American Journal of Condensed Matter Physics 2016, 6(2): 21-26
DOI: 10.5923/j.ajcmp.20160602.01

# Electrical Characteristics of Zn Doped $In_2Se_3$ Thin Films for Phase Change Memory (PRAM) Applications

**Opiyo S. O.[*], Munji M. K., Njoroge W. K., Makori N. E., Obare B. M.**

Department of Physics Kenyatta University, GPO Nairobi, Kenya

---

**Abstract** The effects of Zinc doping on electrical characteristics of $In_2Se_3$ for PRAM applications have been successfully investigated. The results obtained show an increase in sheet resistance for as deposited and annealed films with increase in Zn doping. *In-situ* electrical properties during thermal cycling showed a sharp drop in sheet resistance showing a transition from amorphous to crystalline phase. Zinc doping also affected the resistance contrast with the highest contrast found to be $1.38\text{x}10^5\Omega/\square$ for 4% Zn doping. Crystallization temperature increased linearly with zinc doping. From the study, 4% Zn doping gave the best results for PRAM fabrication as it registered moderately high crystallization temperature as well as high resistance contrast. These properties ensure stability of the cell as well as reduce the RESET current. The PRAM fabricated from 4% Zn doped sample, registered a threshold voltage of 4.60V during I-V testing. The pulsed mode testing resulted in a SET pulse of 2.38V, $15\mu s$ and a RESET pulse of 4.75V, 75ns. The obtained threshold voltage of 4.6V suggests that the material is scalable.

**Keywords** Indium Selenide ($In_2Se_3$), Phase Change Random Access Memory (PRAM), Current Voltage (I-V) test

---

## 1. Introduction

Phase Change Random Access Memory (PRAM) is one of the most promising concepts for the future generations of Non Volatile Memories. Generally PRAM is a non-volatile memory that employs the reversible phase change in material to store bits of information [1]. PRAM utilizes the large resistivity contrast between crystalline (low resistivity) and amorphous (high resistivity) phases of the Phase Change Material (PCM). The SET and the RESET states of the PRAM refer to low and high resistance respectively. The operation speed of PRAM is limited by the SET programming time because it takes finite time to fully crystallize the amorphous region. This idea of using amorphous to crystalline phase transition of chalcogenides for an electronic memory technology has been pursued for many years [2]. PRAMs have desirable characteristics including; fast switching speed, low programmable energy, high endurance, good data retention, improved compatibility with CMOS and excellent scalability [3]. Studies have also shown that PRAM cycling endurance is of the order $10^8$ writes (the number of successive write/erase cycles before the cell fails) which is significantly higher than that of floating gate technology which is reported to be approximately $10^5$ [4]. In addition PRAM is capable of creating new functions and applications of its own which are fast write programming speed and direct overwrite capability [5].

Many researchers have widely studied $Ge_2Sb_2Te_5$ (GST) and optimized it for PRAM applications. However GST has been reported to have some drawbacks for instance, meta-stable face centered cubic (fcc) structure, low crystallization temperature and low crystallization resistance. The low crystallization temperature means it is unable to retain data at high temperature. To eliminate these problems, anew PCM for next generation PRAM applications must have a higher crystallization temperature and also higher crystalline resistance with a faster phase change speed than GST. Research has shown that crystallization temperature is directly proportional to the data stability while crystalline resistance is inversely proportional to the RESET operation power [6]. It is therefore necessary to come up with a material that has high crystallization temperature and also high crystalline resistance. This will ensure an improved data retention capability and reduce the RESET power of the PRAM.

Additives for instance Zinc, Silicon dioxide, Titanium, Nitrogen among others have been reported to have the ability to influence the crystallization temperature of PCM. Addition of carbon has been found to lead to an increase in crystallization temperature and activation energy for crystallization of GeTe [7, 8]. Selenium has been found to have tremendous potential in device technology since it exhibits a unique property of reversible transition. Additives increase the hardness, sensitivity and crystallization

---

* Corresponding author:
samopiyo11@gmail.com (Opiyo S. O.)

temperature of selenium as well as lessening the ageing effect [9]. This study was aimed at finding out the effect of Zn additive at lower percentages (0-8%) on the electrical characteristics of $In_2Se_3$ for PRAM application.

## 2. Experimental Procedures

### 2.1. Zn:$In_2Se_3$ Alloys Synthesis and Thin Film Deposition

Elements of In and Se granules, of purity 99.999% were synthesized in the ratios of 2:3 by atomic mass. Zn of similar purity was then introduced into the sample at different ratios (0%-8%, in steps of 2%) by mass. The composition was then loaded in Pyrex glass tube and then sealed before heating to about 450°C in the presence of argon. During heating there was slight shaking of the tube to obtain homogeneity. The obtained homogenous solid alloy was ground in a porcelain motor.

Edward Auto 306 RF/DC evaporation chamber was employed in the thin film deposition. Thoroughly cleaned ordinary microscope glass slides were used as substrates and mounted on the chamber substrate holder. The chamber pressure was then pumped down to 3.0 x $10^{-5}$ mbar pressure at room temperature. A current of 3A was used to heat up the boat to allow for the evaporation of the sample and a final thin film deposition on the substrate.

### 2.2. Sheet Resistance Determination during Thermal Cycling

The sheet resistance of the sample was obtained at various temperatures (ranging from 25°C to 300°C in steps of 5°C). During thermal cycling, Lindberg Mini-Mite TF55035Atube furnace was used for annealing. Keithley 2400 sourcemeter in four wire mode was used to determine the I-V characteristics of the films the temperature was ramped at a constant rate of 10K/minute [10]. To eliminate chances of oxidation of the film, Argon gas was flown through the Lindbergh furnace continuously at a constant rate of 1sccm.

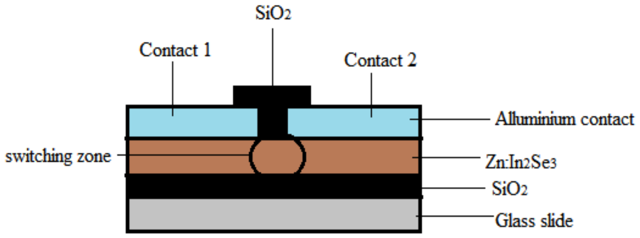

**Figure 1.** Schematic diagram of PRAM cell

### 2.3. Fabrication of a PRAM

A PRAM was fabricated by depositing first a layer of $SiO_2$ on a clean normal glass substrate. This was followed by a layer of Zn:$In_2Se_3$. Aluminum strip of width 1 mm was used to mask the switching zone on the PCM before depositing a thin film of Aluminum to form the two contacts (1 and 2) as shown in figure 1. A further layer of $SiO_2$ was deposited to passivate the switching zone. All the layers were 100nm thick as that was the optimum thickness. The method of deposition for all the layers was evaporation technique.

### 2.4. Characterization of the PRAM

#### 2.4.1. DC Current Sweep Test

DC test was achieved by connecting the PRAM in series with 1 kΩ resistor and a 60V variable voltage supply. Keithley 2400 Sourcemeter was used to measure current through the cell while the digital multimeter was used to determine voltage across the cell. Voltage values were determined while the current was varied from 0 to 5 mA in steps of 0.01mA.

#### 2.4.2. Pulsed Mode Test

For pulsed mode testing Agilent 81104 pulse generator was employed. The pulse width (time) was set at 75ns and 15$\mu s$ for RESET and SET operations respectively.

During RESET operation voltage was varied from 1V to 6V while in the SET operation the voltage was varied from 1V to 3V.

## 3. Results and Discussions

### 3.1. Thermal Cycling

Figure 2 shows variation of sheet resistance of the as deposited Zn:$In_2Se_3$ thin films with temperature. From the graph, the gradual decrease in sheet resistance at lower temperatures and sudden drops in the sheet resistance at specific temperatures values are observed. The specific temperature values where the sudden drops in sheet resistance occur correspond to the crystallization temperatures of the films [11, 12]. The minima of Gaussian fits of the derivative of R-T graph results gave crystallization temperatures as shown in table 1 below.

**Table 1.** Variation of Crystallization Temperature with %Zn on $In_2Se_3$

| Zn doping level | Crystallization temperature (°C) |
|---|---|
| 0% | 107.28 ± 0.20 |
| 2% | 114.63 ± 0.27 |
| 4% | 121.72 ± 0.05 |
| 6% | 141.60 ± 0.13 |
| 8% | 147.51 ± 0.07 |

The sheet resistances drop from a magnitude of $10^8$ to $10^3$ is a reduction of 5 orders of magnitude. The graph also shows a rise crystallization temperature with increase in the zinc doping percentages. This is in line with the research carried out by [6] in which they reported an increase in crystallization temperature of GST from 149°C for 0% Zn doping to 272°C for 19.78% Zn doping. The addition of zinc in the alloy stabilizes the alloy as the zinc atoms disorganizes the coordination of In and Se atoms leading to bond recombination between Zn, In and Se atoms. This may have been the cause of the delayed transition with addition of zinc.

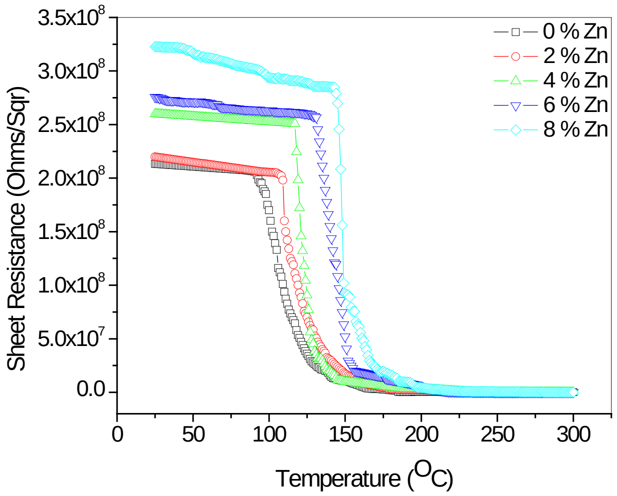

**Figure 2.** R-T curves of $In_2Se_3$ doped with different (%) concentration of Zn

The steep slope observed for the 4% Zinc doping indicates faster crystallization speed. [13] reported that the crystallization speed is directly proportional to the gradient of R-T curve. Crystallization speed is a very important factor in phase change materials since it influences the operation speed of the PCM device.

Figure 3 shows the variation of crystallization temperature with Zn doping. A clear trend on the dependence of crystallization temperature on Zn doping is observed.

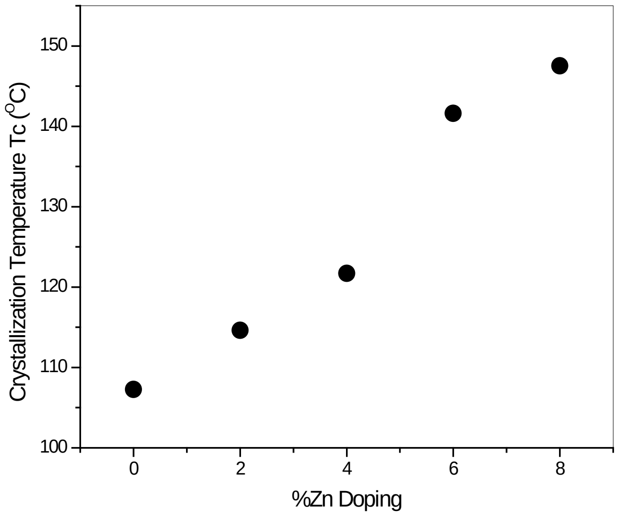

**Figure 3.** Variation of crystallization temperature with % Zinc doping

Increase in % Zinc doping led to considerable increase in crystallization temperature. The increase in crystallization temperature may be attributed to the raise in glass transition temperature of In and Se due to higher glass transition temperature of Zn. Generally an additive with a greater glass transition temperature would greatly increase the crystallization of an alloy consisting of elements with lesser glass transition temperatures in comparison with the additive. Another phenomenon which may have been at play is the electronegativity difference between Zn and InSe. Large difference in electronegativity facilitate more dopant to reduce diffusion resulting from introduced covalent bond which further reinforce the cohesion of the atomic network leading to increased crystallization temperature [14].

Higher crystallization temperature means thermal stability of the material and hence longer data storage capability of a PCM device. However, very high crystallization temperature may lead to low crystallization speed.

Table 2 shows variation of sheet resistance of the thin film at different Zn doping levels.

**Table 2.** Variation of Sheet Resistance with Zn Doping

| %Zn doping | Amorphous Sheet Resistance $(\Omega/sqr)$ | Crystalline Sheet Resistance $(\Omega/sqr)$ |
|---|---|---|
| 0 | $2.130\text{x}10^8$ | $1.590\text{x}10^3$ |
| 2 | $2.199\text{x}10^8$ | $1.629\text{x}10^3$ |
| 4 | $2.599\text{x}10^8$ | $1.883\text{x}10^3$ |
| 6 | $2.756\text{x}10^8$ | $2.493\text{x}10^3$ |
| 8 | $3.227\text{x}10^8$ | $3.443\text{x}10^3$ |

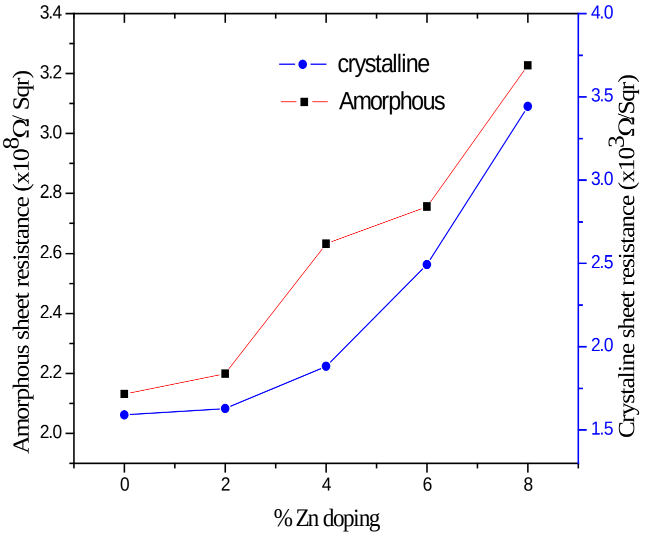

**Figure 4.** Variation of amorphous/crystalline resistance with %Zn doping levels

Table 2 and Figure 4 show variation of amorphous and crystalline sheet resistance with different zinc doping levels. It is observed that an increase in zinc doping raised both amorphous and crystalline sheet resistance. The highest and the lowest sheet resistances are $2.130 \text{ x } 10^8\ \Omega/\square$ and $3.227 \text{ x } 10^8\ \Omega/\square$ for 0% Zn and 8% Zn doping respectively. The increase in sheet resistance may be attributed to the disruption of coordination of the atoms of $In_2Se_3$ as the zinc doping increases.

It’s clear from figure 4 that there is a slight change in sheet resistance at lower zinc percentages (0-4%) after which there is a larger change at higher zinc doping (6-8%). This behaviour may be attributed to non-uniform crystallinity or poor crystallinity at high zinc doping levels.

The stability of data in a memory cell is not only a function of the crystallization temperatures of the material of the cell, but also the resistance contrast (ratio of the amorphous to crystalline sheet resistance).

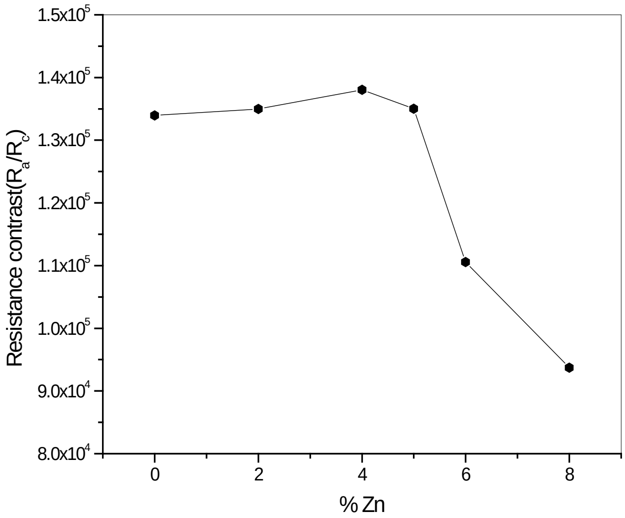

**Figure 5.** Graph of resistance contrast with increase in % Zn doping on $In_2Se_3$

Figure 5 shows a graph of resistance contrast with increase in % Zn doping. The graph shows a gradual rise in resistance contrast with increase in Zinc doping up to 4% Zn doping. Further increase in Zinc doping results in relatively faster drop in resistance contrast as observed for 6% and 8% Zn doping. The highest contrast is registered at 4% Zn doping ($1.38x10^5$) meaning that 4% Zn doping will form much stable memory cell due to the higher ratio of amorphous and crystalline resistance. [15] reported that higher amorphous to crystalline resistance ratio is an excellent property and helpful to achieve lower RESET current and higher ON/OFF ratio. Resistance contrast also has effect on the data stability of a PCM device. An increase in contrast increases data stability.

A PRAM was fabricated employing the 4% Zn doped $In_2Se_3$ films as the active layer. 4% Zn doped $In_2Se_3$ film was used because it exhibited most of the desired characteristics for PRAM applications which include: moderately high crystalline resistance, moderately high crystallization temperature and high resistance contrast which are useful in reducing RESET current, raising data stability and reducing data disturbance in the PCM device respectively.

Figure 6 shows how the voltage varied with current for different current sweeps on Zn:$In_2Se_3$ PRAM. During the first sweep the current remains almost unchanged and at very low level up to about 4.6V when the current suddenly starts to increase. Before 4.6V, there is high resistance since the material is still in the amorphous phase. However, at 4.6V the current generated is enough to crystallize the material hence creating a conduction path [16]. This eventually leads to a sudden drop in the voltage as very little energy is now needed to drive the current.

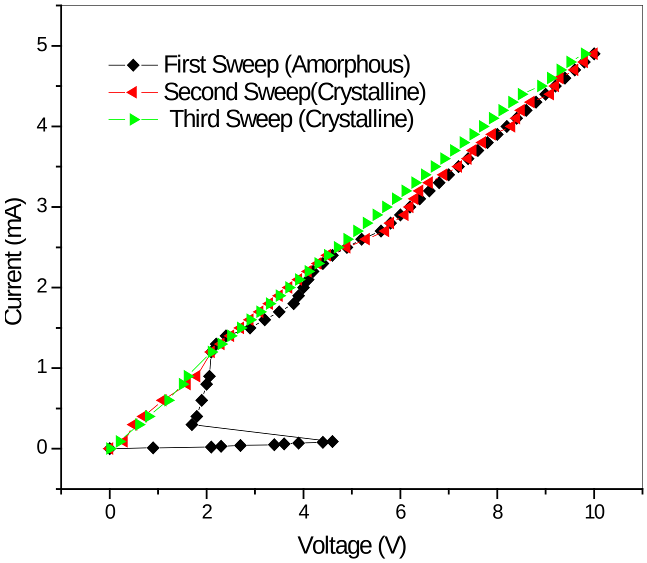

**Figure 6.** I-V curve for 4%Zn-$In_2Se_3$ PRAM

A critical property of phase change materials is the threshold switching. Without this effect PCM would simply not be a feasible technology, because in the high resistance state extremely high voltages would be required to deliver enough power to the cell to heat it above the crystallization temperature [17]. At the threshold voltage most of the current flows through the critical current path, the joule heat is generated from the path and begins to crystallize the surrounding area. As a result, amorphous phase-change resistor switches to a crystalline state [18]. Second and third sweeps clearly show ohmic behavior since the formation of critical current path and crystallization of phase-change resistor is done by the first sweep.

Figure 7 shows the plot for variation of the resistance with 75ns RESET pulse. Almost constant crystalline resistance of 3 orders with increasing voltage up to about 4.75V when the resistance suddenly rises to 8 orders of magnitude is observed. The voltage at which the switching from low to high resistance occurs is called the RESET voltage. At this voltage the material is heated above its melting point and due to the short pulse duration, it is rapidly cooled hence changing from low resistance crystalline state to high resistance amorphous state.

Figure 8 shows the variation of the resistance with 15$\mu$s SET pulse. The resistance of the PRAM remained almost constant at an average of about 2.6 $x10^8\Omega/\square$ for voltages less than 2V. However, at 2.38V the resistance of the cell drastically dropped from 8 orders to 3 orders of magnitude. This voltage is called the SET voltage as the switching region is set to low resistance. This phenomenon occurs due to joule heating of the switching area hence creating a conduction path that switches the material from highly resistance to low resistance.

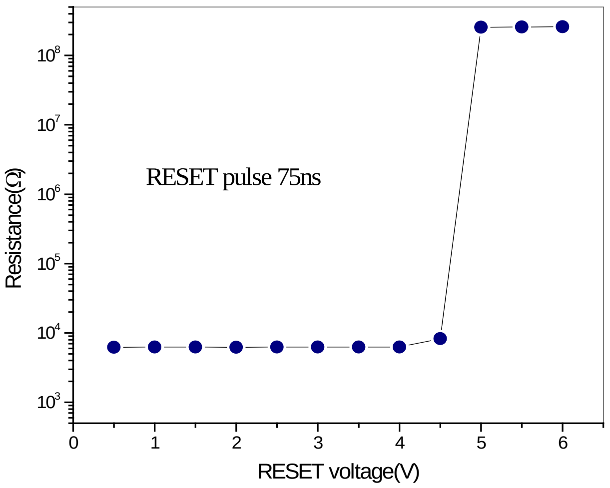

**Figure 7.** RESET Pulsed-mode switching behavior of Zn:$In_2Se_3$ PRAM

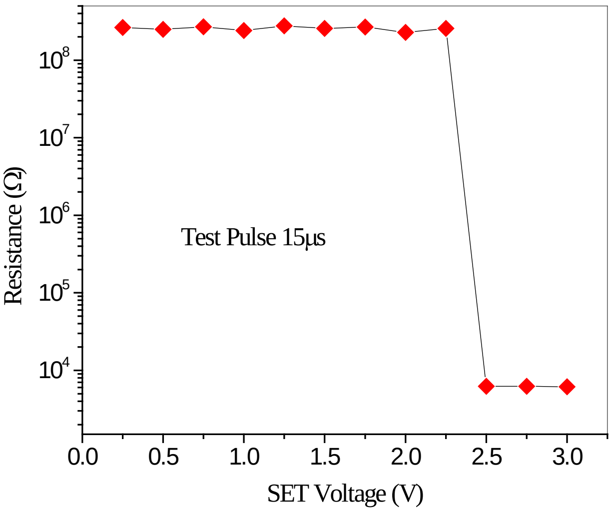

**Figure 8.** SET pulsed-mode switching behavior of Zn:$In_2Se_3$ PRAM

For the cell to be SET to low resistance then a considerably low pulse has to be passed through the cell for a relatively longer period that will allow slow cooling and hence crystallization of the switching region of the cell [19]. As can be seen in figure 8, after 2.38V the resistance remains low even with continuous pulsing. This indicates that the material is already in the crystalline state.

## 4. Conclusions

The effect of low percentage Zn doping (0%-8%) on $In_2Se_3$ thin films for phase change memory application has been successfully investigated in this work. Zn doping raised both amorphous and crystalline sheet resistance of $In_2Se_3$ thin film. Crystallization temperature also increased with increase in Zinc doping from 107.28°C to 147.51°C for 0% to 8% doping levels respectively. This indicated an increased stability of the thin films with Zn doping. Four percent (4%) Zn:$In_2Se_3$ registered the highest amorphous/crystalline resistance contrast indicating reduced noise in the PRAM as well as considerable increase in stability. The I-V characterization of the PRAM resulted in a threshold voltage of 4.60V while the pulsed mode test yielded a RESET pulse of 75 ns, 4.75V and a SET pulse of 15$\mu s$, 2.38V.

## ACKNOWLEDGEMENTS

We would want to say special thanks to the Vice Chancellor Kenyatta University, Prof. Olive Mugenda for availing laboratory resources and for creating an ample environment for science research. Thanks to entire staff of physics department, Kenyatta University lead by the chairman Dr. Walter Njoroge (2011-2015) for their continuous guidance in the laboratory during experiments as well as during the departmental seminars. They surely played a major role in the success of this work.

---

## REFERENCES

[1] Wong, S., Raoux, S., Kim, J. Liang. (2010). Proceedings of the Institute of Electrical and Electronics Engineering (IEEE), 98, 2201.

[2] Ovshinksy S. R. (1968). Reversible electrical switching phenomena in disordered structures. Proceedings of the Electrical and Electronics Engineering (IEEE), 98, 18-19.

[3] Qiao, B., Yun, L., Lin, Y., Lai, L., Feng, J., Chen, B. and Tang, T. (2006). The performance of GeSbTe material for PCRAM device. Integrated Ferroelectronics Journal,10, 261-270.

[4] Gleixner, B., Pellizzer, F. and Bez R. (2009). Reliability Characterization of Phase Change Memory. In the proceedings of Non-Volatile Memory Technology Symposium (NVMTS), 2009 10th Annual. DOI: 10.1109/NVMT.2009.5429783.

[5] Daewon, H. and Kinam K. (2007). Recent advances in high density phase change memory (PRAM). Advanced Technology Development Team Invited Paper, 2, 9-11M.

[6] Heone, L. and Dae-Hwan, K. (2005). Indium selenide thin film for phase change memory. Material science and Engineering B, 119, 196-201.

[7] Sousa V., Perniola, L., Navarro, G., Pashkov, N., Suri, M., Persico, A., Henaff, E., Fillot F., Pierre, F., Roule, A., Maitrejean, S., Feldis, H., Jahan, C., Nodin, F., Toffoli, A., Blachier, D., Bastard, A., Bastien, J-C., Hyot, B., André, B., Reimbold, G., De Salvo, B., Faynot, O., Zuliani, P. and Annunziata, R. (2011). GeTe-based Phase Change Memories: Effect of stoichiometric variations and N or C addition. European Phase Change Ovonic Science (EPCOS) 2011.

[8] Ramesh, K., Asokan, S., Sanguni, K. (2011). Electrical switching in GeTe glasses doped with Cu and Ag. Indian institute of science. IIS560012.2011.

[9] Sushama, D., Achama, G., Predep, P. (2006). Effect of doping on binary Se-In chalcogenide glasses. Journal of Optoelectronics and advanced Materials, 8, 1639-1640.

[10] Keithly Instruments 2400 Series Source Meter User's Manual, 2400S-900-01 Revision G. USA, (1998).

[11] Guoxing, W., Qiuhua, N., Xiang, S., Wang, R., Liangcai, W., Jing, F., Tiefeng, X. and Shixun D. (2012). Phase change behavior of Zinc doped $Ge_2Sb_2Te_3$ film. Applied Physics Letters, 101, 051906.

[12] Muchira, I., Njoroge, W. K. and Karimi P.M. (2015). Crystallization Kinetics of $In_{40}Se_{60}$ Thin Films for Phase Change Random Access Memory (PRAM) Applications. Journal of Ovonic Research.

[13] Lee, B., Lee, C., Ping, Z., Jun, Y., Youtao, Z., Bo Z., Engin, I., Onur, M. and Doug B. (2010). Phase-change technology and the future of main memory. Institute of Electrical and Electronics Engineering (IEEE) Computer Society. IEEE Micro White paper 0272-1732/10.

[14] Gu, Y., Sannian, S., Zhitang, S., Yan, C., Xiaofeng, D., Liu, B. and Songlin, F. (2012). $Si_xSb_2Te$ materials with stable phase for phase change random access memory applications.Journal of Applied Physics, 111, 1-9.

[15] Heon, LEE and Dae-Hwan K. (2005) Switching Characterization and Failure Analysis of $In_2Se_3$ Based Phase Change Memory. Japanese Journal of Applied Physics, 44, 4759–4763.

[16] Xiang, S., Guoxiang, W., Wang, P., Shixun, D., Liangcai, W., Yimin, C., Tiefeng, X. and Qiuhua, N. (2013). Enhanced thermal stability and electrical behavior of Zn-doped Sb2Te films for phase change memory application. Applied Physics Letters, 102,1-3.

[17] Geoffrey, W., Matthew, J., Michele, F., Davide, G., Kailash, G., Bryan, J., Kurdi, B., Chung, L., Luis, A., Alvaro, P., Bipin, R., Simone, R. and Rohit S. (2010). Phase change memory technology. Journal of Vacuum Science and Technology B, 28, 223-262.

[18] Barclay, J. (2009). Electrical switching properties of ternary and layered chalcogenide phase-change memory devices. Master of Science thesis. Boise State University, December, 2009.

[19] Raoux, S., Burr, G. W., Breitwisch, M. J., Rettner, C. T., Chen, Y.-C., Shelby, R. M., Salinga, M., Krebs, D., Chen, S.-H, Lung, H.-L., Lam, C. H. ( 2008). Phase-change random access memory: A scalable technology, IBM J. RES. & DEV, 52, 465-479.