Exploring the Dynamics of Threshold Switching and Electronic Properties of Ag, In-doped Sb_2Te Phase Change Material for Universal Memory

Synopsis of the thesis
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DOCTOR OF PHILOSOPHY

by
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1. Introduction

Modern electronics with a key component of non-volatile memory has remarkably pervaded our day-to-day lives, starting from music players, to digital cameras, information stored in smart phones and portable external storage devices. High speed and high-density non-volatile memory is the essential component widely used to preserve information in the local servers, hard disc drives (HDD), solid state drives (SSD), external storage devices including rewritable CDs, DVDs and Blu-ray discs. Online data storage refers to store information on the host servers. These servers typically store massive amounts of data that are housed in one or more data centers. All these information needs to be either stored or processed with the help of memory devices. This demands a large capacity of high-speed non-volatile digital data storage media. Despite the existing memories such as HDD, SSD satisfy current demand they suffer to meet high performance computing, due to slow programming characteristics. In order to enable high speed non-volatile memory for future, there are numerous technologies have been explored in the last few decades. Among various emerging memory technologies, chalcogenide based phase change memory (*PCM*) is considered as a potential candidate for the next-generation non-volatile memory, owing to better scalability, longer data retention, higher endurance and fast programming compared to the other emerging memory technologies [1-4].

Chalcogenide based phase change materials exhibit a unique behavior of rapid and reversible switching between a high resistance amorphous state (*binary '0'*) to a low resistance crystalline state (*binary '1'*) which forms the basis of information storage. These states are achieved by means of applying appropriate nanosecond (ns) electrical pulses to switch the material between amorphous (*RESET*) and crystalline (*SET*) states as shown in Fig. 1 [1,2].

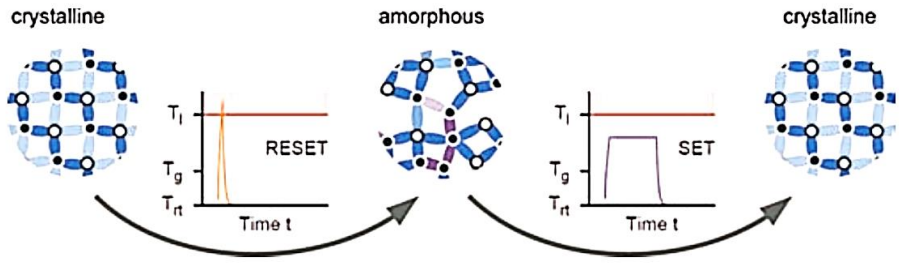

Figure 1. *Principle of operation of Phase change memory technology [5].*

The high resistance amorphous state (RESET) is achieved by applying the larger amplitude RESET pulse, which raises the temperature of the material above melting temperature within the short duration of 400 ps [6]. Subsequently, a rapid cooling takes place during the sharp

trailing edge, wherein atoms are quenches in the disordered state. However, to achieve the low resistance crystalline state (SET) a longer pulse-width of a few ns [7] is required to essentially surpass an event of threshold-switching from the amorphous off-to-on state. Thereafter, the Joule heating takes place and raises the local temperature above crystallization temperature. Hence, the speed of crystallization achieved by the SET pulse is inherently governed by a combined effect of ultrafast threshold-switching dynamics and crystallization kinetics of phase-change (PC) material.

Furthermore, the speed of threshold-switching is primarily decided by transient parameters including delay time (t_d). The delay time decreases rapidly over the threshold voltages [8-10]. The reported delay time value for the chalcogenide-based memory devices is in the order of 1-10 ns and these transient parameters are limited by the response time of the experimental setup [7-10]. Owing to these facts, achieving a faster set process is primarily hindered by the voltage dependent transient parameters and therefore the speed of crystallization is much slower compared to that of amorphization, which is the main drawback keeping us from realizing ps-programming characteristics of PCM devices.

Figure 2 displays various families of phase change materials. The first family of materials is primarily located in the pseudo-binary line between GeTe and Sb_2Te_3. These materials found to show nucleation-dominated crystallization and have been employed in various optical data storage products [2].

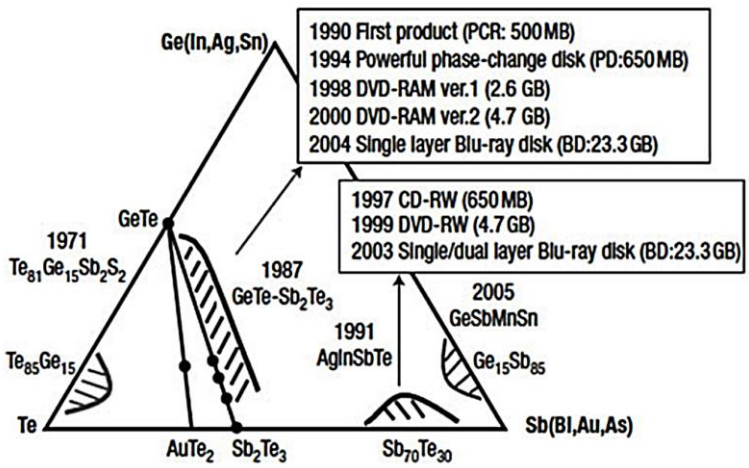

Figure 2. *Ternary phase diagram of the phase change memory material families [2].*

The second family mainly includes Ag and/or In-doped Sb_2Te. The AgInSbTe (AIST) material is the most prominent candidate of the doped Sb_2Te family, which shows ultrafast crystallization based on the growth-dominated crystallization mechanism and is extensively

used in rewritable memory products [2]. The third family is Ge doped Sb. The $Ge_{15}Sb_{85}$ is the eutectic composition, which shows higher thermal stability and faster crystallization time compared to other families [2]. Therefore, exploring phase change materials with faster switching dynamics by means of a systematic understanding of threshold-switching dynamics and the crystallization process of PCM device together in ps-timescale is essential.

2. Motivation of this thesis

PCM offers promising attributes such as DRAM like speed and non-volatility for '*universal memory*' owing to its all-round characteristics. However, some of the most critical issues including threshold switching dynamics, fast crystallization and structural stability of phase change material is poorly understood.

a) The crystallization process in the phase change materials is either nucleation dominated or growth dominated. The crystal growth rate is found to be 1m/sec for the nucleation dominated $Ge_2Sb_2Te_5$ material, while growth-dominated crystallization in AIST material, shows a very high crystal growth velocity of 100 m/sec [11]. Therefore, AIST having higher crystallization growth velocities is ideally suitable for achieving high-speed programming characteristics. A systematic study of rapid switching dynamics of AIST and electronic properties would be helpful for universal memory applications.

b) The programming speed of memory is primarily governed by rapid and reversible phase change behavior of active material. Re-amorphized phase (*RESET*) is achieved within a duration as small as 400 ps [6]. However, to achieve a crystalline phase (*SET*), a longer pulse-width of a few ns is required to essentially surpass an event of threshold-switching from amorphous off-to-on state [7-10]. Owing to this, achieving an ultrafast SET process is primarily hindered by the voltage-dependent transient parameters and therefore the speed of crystallization is much slower compared to that of amorphization and found to be main drawback keeping us from realizing ps-programming characteristics of PCM devices. Therefore, exploring ultrafast switching dynamics by means of a systematic understanding of threshold-switching and the crystallization process in Ag, In-doped Sb_2Te based memory devices at ps-timescale is essential for the universal memory.

c) For testing memory cells with ns electrical pulses, carefully designed high-frequency contact-boards are usually employed that allow realization of time-resolved electrical quantities. However, in case of PCM, owing to threshold-switching a rapid change from its high resistance to a low resistance (from ~1 MΩ to a few 100 Ω) state causes loading and

unloading of parasitic capacitances in ps, which limits realization of the actual response of the device. Therefore, development of an unconventional custom-built electrical setup with the capability of capturing time-resolved electrical pulse measurements of threshold-switching dynamics and *SET* process of PCM devices together in ps timescale is essential.

d) The fundamental origin of a pronounced contrast in resistivity and reflectivity is predominantly attributed to the electronic states of amorphous and crystalline phases. The disordered structure of the amorphous phase depends on the bonding nature of the material. The amorphous phase possesses purely covalent bond, while crystalline phase consists of resonant bonding. The degree of disorder is known to impose a profound effect on band structure and hence change in the electronic properties of the material can be observed. Therefore, insights on systematic evolution local structure and band gap during phase transition AIST materials using in situ measurements would be extremely useful for achieving a stable reversible switching between amorphous and crystalline phases.

3. Objectives and the scope of the present thesis work

In the view of the major concerns mentioned above, it is necessary for a systematic study on the following objectives.

I. Development of an advanced programmable electrical test (PET) setup to explore the electrical switching and programming characteristics at the picosecond timescale of nano-scale memory devices.
II. Systematic investigation of the structural properties of the Ag, In-doped Sb_2Te (AIST) phase change material for their suitability for the ultrafast memory application.
III. Investigation of ultrafast threshold switching dynamics and transient characteristics of AIST devices for enabling the ultimate programming speed for the universal memory.
IV. Exploring the electronic properties of the amorphous and crystalline phase of the AIST material by systematic evolution of optical band gap and local disorderness by means of in situ measurements.

4. Major contributions

4.1 Fabrication of device and experimental details

The thin films of AIST material of various thicknesses are deposited by using the RF/DC magnetron sputtering system for various measurements such as X-ray Diffraction (XRD), X-ray Reflectometry (XRR), Scanning Electron Microscopy (SEM) and UV-Vis-NIR

Spectroscopy. The temperature dependent sheet resistance measurements (van der Pauw method) were carried out on the thin AIST films. The custom-built advanced programmable electrical test setup was employed to perform ultrafast electrical switching measurements and programming on AIST devices. Such devices are fabricated by using the three different mechanical masks (top electrode, a bottom electrode, and PCM layer mask), in which the active layer of the AIST material is sandwiched between the top and bottom electrodes.

4.2 Development of ultrafast programmable electrical tester

To capture the ultrafast electrical switching dynamics of PCM devices a carefully designed advanced programmable electrical test (PET) setup is essential. The PET setup must be able to resolve the major challenges involved in the measurement technique. First, the rapid change in the dynamic resistance due to threshold switching causes the loading and unloading of the parasitic capacitance in ps involved in the circuit, which limits the actual realization of the switching response of the device and may also generate high current spikes which can destroy the device and/or setup. Secondly, to understand the threshold switching dynamics, it requires capturing the time-resolved measurement of sub-threshold current. These issues were carefully tackled in the designing of advanced PET setup. The custom designed PET setup consist an arbitrary waveform generator (AWG, *Agilent*), Digital storage oscilloscope (DSO, *Teledyne Lecory*) and custom-designed probe station with two high-frequency contact-boards namely source side contact board and sense side contact board. The sourcing side contact board consist of impedance matching circuit (IMC) while sensing side contact board consists of a direct output line and low noise high-speed amplifier circuit as shown in Fig. 3. The entire setup is controlled though LabVIEW program to perform various operations such as (*SET*, *RESET*, *READ*) and allow measurement of time resolved current-voltage characteristics at the ps timescale.

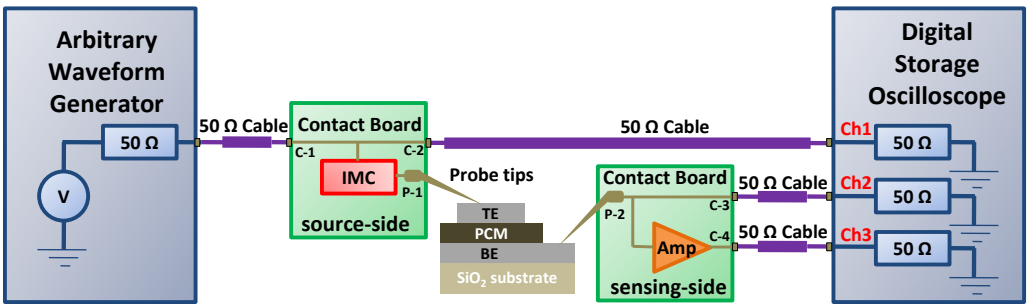

Figure 3. *Schematic of the custom-designed PET setup.*

The performance of the setup is measured by the testing the contact boards, probe tips and cables at ps timescale. A standard test pulse (STP) of rise time (20% to 80%) and fall time (80% to 20%) of 100 ps with the pulse width of 100 ns and 0.5 amplitude is sent through the cables and the output response is recorded by the DSO. The cable response time is found to be 100 ± 25 ps, which is same as STP. Furthermore, the output response of the contact boards including the probe tips, measured on the gold strip for STP is captured by the DSO as shown in Fig. 4. The inset images show the response time of the contact boards, which are 200 ± 25 ps i.e. 20% to 80% of rise time or 80% to 20% of fall time. The setup enables capturing ultrafast threshold switching transitions of PCM devices at ps timescale.

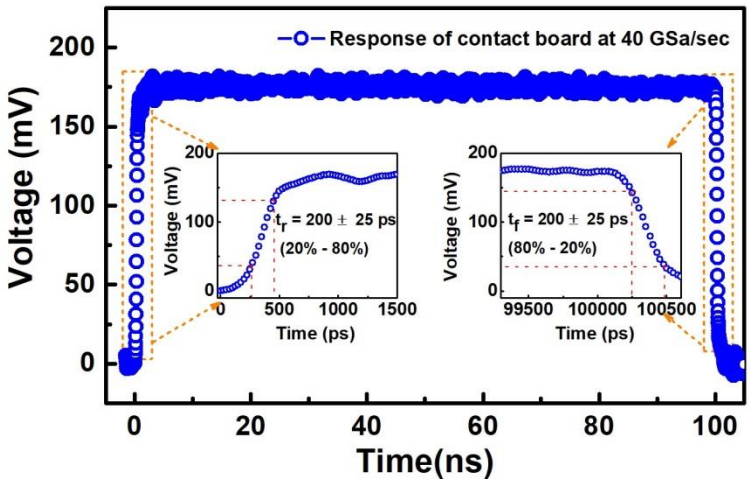

Figure 4. *The output response of the high-frequency contact boards for the standard test pulse (STP).*

4.3 Structural suitability of AIST for ultrafast memory application

The dependency of resistance on the temperature of the as-deposited amorphous phase was carried out by performing the sheet resistance measurement on 100 nm thin film of AIST. The resistance of the amorphous phase decreases with increasing the temperature owing to semiconductor nature of the amorphous phase along with a sudden drop in the resistance value at phase transition temperature (T_c = 175 °C) due to the structural change in the structure. The amorphous nature of as-deposited thin film was confirmed using X-ray diffraction, while XRD pattern of the AIST sample annealed at 250 °C indicates the crystalline (hexagonal phase) nature of the film.

The activation energy of the crystallization is calculated by the Kissinger plot by calculating the crystallization temperature T_c at different heating rates and it is found to be 2.4 eV, which shows the better thermal stability of the AIST material. Furthermore, the activation energy (E_a) of the conduction is estimated by the temperature dependent current plot. The Arrhenius

equation of conduction is applied to extract the activation energy of conduction and it is found to be 0.35 eV for various heating rates.

4.4 Investigations on ultrafast threshold switching dynamics of AIST

To understand the threshold switching dynamics of AIST device, a voltage pulse having amplitude of 1.8 V and the leading and trailing edge of 30 ns was applied on the AIST memory cells. During the leading edge of V_A, the device remains in a high-resistance off state until reaching the threshold voltage (V_T) of 1.6 V. Above this V_T, the device current (I_D) rapidly increased and lead to conducting on state. Furthermore, to investigate the delay time and its dependency of the applied voltage, a trapezoidal pulse heaving the rise time of 1 ns and fall time of 100 ns with the pulse width of 100 ns of different amplitude (1.8 V, 2.1 V, and 2.6 V) are applied on the different memory cells. Interestingly, it is observed that all the cells are switched at V_T 1.6 V without introducing any delay as shown in Fig. 5 (a). The current response curve unveil two different slopes of I_D, first a steep current rise indicating the breakdown of the electronic resistivity without further measurable delay and the switching time (t_s) from amorphous off-to-on state was achieved within 250 ps. Subsequent to this, I_D increases with a distinctly lower slope until reaching saturation within 700 ps prescribed as the crystallization time (t_c) of AIST. In order to further substantiate on steep threshold-switching characteristics in AIST cells, very short duration electrical pulses having a pulse width of 1.5 ns (FWHM) is used. Figure 5 (b) demonstrates a similar threshold-switching characteristics of a steep current-rise at V_T as described above, for the V_A of 1.6 V 2.1 V and 2.6 V. Hence, these results of threshold switching dynamics would be ideally suitable for universal memory owing to its steep switching characteristics.

To further corroborate the nature of the threshold-switching mechanism, the numerical solution for threshold-switching based on trap-limited conduction assisted by hot-electrons effects is computed using our experimental data. The normalized carrier temperature (T_e/T_o) is simulated using time-dependent experimental voltage. It is found, that the signature of the T_e/T_o is unity up to a steep current-rise from the off-to-on state as initiated by threshold-switching even with various applied voltages. This confirms that the well-acclaimed origin of threshold-switching is primarily governed by the electronic mechanism.

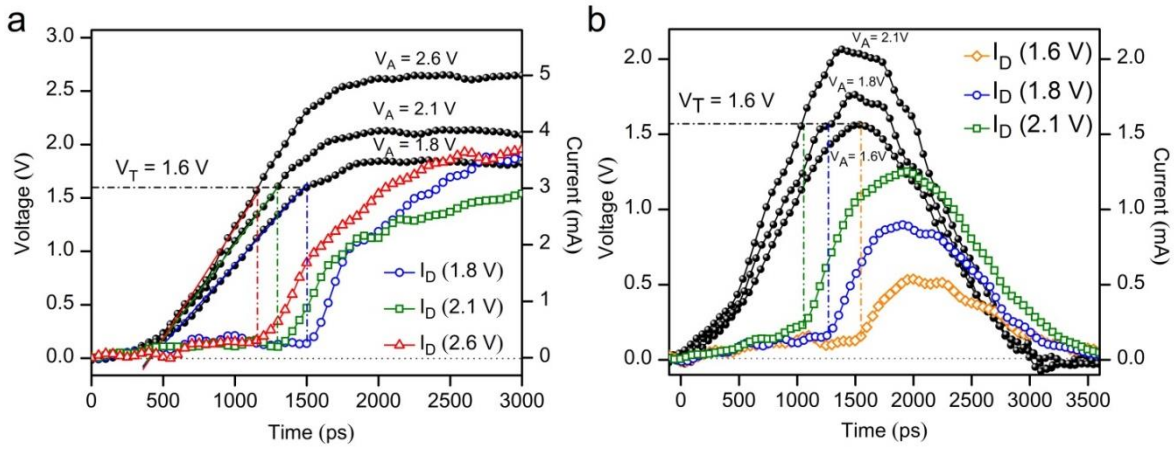

Figure 5. *Transient responses for different VA of 1.8 V, 2.1V and 2.6V (a) for pulse having the rise time of 1 ns, fall time of 100 ns and pulse width of 100 ns. (b) for a pulse having the rise and fall time of 1 ns with the pulse width of 1.5 ns (FWHM).*

4.5 Evaluation of the optical band gap and disorderness

The systematic study of the evolution of the band gap (E_g) and disordeness from as-deposited amorphous to crystalline state was performed using *in situ* UV-Vis-NIR measurement technique in the temperature range from 90 K to 480 K. The AIST material has shown best fitting of the Tauc plot for n= 3/2 for both the phases. The value of n= 3/2 corresponds to the direct forbidden transitions in the AIST as compared to the indirect allowed transitions as reported for the GeSbTe material. These well-known forbidden transitions are mainly due to the transitions between the localized states rather than the extended states, which reflects that the density of the localized states are relatively higher near the band edges of the conduction band and valence band. The band gap of as-deposited amorphous phase and crystalline phase at the 300 K are 0.48 eV and 0.18 eV respectively. Figure 6(a) display the parabolic reduction of the E_g below room temperature following the Varshni's relation and linear reduction above room temperature owes to the semiconducting nature of both amorphous and crystalline phases. The change in band gap with temperature in the crystalline state is due to the thermal excitation of the carriers as well as lattice distortion. These effects are more pronounced at the higher temperature while at the lower temperature the overall effects are freezing out. The more interesting observation was made by analyzing temperature dependence of Tauc parameter, β regarded as a measure of short-range disorder. Interestingly, the value of β decreases with increasing the temperature. The β increase rapidly at the crystallization, indicating the long-range structural order in hexagonal phase as compared to the amorphous phase. A notable increment of mere 2.7 % in the β has shown in Fig. 6(b), which reveals the

higher degree of short-range disorder in the crystalline AIST than that of crystalline GST due to the higher degree of the resonant bonds in the Sb-rich material.

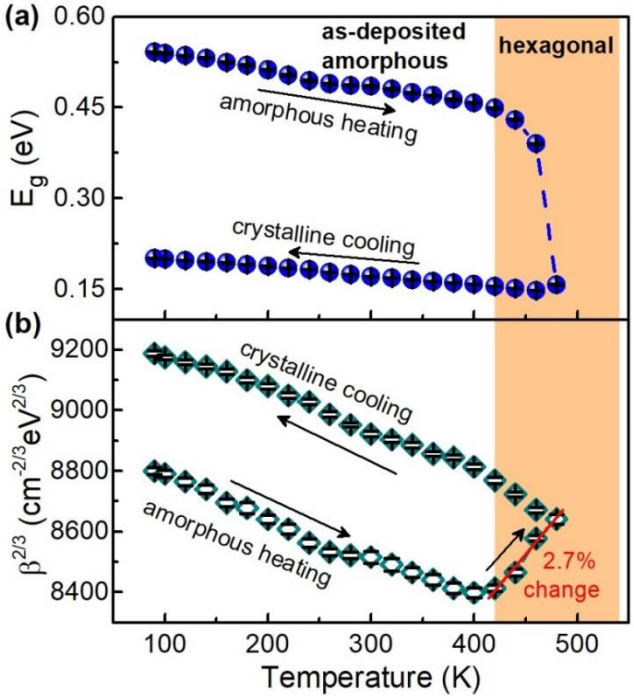

Figure 6. *Temperature-dependence of* ***(a)*** *band gap* E_g *and* ***(b)*** *short-range disorder measured by the Tauc parameter* $\beta^{2/3}$.

Furthermore, the Urbach energy of the amorphous phase is found to decrease upon increasing the temperature, the medium-range order enhances and hence the dynamic structural disordering $(E_U)_{X,dyn}$, which reveal the effect of the $(E_U)_{X,dyn}$ is much more prominent over the effect of the temperature related parameter $(E_U)_{T.}$

5. Summary of contributions

The major contributions of the thesis are summarized as follows:

i. A custom-designed ultrafast programmable electrical test setup was developed, for capturing ultrafast electrical switching at picosecond timescale and also measure the time-resolved current-voltage characteristic with the minimum current value of 1 µA in the sub-threshold conduction.

ii. The structural properties of the Ag, In-doped Sb_2Te (AIST) phase change material are investigated. The AIST material shows fast crystallization and a relatively small change in the density at phase transition temperature, which proved their suitability for electronic memory applications.

iii. The dynamics of the threshold switching in the AIST material is systematically explored. AIST material exhibit a unique and ultrafast threshold switching at 1.6 V without introducing any delay in the response as compared to other family of phase change materials. The device switches strikingly fast from a-off to a-on state within 250 ps and leading to ultrafast crystallization in 700 ps.

iv. Direct observation of the electronic states by the systematic study of the optical band gap and disorderness. The AIST unveiled the direct forbidden transitions in the amorphous and crystalline phase.

6. Conclusions

An ultrafast programmable electrical test setup has been developed, that offers an exceptional capability to explore the threshold switching dynamics at picosecond time scale in the nanoscale memory devices. The structural properties of AIST material were carried out using XRD and XRR measurements. The ultrafast threshold switching dynamics without introducing any significant delay in AIST devices promote the ability to accomplish the faster crystallization and hence programming in sub-nanosecond timescale is viable to achieve universal memory. The rate-independent ultrafast threshold-switching dynamics of AIST devices investigated in this work is very different from other families of PC materials. Furthermore, the electronic structure of AIST, studied by the temperature dependent optical band gap measurement reveal direct forbidden transitions in both the phases. This unique behavior of the electronic states could be responsible for accomplishment of rapid threshold switching dynamics in AIST. Hence, these findings of steep threshold-switching dynamics and the structural properties of AIST device pave a way for high-speed non-volatile memory for future computing.

References

[1] S. R. Ovshinsky, *Reversible electrical switching phenomena in disordered structures,* Phys. Rev. Lett. **21,** 1450 (1968).

[2] M. Wuttig and N. Yamada, *Phase Change Materials for rewritable data storage*, Nat. Mater. **6**, 824 (2007).

[3] D. Loke, T. H. Lee, W. J. Wang, L. P. Shi, R. Zhao, Y. C. Yeo, T. C. Chong, and S. R. Elliot, *Breaking the speed limits of Phase-Change Memory*, Science **336**, 1566 (2012).

[4] N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira and M. Takao, *Rapid-phase transitions of GeTe-Sb_2Te_3 pseudobinary amorphous thin films for an optical disk memory*, J. Appl. Phys. **69**, 2849 (1991).

[5] D. Lencer, M. Salinga, and M. Wuttig, *Design Rules for Phase-Change Materials in Data Storage Applications* Adv. Mater. **23**, 2030 (2011).

[6] W. J. Wang, *et al*. *Fast phase transitions induced by picosecond electrical pulses on phase change memory cells*. *Appl. Phys. Lett.* **93,** 043121 (2008).

[7] G. Bruns, *et al*. *Nanosecond switching in GeTe phase change memory cells*. Appl. Phys. Lett. **95,** 043108 (2009).

[8] D. Adler, M. S. Shur, M. Silver, and S. R. Ovshinsky, Threshold-switching in chalcogenide glass thin films. *J. Appl. Phys.* **51,** 3289-3309 (1980).

[9] M. Anbarasu, M. Wimmer, G. Bruns, M. Salinga, and M. Wuttig, *Nanosecond threshold-switching of $GeTe_6$ cells and their potential as selector devices.* Appl. Phys. Lett. **100,** 143505 (2012).

[10] M. Wimmer and M. Salinga, *The gradual nature of threshold switching*, New J. Phys. **16**, 113044 (2014).

[11] M. Salinga1, *et al*. *Measurement of crystal growth velocity in a melt-quenched phase-change material*, Nat. Commun. **4**, 2371 (2013).

List of Publications (from the thesis work)

Journals:

1. **Krishna Dayal Shukla**, Nishant Saxena, Suresh Durai, and Anbarasu Manivannan; "*Redefining the Speed Limit of Phase Change Memory Revealed by Time-resolved Steep Threshold-Switching Dynamics of AgInSbTe Devices*"; ***Sci. Rep.,*** 6, 37868 (2016). DOI: 10.1038/srep37868. Impact factor 5.12.
2. **Krishna Dayal Shukla**, Smriti Sahu, Anbarasu Manivannan, and Uday Deshpandey; "*Direct Evidence for a Systematic Evolution of Optical Band Gap and Local Disorder in Ag, In Doped Sb2Te Phase Change Material*"; ***Phys. Status Solidi RRL***, 1700273 (2017,). DOI: 10.1002/pssr.201700273. Impact factor 3.06.
3. **Krishna Dayal Shukla**, Nishant Saxena, and Anbarasu Manivannan; "*An ultrafast programmable electrical tester for enabling time-resolved, sub-nanosecond switching dynamics and programming of nanoscale memory devices*"; **Rev. Sci. Instrum.**, 88, 123906 (2017). DOI: 10.1063/1.4999522. Impact factor 1.515.

Conference Proceedings:

1. M. Anbarasu, **Krishna Dayal Shukla**, and Suresh Durai; "*Theoretical and Experimental Investigation of Electrical Switching Properties of AgInSbTe Phase Change Memory Devices*"; *Proceeding of International workshop on Physics of Semiconductor Devices* ***(IWPSD)***, pp. 408, Dec 2015.
2. Gaurav Bishnoi, K. Harish Kumar, **Krishna Dayal Shukla**, and M. Anbarasu; "*LabVIEW controlled Ultrafast Programmable Electrical Tester for Nanoscale Device Characterization*"; *Conference on Intelligent Robotics, Automation and Manufacturing* ***(IRAM)***, pp. 82, Dec 2013.

Patent:

1. Anbarasu Manivannan, **Krishna Dayal Shukla,** and Nishant Saxena; "*Ultrafast Programmable Electrical Test System*"; ***Indian patent, filed*** No. 201721016295 (2017).