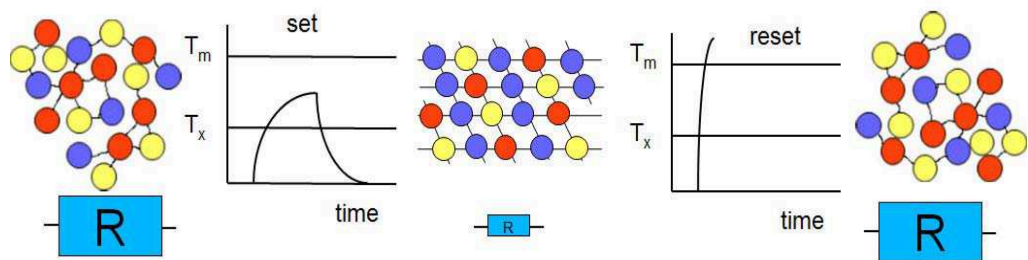

Figure 4

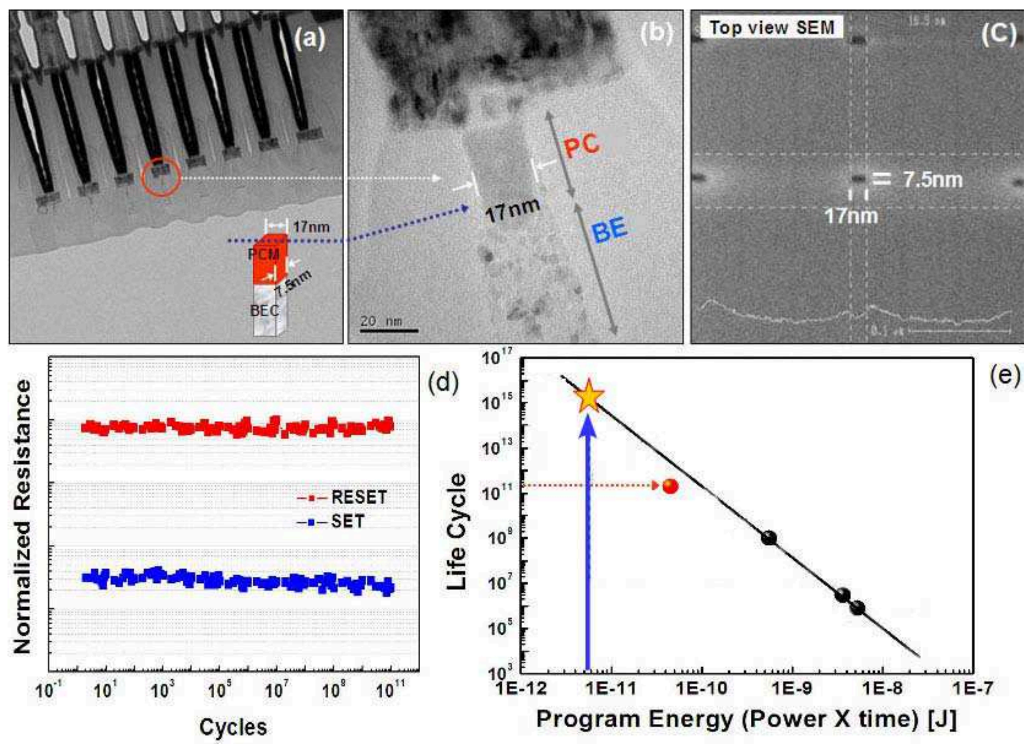

Figure 5