

Electronic Study Comparison of Dopants on GST Material for Improved Efficiency of PC Memory Cell

Jashangeet Kaur¹, Ankush¹, Kanika¹, Manoj Bali², Manish Dev Sharma¹, NavdeepGoyal¹

¹Department of Physics, Centre of Advanced Study in Physics,
Panjab University, Chandigarh, India

²B.H.S.B.I.E.T.LehragagaSangrur,Maharaja Ranjeet Singh State Technical University
E-mail:¹jashan2191@yahoo.com

Abstract. Ge-Sb-Te(GST) has gathered immense interest in memory applications due to its modifiable physical and electrical properties. A phase change memory (PCM) cell made up of pure GST has better data retention, switching speed and power consumption than conventional storage devices. A further improvement in these properties can be accomplished by doping with various elements. To comprehend the present scenario of GSTbased phase change memories, it is vital to know about the doping trends. Foreign elements engineer the material properties to produce a PCM device with better physical and electrical properties. This manuscript constructs a comparison of various elements which will serve as a key in research while determining the most advantageous impurity. C, N, O, Si, Se and some transition metals are also examined. A tabular illustration yields correlated effects on physical and electrical properties of dopants on pure GST. Suggestions for future advancements are also specified and substantial conclusions are inferred from the literature review.

Keywords:Phase change memory, GeSbTe, Chalcogenides, dopant effect, material properties.

1. Introduction

The incalculable demand of high density storage media has resulted in the development of phase change random access memory (PCRAM). This has been proved to be a milestone in the information-oriented community. The main component of PCRAM device is its phase change memory (PCM) cell made up of chalcogenide alloys which have a unique property of phase transformation from amorphous to crystalline state[1]. This switching occurs rapidly at a certain threshold voltage, known as threshold switching. The chalcogenides that are mostly investigated as phase change materials are Ge-Sb-Te ternary alloys. The alloys phase diagram shows a pseudo-binary line connecting Sb₂Te₃ and GeTe. The stoichiometric compositions lying on this line have been examined as phase change materials. Ge₂Sb₂Te₅ (GST) is by far the most promising nominee for storage applications. It exists in three phases, one amorphous and two crystalline namely face centred cubic (fcc) and hexagonal closed packing (hcp). The amorphous to fcc transition occurs at 120°-180°C, this is a meta-stable state having high resistivity and low reflectivity. On annealing upto ~250°C, fcc-hcp transition is observed, this phase is more stable with low resistance and high reflectivity. Exploiting this unique property of GST, a PCM cell is grown as shown in Fig.1. The operation of this cell can be summarized in three stages as described in Table 1.

Table 1.PCM Cell Operation.

Stage	Mode	Operation
Stage 1	Reset (Writing)	Melt-quenching the programmable region above melting temperature (T_m) with a short pulse of high intensity (I_{RESET}).
Stage 2	Set (Erasing)	Local annealing above crystallization temperature (T_c) with a long pulse of low intensity (I_{SET}).
Stage 3	Read (Reading)	Applying a lower pulse to measure the resistance without disturbing the state of device.



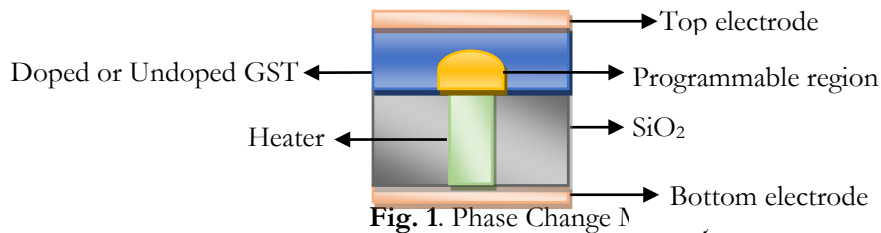


Fig. 1. Phase Change Memory

GST-PCM cell has high resistance contrast between the two stages with high switching speed. It is reliable, inexpensive, non-volatile and has a low threshold voltage [2]. In spite of all these benefits, several drawbacks are encountered when we move to nano-size confinement of this cell. These include large reset current (I_{RESET}), short data retention time and high power consumption. To overcome this, alteration of crystal structure is accomplished by doping. O, N, Si, Cu, C are some commonly used dopants. In this work, we summarize and compare the effect of different dopants on device characteristics.

2. Literature Survey

A phase change material with low crystalline temperature ensures a high speed device, whereas a high T_C material ensures better stability. A low T_M material assures a reduction in power consumption. This propagates a demand of several exclusive dopants that calibrate the material properties of GST. By this motivation, we structured an inter-connection between dopants and modifications in material properties.

2.1. Carbon (C)

Carbon incorporation into GST films leads to a more thermally stable, reliable and low power PCM device. A large decrement in I_{RESET} and improved endurance properties are observed [3]. Various properties of carbon lead to such advancement in GST based memory devices. Firstly, carbon dopant alters the Ge-Te network by disordering its local environment which postpones the crystallization process or stabilizes the amorphous phase. The ABAB type 4-membered arrangement is suppressed by the breakage of Ge-Te bonds and formation of C-Ge bonds. The amount of C-Ge bonding is directly proportional to the carbon content in the doped films [4]. Secondly, carbon gets segregated and forms amorphous clusters at the grain boundaries which retard the crystal growth leading to enhanced thermal stability. Moreover, during the fabrication of high scaled PCM device, conformal deposition of phase change material is desired. For this, C-GST is a potential contender as carbon can be easily introduced from precursors and co-reactants [5]. Researchers propose that GST alloy with reasonable carbon doping is preferred for high density storage devices.

2.2. Nitrogen (N)

This is the most widely studied dopant so far. Nitrogen is a common choice because it increases the set state resistance, E_a and thermal stability. The memory cell so formed has low I_{RESET} and on-voltage with respect to pure GST. N-GST films exhibit a resistance contrast of as large as three orders of magnitude which is the highest according to present accessible literature [6]. The first and second crystallization temperatures are found to increase. There can be two possibilities for such a behavior, firstly, the condensation of nitrides (GeN_x) near grain boundaries and secondly, the increment in covalent bonding. This further suppresses the grain size and atomic diffusion. Nitrogen doesn't amend the amorphous resistivity but it boosts the crystalline resistivity thereby lessening the on/off ratio of PCM cell. Zhen Xu et al. explained the transformation mechanism with the help of density variations in the lattice. A large variation in the densities of amorphous and crystalline phases in undoped GST is a drawback for storage applications. By introducing low density compounds like GeN_x and N_2 , this contrast can be largely reduced. As a result, both amorphous and crystalline state densities decrease with more nitrogen content [7]. An enhancement in both physical and electrical properties is observed with nitrogen incorporation. Low power, highly stable and much more reliable phase change device can be constructed with N-GST films.

2.3. Oxygen (O)

Oxygen incorporation enhances the thermal efficiency but reduces the power hunger as well as conductivity of the PCM cells. This happens as a result of increment in the incubation span and E_a for conduction. Crystalline temperature (T_C)

and grain size is decreased in O-GST films. The suppression of crystallization process at low doping concentration is due to the formation of Ge-O bonds which replace Ge-Te bonds. As an annealing aftereffect, new hexagonal phases comprising GeSb_2Te_4 and Sb_2Te_3 emerge. M.H Jang et al. reported that the augmentation in doping concentration indicates the formation of stoichiometric Sb_2O_3 phase rather than GeO_2 phase which is in disagreement with the previous findings [8]. The author has explained the preferred formation of Sb_2O_3 with the fact that the bond energy of Ge-Te bond is greater than Sb-Te bond. Therefore, the chances of GeO_2 phase formation are lower than that of Sb_2O_3 . S.Privitera et al. has studied the difference in Oxygen (O), Nitrogen (N) and Fluorine (F) dopants on GST films. N succeeded O and F in producing the desired results. The elevation of T_C was more in the case of N-GST as compared to O-GST. This can be justified in view of the larger strain fields and more covalency in case of nitrogen which is well explained by two models proclaimed in literature [9]. A large increase in phase transformation time and smaller grain size has been observed in case of nitrogen. On the other hand, elements like fluorine (F) tend to decrease the T_C and incubation time. Therefore, F is not a potential dopant candidate [10].

2.4. Bismuth (Bi)

Bismuth doping can vary the electrical and optical properties of GST phase change material. A deduction in T_C as well as melting temperature (T_M) is observed. Being isomorphous with Sb, bigger Bi atoms replace Sb and form Bi-Te weaker bonds. This leads to fast crystallization speed and expansion of lattice parameter [11]. The available literature suggests that there is a critical doping concentration (< 1 at.% of Bi) below which Bi-GST shows unexpected performance. This can be understood with the help of percolation theory [12]. The activation energy of Bi-GST films rises rapidly at low concentrations but falls down to original GST values at higher concentrations. Thus, Bi-GST with low Bi concentration is more reliable than the one with high concentration.

2.5. Silicon (Si)

Silicon substitutes Ge and forms Si-Te bond in Si-GST films. This leads to distortion of crystal structure and reduction in I_{RESET} . Confinement of this cell to nano-sizes further reduces the reset current. Silicon doping does not affect the on/off ratio of GST cell by simultaneously increasing the resistivities of crystalline and amorphous phases. Liang et al. found an increase in E_a at the cost of slower crystallization speed and higher on-voltage [13]. In contrast to this, Sung-Jin Park et al. observed a curtailment in E_a causing a low threshold voltage [14]. The reason of less I_{RESET} ability is that the fusion of Si atoms in GST lattice gives rise to Si-rich high resistivity phases which segregate during the reset process. These phases serve as virtual heaters and provide more joule heating to the active region for less I_{RESET} values.

2.6. Tin (Sn)

Sn being in the same group as Ge but having a larger size, takes the place of Ge in the GST lattice. The crystal structure remains unamended whereas the lattice parameter is expanded. The stronger Ge-Te bonds are substituted with relatively weaker Sn-Te bonds which results in super-fast crystallization and low T_C from amorphous to cubic phase [15]. T_C can be increased linearly with the heating rate which can be attributed to insufficient time for crystallization. The T_M and E_a also decrease in a Sn doped film which makes it favorable for high speed, low power and high stability PCM devices. Y.C Chen et al. examined that Sn-GST can be reset and set with much lower pulse width duration producing a high programming speed device [16].

2.7. Selenium (Se)

When selenium forms an alloy with GST, Ge-Se bonds are formed which augment the global bond energy of the structure. Se doping procreates a more thermally stable and high resistance PCM device with a drawback of increased threshold voltage. Vinod et al. proposed that when concentration of Se is between 0.10 at.% and 0.20 at.%, the NaCl phase is skipped and the film shows direct transition from amorphous to hcp phase. This improves the crystalline temperature and on/off ratio [17].

2.8. Transition Metals

2.8.1. Copper (Cu)



The high power consumption of undoped GST is a direct consequence of the high melting temperature (625°C) of this alloy. Therefore, by decreasing the T_m , the energy required to reset the PCM cell is reduced. This is achieved by incorporation of Cu as a dopant. Cu decreases T_m but increases T_C resulting in highly stable phase change films. Cu₂Te phase segregation is observed in Cu-GST alloys during the reset stage because high temperature is required to get Cu into the GST lattice. This phenomenon weakens at higher temperatures and as a consequence the energies for set and reset operations might not degenerate [18].

2.8.2. Magnesium(Mg)

Mg forms covalent bonds with Sb and Te when it enters the crystal lattice of GST. This leads to enhancement in T_C and E_a of doped films. The increased E_a accounts for improved thermal stability and more archival life time. Mg dopant suppresses the formation of hcp phase which increases the amorphous phase stability [19].

2.8.3. Zinc (Zn)

Zinc addition can lead to phase change device which can preserve data for a longer time. The onset temperature and switching speed increases at the cost of upgraded threshold voltage. A modest change in resistance contrast is observed in Zn-GST films which are bettered with more zinc content. Increasing the dopant concentration may also decrease threshold voltage (V_{th}) [20]. Therefore, zinc is a good contender for a high speed device with better 10 year data retention (167.5° C).

2.8.4. Titanium(Ti)

Ti dopant elevates the T_C and E_a of GST films. The reset operation in Ti-GST PCM device has higher 10 year data retention ability with good endurance property. Moreover, it decreases the set and reset voltages which further lowers the power consumption. Introduction of Ti atom in GST lattice leads to Ti-Te bond formation whose bond length is shorter than others. This causes suppression of the volume of supercell. The phase transition from amorphous to crystalline is delayed and from cubic/fcc to hcp is restrained with Ti addition. This benefits for reduction in I_{RESET} because hcp is more stable and provides less resistance whereas fcc is meta-stable with higher value of resistance. Therefore, a Ti-GST cell can be switched on at a V_{th} lower than that of an undoped cell. Moreover, augmentation in doping concentration leads to stronger restrain in cubic to hexagonal phase transition and an increment in T_C [21]. Shershenkov et al. studied and compared the effect of Ti and Bi (Bismuth) dopants on GST film and found that Bi-GST with 0.5 at.% has better kinetic characteristics than all other concentrations of Ti and Bi under observation. Bismuth doping can provide very low switching time but it lowers T_C . This happens because Bi replaces Sb atoms from the GST lattice. As the atomic radius of Bi is more than Sb, substitution of Sb by Bi reduces the average bond energy and hence the crystallization temperature [22].

2.8.5. Tungsten(W)

Though there has been very less research on W as a dopant but available research reveals much better performance characteristics with W-GST films. Due to comparable atomic radius of W with Ge, Sb and Te, it can enter the GST lattice as a substitutional dopant leading to more disorder. Xiaonongchen et al. showed that W-GST films improve the 10 year data retention to 183° C which can increase upto 204° C by incrementing the dopant concentration. The T_C , endurance, nucleation probability and operation speed was also elevated. A decline in grain size implying improved crystalline state resistivity was observed. A complete suppression of hexagonal phase observed, proves to be breakthrough in phase change applications. 7.1% doped W-GST is better for memory applications, according to present work [23].

2.8.6. Nickel (Ni)

Nickel doping gives birth to high speed PCM device which can be reset with a very short pulse width (6 ns). Better 10 year data retention ability (113°C for 0.1at.% & 135°C for 0.3at.%) and elevation in T_C (217°C) are accomplished even with low concentration of Ni [24]. Therefore, Ni can enhance the speed, cyclic ability and thermal stability of PCM cell.



3. Conclusion

Table 2 and 3 summarizes the effect of considered dopants on various physical and electrical properties which are essential for upgradation of phase change memories.

Table 2. Comparative Analysis of Doping Trend.

Dopants	T _c	Switching Speed	E _a	Power Consumption	Thermal Stability	I _{RESET}	V _{th}
Tin	↓	↑	↓	↓	↑	-	-
Bismuth	*↓	*↑	↓ (at low conc.) ↑ (at high conc.)	-	↑	↓	-
Copper	↑	-*	-	↓	↑	-	-
Oxygen	↑	↓	↑ (slightly)	↓	↑	-	-
Carbon	↑	↓	↑	↓	↑	↓	↓
Titanium	↑	↓	↑	↓	↑	↓	-
Tungsten	↑	↑	-	-	-	↓	-
Silicon	↑	↓	↑	↑	↑	↓	↑
Magnesium	↑	↑	↑	↑	↑	↑	↑
Nitrogen	↑	↓	↑	↓	↑	↓	↓
Nickel	↑	↑	↑	-	↑	↓	↓
Zinc	↑	-	↑	↑	↑	-	↑ (Large)

(* ↑ means Increases, ↓ means decreases, - means literature not available)

Table 3. Variation in lifetime of a PCM cell with doping.

Phase Change Material	Dopant Concentration (at.%)	Data Retention Ability (10 year)
GST	0	85°C
Zn-GST	15.16	167.5°C
Cu-GST	10	134°C
Ti-GST	5.67	134°C
W-GST	8	183°C
Ni-GST	3	135°C
N-GST	2.02	97°C

From this illustration, it can be inferred that:

1. Ni, Zn, Cu, Ti and N are the best options for better data retention ability.
2. Sn, Bi, W, Mg and Ni can be preferred for high switching speed.



3. Sn, Cu, O, C, Ti and N can be picked for low power consuming memory devices.

In addition to this, we propose that co-doping can prove to be a valuable breakthrough in achieving better outcomes. Co-doping may blend the advantages of the elements, surpassing the shortcomings of each other. Si-N co-doping has been documented in recent research [25]. We advice that C-O, N-O and many such permutations and combinations can be attempted.

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