

# Doped GeSe Selector Materials

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**Abstract**—We report on the thermal and electrical performance of nitrogen(N) and carbon(C) doped GeSe thin films for selector applications and tuning of their electrical performance. Doping GeSe successfully improved its thermal stability to 450C. Nitrogen doping led to decrease in off-state leakage and an increase in  $V_{th}$ , while Carbon doping increases leakage and reduces  $V_{th}$ . Hence, we show an effective method to tune the electrical parameters of GeSe selectors by using nitrogen and carbon as dopants.

**Keywords**— Selector; Ovonic Threshold Switching(OTS); GeSe; Doping; Threshold voltage; Nitrogen; Carbon

## I. INTRODUCTION

The emergence of 3D stackable memory in cross bar architecture has been receiving attention as a viable candidate for storage class memory. Selectors become essential as the density of arrays increases to avoid sneak path issues which lead to lower noise margins[1]. Ovonic threshold switching (OTS) materials have gained prominence as selectors ever since Ovshinsky[2] first demonstrated them. They exhibit high on current density which enables larger arrays and fast nanosecond switching

$Ge_xSe_{1-x}$  glasses are promising OTS materials. The modulation of OTS switching by varying the Ge concentration in  $Ge_xSe_{1-x}$  has been demonstrated [3], [4]. Varying the thickness of the layer also reduces the  $V_{th}$  at the cost of increased  $I_{off}$  [5]. The effect of dopants, Sb[6], N[7] and Bi[8] on the switching characteristics of  $Ge_xSe_{1-x}$  have been studied before for different values of  $x$  ranging from 0.4-0.7. These dopants were used to modulate the threshold voltage of GeSe. In addition to tunable operation parameters, to implement selectors on memory arrays, improving the thermal stability of these glasses is essential.

In this work, we study the effect of C and N doping of GeSe on its OTS functionality. The high co-ordination number (C=4, N=3) of these dopants would increase the average co-ordination number of the network and enhance the network connectivity [5]. This is expected to strengthen the amorphous network and postpone crystallization.

## II. EXPERIMENTAL

The selector devices studied in this work are cross-bar structures with the overlap area between a bottom and a top electrode defining the active device area. The stack consists of Ru/20nm GeSe/20nm TiN as illustrated in Fig. 1 (a). The devices have been processed using a 300mm substrate, which

includes patterning of the BE, followed by an e-beam write

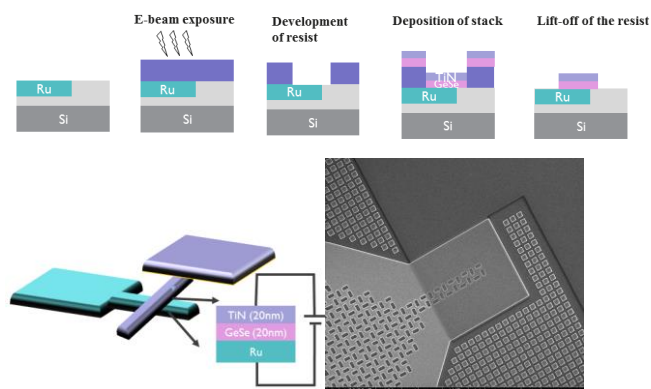


Fig. 1. (a) Process flow for the fabrication of the device (b) Top-down SEM of the cross-bar selector devices which a overlap are of 3umx3um.

process, defining the top electrode (TE). PMMA resist was then spun on Ru bottom electrode (BE) and written by ebeam lithography. The resist was developed for 1 minute in a solution of Mehtyl Iso Butyl Ketone and Iso Propanol Alcohol. GeSe films were deposited by co-sputtering from Ge and GeSe<sub>2</sub> targets, at room temperature. Nitrogen gas was introduced along with the Ar carrier gas in the chamber to dope GeSe with N. The content of N in the deposited GeSe film has been controlled by adjusting the N<sub>2</sub> partial pressure in the gas flow. C was introduced by co-sputtering with a graphite sputter target. The amount of C in the GeSe film has been controlled by adjusting the sputtering power during the deposition.

## III. RESULTS AND DISCUSSION

### A. N doping

Three N doping concentrations, N1, N2 and N3 are studied in this work with N1<N2<N3. To determine the crystallization temperature of the amorphous material, an in situ XRD technique was used, which allowed taking XRD spectra while heating the samples with a specific temperature ramp rate. While the  $T_c$  of pure GeSe is 350C, the addition of N inhibits crystallization and retains amorphous state beyond 450C. Hence N is very effective in delaying crystallization and improving the thermal stability of GeSe.

## B. Electrical Characterisation

The sub-threshold leakage of the pristine samples is plotted in Fig. 2(a) while the distribution of current at 2V across 8 devices for each sample is shown in Fig. 2(b). The initial leakage is symmetric in both directions despite the asymmetry in the stack, suggesting that the electrode material

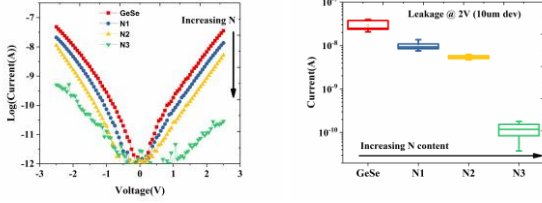


Fig. 2. (a) I-V characteristics of N doped selector devices (b) Current @ 2V for different N contents

plays a marginal role, for this stack configuration, which is consistent with a bulk-limited conduction mechanism. The addition of N decreases the  $I_{off}$  of the device.

The switching characteristics of the N doped OTS devices are plotted in Fig 3. To initiate switching in the devices, a forming voltage ( $V_{form}$ ) is required for the first cycle which is higher than the stabilized switching voltage observed for the

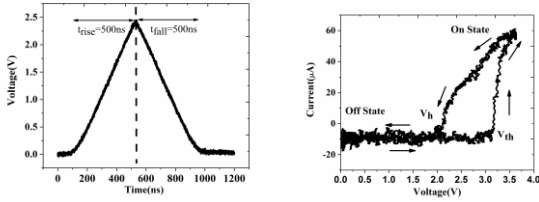


Fig. 3. (a) Schematic of the triangular voltage pulse applied on the device (b) Representative switching I-V curve of the device

subsequent cycles[9]. The forming in our devices was achieved by applying a triangular pulse of amplitude 7V with a rise and fall time of 100ns. Applying a DC sweep led to an irreversible decrease in the resistance of the material and hence a lower pulse width of 100ns was used for the first fire to minimize the structural change in the material. In contrast, the sample N3 could not be initiated with triangular pulses and needed a DC sweep to initiate it.

Post the forming step, triangular voltage pulses with a rise and fall time of 500ns were applied across the device as shown in Fig. 3(a) while the current across the device is calculated by the voltage drop across a 50Ω load resistor. The devices exhibit good OTS behavior with a transition to lower resistance above the transition voltage ( $V_{th}$ ) and regaining the high resistance state when the voltage drops below the hold voltage ( $V_h$ ). The mean switching curves for each sample are compared in Fig. 4(a). After the initial leakage, the devices

switched at lower voltages for subsequent cycles. Continuing the trend observed for the initial leakage, addition of N increases  $V_{th}$ .

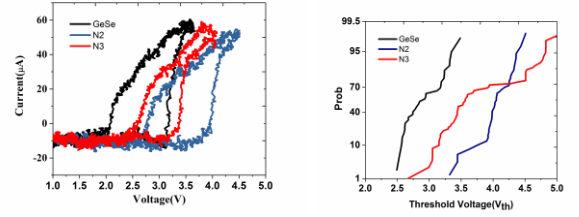


Fig. 4. (a) Switching curves at 500ns triangular pulse width (b)  $V_{th}$  of N doped samples

## C. C doping

Two different doping concentrations of C, C1 and C2 are studied in this work with  $C1 < C2$ . Addition of C increases  $T_c$  with an increase of 150C for C2. Hence C is also effective in delaying crystallization and improving the thermal stability of GeSe.

## D. Electrical Characterisation

The initial leakage of the C doped samples is plotted in Fig. 5. The addition of C increases the  $I_{off}$  of the device in

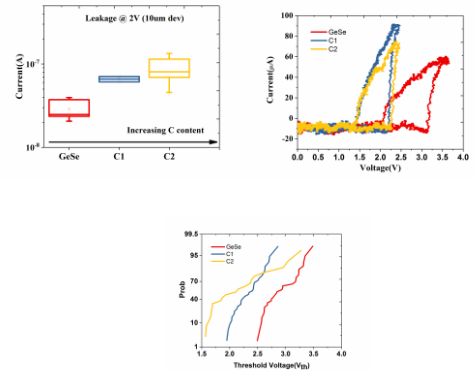


Fig. 5. (a) Leakage @ 2V (b) Switching Curves and (c)  $V_{th}$  across devices for different C contents

contrast to N. The increase in leakage with increasing C content is insignificant. The  $V_{th}$  also reduces with C doping.

The sub-threshold conduction in the samples, was measured at 25°C, 45°C, 65°C and 85°C as plotted in Fig. 6(a).  $J-E$  vs  $\sqrt{E}$  (Fig. 6(b)) in the voltage range 1.5-2.5 V shows a linear fit indicating that Poole-Frenkel conduction is dominant at this voltage range. The barrier depth is given by the slope of the plot  $\log(J/E)$  vs  $1/T$  while the intercept of the plot gives the trap density,  $N_T$ .

$$\log\left(\frac{J}{E}\right) = \log(q\mu N_T) + \frac{q}{kT} \left( \sqrt{\frac{qE}{\pi\epsilon_r\epsilon_0}} - \phi_T \right)$$

The extracted parameters are given in Table 1.

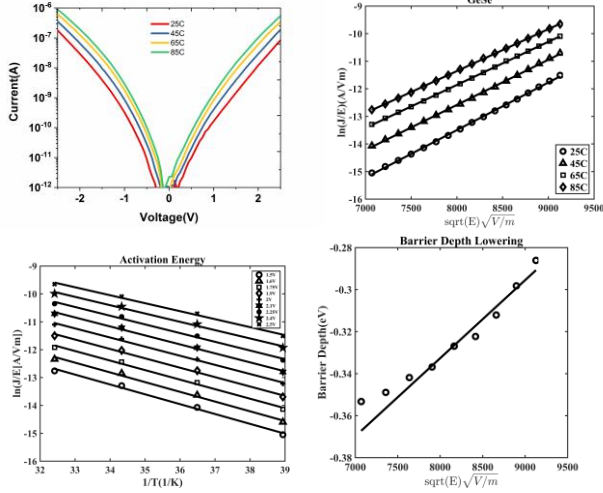


Fig. 6. (a) T dependence of sub-threshold conduction in pristine devices (b)  $\ln(J/E)$  vs  $\sqrt{E}$  shows a linear fit confirming Poole-Frenkel conduction (c) Activation Energy for conduction for different field across stacks (d) Barrier depth lowering vs  $\sqrt{E}$ . Poole Frenkel model predicts that the barrier depth is reduced as a function of the square root of the field with the intercept giving the trap depth

Table 1: Extracted values from Poole Frenkel model

| Sample | $\phi_T(\text{eV})$ | $q\mu N_T$ |
|--------|---------------------|------------|
| GeSe   | 0.54                | 0.2        |
| N1     | 0.55                | 0.019      |
| N2     | 0.6                 | 0.018      |
| C2     | 0.53                | 0.5        |

#### IV. DISCUSSION

To understand the effect of dopant on the thermal and electrical properties of GeSe, it is necessary to understand the bonding in the network and how it is influenced by the dopant. Amorphous GeSe has been shown to consist of corner sharing  $\text{Ge}(\text{Se}_{(1/2)})_4$  tetrahedra units which comply with the 8-N rule for both Ge and Se[10].

The homopolar and heteropolar bond energies have been calculated from the model outlined by Lankhorst[11] and listed in Table 2. Both C and N form stronger bonds with Ge than Se, Ge-C and Ge-N being the strongest in the system followed by Ge-Se, Se-Se and Ge-Ge. Hence Ge-N and Ge-C bonds are expected to be formed. For the composition used in this work, GeSe, majority of the Se co-ordination is expected to be satisfied by Ge, there would be minimal formation of Se-Se chalcogen chain of atoms.

The formation of Valence Alternation Pairs(VAPs) by the lone pair electrons in chains of chalcogen atoms has been identified as the traps resulting in OTS switching. However, in the equiatomic composition of GeSe, there are expected to

be very few homopolar Se-Se bonds as discussed. Hence, another type of defect, probably Ge dangling bonds could be responsible for the OTS switching

With the addition of N, the amorphous network which previously consisted of weakly 2-fold co-ordinated chalcogen atoms now has the increased 3-fold co-ordination of N increasing cross linking in the network[12]. N is incorporated into the matrix and forms bonds with Ge [13]. The high Ge-N bond energy partially arises from the huge electronegativity difference between Ge and N which also leads a partial ionic character to the bond. The presence of N also trades weaker homopolar Ge-Ge bonds for the stronger Ge-N bonds. The kinetic barriers to break these bonds would strengthen the network, hinder diffusion and combined with the increased entropy will postpone crystallization.

Table 2: Bond Enthalpies from Lankhorst Model

| Bond              | Ge-Se | Ge-Ge | Se-Se |      |
|-------------------|-------|-------|-------|------|
| Enthalpy(KJ/mole) | 234.5 | 186   | 227   |      |
| Bond              | Ge-N  | Se-N  | Ge-C  | Se-C |
| Enthalpy(KJ/mole) | 354.1 | 295.7 | 269.5 | 262  |

N passivates the Ge dangling bonds and pushes the edge states deeper into the band increasing the mobility gap of the material. This also leads to a reduction in the number of traps contributing to conduction. At the highest N content,  $\text{Ge}_3\text{N}_4$  structural units might be formed[12]. The values extracted in Table 1 also indicate that with the addition of N there is a small increase in the trap depth,  $\phi_T$  and a drop in the density of trap states,  $N_T$ . Both contribute to a decrease in leakage and increase in  $V_{th}$ . The necessity of a DC forming step for higher N contents, N3, is also a consequence of the increased rigidity of the network. However, after the forming step, N3 undergoes transformation and switches at lower  $V_{th}$ .

The addition of C also increases  $T_c$  like N. However, the magnitude of increase in  $T_c$  is lower for C because the Ge-C bond is weaker than the Ge-N bond. It is to be noted that C forms strong homopolar bonds has the tendency of forming  $sp^2$  hybridized graphitic C chains which could also delay crystallization due to the high energy required to break the C bonds. Evidence of C-C[14] bonds C-C bonds have been confirmed in Ge-C systems previously.

The values extracted in Table 1 also indicate that with the addition of C there is an increase in the density of trap states,  $N_T$ . This accounts for the increased leakage and decrease in  $V_{th}$  observed with addition of C. The nature and source of these trap states is not clear yet and is under investigation. It is probable there exist triple co-ordinated C- $\text{Ge}_3$  with C 2p states forming gap states or tail states. Another possibility is that C-C chains form states within the band gap and lead to increased  $N_T$ .

## V. CONCLUSIONS

We have demonstrated the effect of N and C on the switching behavior of GeSe. N decreases the off-state leakage which is crucial for application in cross-bar devices while increasing the  $V_{th}$  of the selector. In contrast, C increases the off-state leakage while reducing  $V_{th}$ . Hence switching parameters of GeSe selector can be tailored by adding C and N. Both dopants increase the  $T_c$  of the selector improving the thermal stability of the device.

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