The Role of Arsenic in the Operation of Electrical Threshold Switches

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Abstract

Arsenic is one of the most frequently used elements for doping conventional silicon-based semiconductors and particularly in emerging phase-change-memory (PCM) chips, yet the detailed functional mechanism as well as its experimental demonstration is still lacking in the latter in spite of its wide application. Here, we fabricate chalcogenide-based ovonic threshold switching (OTS) selectors, which are essential units for suppressing sneak currents in 3D PCM arrays, with various As concentrations. We discovered that incorporation of 20 at. % As brings a more than 100 °C increase in crystallization temperature, remarkably improving the switching repeatability and prolonging the device lifetime. These benefits arise from strengthened As-S bonds and sluggish atomic migration after As incorporation, as demonstrated by molecular-dynamics simulations. As a result, the addition of As reduces the leakage current by more than an order of magnitude and significantly suppresses the operational voltage drift, ultimately enabling a backend-of-the-line (BEOL)-compatible OTS selector with >12 MA/cm² on-current, >10⁴ on/off ratio, ~10 ns speed, and a lifetime approaching 10¹⁰ cycles after 450 °C annealing. These performance enhancements can be explained by an As-induced increase of the band gap and of trap states, as determined by experimental photothermal deflection spectroscopy. Mechanistically, this is due to abundant defect states associated with Ge-Ge chains introduced by As-Ge and As-S bonds. These findings allow the use of precise control of the As concentration in OTS materials for improved-performance high-density 3D PCM applications.

Full Text

Arsenic (As) is a hypertoxic element, yet it has long been extensively used in semiconductor manufacturing¹; e.g., the n-type semiconductors fabricated by ion implantation of As into silicon substrates are the building blocks of modern transistors². Meanwhile, As is also a principal component of gallium arsenide, the landmark material of second-generation semiconductors³. Moreover, As has never been absent in the discovery, development, and eventual commercialization of phase-change memory (PCM)⁴–⁶, an emerging memory technology to bridge the large performance gap between Flash and DRAM in modern computers⁷,⁸. Electrical-switching behavior⁹ was discovered as early as 1964 in arsenic-based chalcogenides, i.e., As-Te-I, by Northover and Pearson¹⁰, as well as in the As-Te-Se system by Dennard in 1966¹¹. Two years later, Ovshinsky reported the repeatable ovonic threshold switching (OTS) phenomenon in the amorphous state of As₃₀Te₄₈Si₁₂Ge₁₀¹², that is, the material becomes highly conductive abruptly once the voltage bias reaches a threshold value and it returns to the low-conductance state when the voltage is removed. Interestingly, if the concentration of As is reduced below 5 at. %, the large current at the threshold-switching point could heat up and crystallize the material, turning it into a permanent low-resistance state. One only needs to melt and quench the crystal to obtain the high-resistance amorphous state again; this is the working principle of PCM.

The OTS device, however, has no memory effect, and nowadays is usually used as a key selector component in 3D PCM integration. In traditional PCM chips, each memory unit is connected with a
transistor to control the opening and shutting of this unit, while in 3D PCM chips, a three-terminal transistor is too bulky to fit into the compact structure, and thus an OTS selector, due to its easy fabrication and high compatibility with PCM, becomes the best replacement. Yet, the performance of OTS selectors is not as satisfactory as traditional transistors, particularly in terms of their stability and on/off ratios; for example, most OTS materials can hardly withstand the backend-of-the-line (BEOL) processing temperature (400-450 °C)\(^8\). Thus, searching for OTS materials with high crystallization temperatures, and without compromising their other performance, is the key task to fully commercialize 3D PCM devices. To date, a lot of materials have been discovered which exhibit OTS behavior, including arsenic-free materials, such as Se-Te\(^{13}\), Zn-Se\(^{13}\), GeTe\(_6\)\(^{14}\), Ge-Se\(_{15}\)\(^{15}\), Si-Te\(_6\)\(^{16}\), GeS\(_{17}\) etc., but an As-based OTS material (As-Se-Ge-Si)\(^{18}\) is the only one that has been successfully used in actual 3D PCM chips (e.g., two decks, 128 Gb, by Intel in 2017).\(^{19}\) Thanks to the vertical stacking ability of OTS selectors on the PCM layer, unlike silicon-based selectors that only survive on silicon substrates, a four-deck stacked PCM with a 256 GB device was recently released\(^{18}\), comparable with advanced 3D Flash memory.

The function of As in traditional \(n\)-type semiconductors (e.g. crystalline Si) has been well studied, that is, providing extra free electrons for conduction via the substitution of Si (four outer electrons) by As atom dopants (five outer electrons), while the role that As plays in OTS materials is still the subject of heated debate. Cheng \textit{et al.} attributed the increase in the thermal stability of Ge-As-Se to the presence of As\(^{20}\). Garbin \textit{et al.} showed that the incorporation of As made a difference in inhibiting elemental segregation from elemental mappings, thus extending the device lifetime\(^{21}\). Noé \textit{et al.} believed that As would help prevent oxidation, thereby ameliorating the endurance or thermal stability of the device\(^{22}\). From the perspective of electron energy bands, Adriaenssens\(^{23}\) argued that the introduction of arsenic would bring new defect states into the band gap. Although reports of previous research have partly mentioned the function of arsenic, precisely how it works in OTS materials and the mechanism behind it is still lacking, which has remarkably slowed down the research and development of next-generation 3D PCM devices.

To reveal the role of As in the performance of OTS selectors, we employed GeS as a prototype material, for which there are already clear device-performance parameters and energy-band data\(^{17,24}\). We added \(x = 0, 20, 25\) and 43 at. % As into \((\text{GeS})_{1-x}\text{As}_x\) abbreviated as GeS, GeSAs\(_{20}\), GeSAs\(_{25}\) and GeSAs\(_{43}\), respectively. T-shaped devices for each composition were fabricated, and TEM photos of them are shown in \textbf{Fig. 1}a, in which we deposited 40 nm TiN as the top electrode, and the 5 nm thick carbon layer below serves as a buffer layer to prevent elemental diffusion. The bottom electrode is a cylindrical TiN electrode with a diameter of 200 nm. As displayed in energy-dispersive spectroscopy (EDS) mappings, Ti, C, Ge, As, and S elements are homogeneously distributed, without segregation or diffusion, even after multiple operations. \textbf{Fig. 1}b displays DC current-voltage (\(I-V\)) curves of Ge-S-As devices with different arsenic contents, in which a series-connected 3 kΩ resistor was embedded to avoid surge currents. Before regular threshold-switching operation, a 3.8 V fire voltage (\(V_{\text{fire}}\)) initializes the Ge-S-As devices, as described by the dotted lines. Then, the switching voltage, denoted the threshold voltage (\(V_{\text{th}}\)), sharply decreases to \(~1.5\) V for pure GeS devices, as described by the solid lines. Interestingly, GeSAs\(_{20}\) cells exhibited a \(V_{\text{th}}\) of
~3.0 V $V_{th}$, increased by 1.5 V, which further drop to ~2.4 V and to ~2 V for GeSAs$_{25}$ and GeSAs$_{43}$ cells, respectively. Obviously, the incorporation of 20 at. % As increases $V_{th}$ the most but then it decreases as one continues to add more As. Meanwhile, the leakage current at 1/2$V_{th}$, known as $I_{off}$, is the smallest in GeSAs$_{20}$ devices. $I_{off}$ is only ~11 nA in this device, about a factor of ten better than that in pure GeS devices (~160 nA). However, continuing to increase the As concentration fails to further reduce the leakage current, e.g., $I_{off}$ increases to 20 nA for GeSAs$_{43}$ devices.

Arsenic also plays an important role in the uniformity and endurance of selector devices, as shown in the current-voltage ($I$-$V$) curves of Ge-S-As devices, which have had applied 100 continuous triangular pulses (Fig. 1c), and the performance statistics of individual devices (Fig. S1). All the devices were successfully switched on at around 2 V and turned off at around 1.5 V (the holding voltage, $V_h$). $V_{th}$ of pure GeS devices fluctuates within a range of 0.7 V (1.6-2.3 V), while the range is just 0.4 V (1.6-2 V) for GeSAs$_{43}$ cells, indicating that the addition of As can indeed improve the switching repeatability, whereas it hardly influences $V_h$ for all devices. Nevertheless, it does affect the on-current ($I_{on}$), captured at the point of threshold switching. It is known that the RESET switching of PCMs needs sufficient energy to melt the memory materials, thus requiring a large $I_{on}$ to be provided by the selectors. The average value of $I_{on}$ goes up from 0.59 mA for GeS devices to 1.36 mA for GeSAs$_{20}$ devices and then slightly down to 1.11 mA for the devices with 43 at. % As concentration (Fig. S2). The value of $I_{on}$ for GeS in this work differs from the DC results of a previous study$^{17}$, due to the series resistance (1.1 k$\Omega$) employed and the different device structures (TiN/Al top electrode and W bottom electrode in previous work), but is consistent with the $I$-$V$ curves from subsequent work with the same structure$^{24}$. Since $I_{on}$ is almost size-independent, the current density of GeSAs devices sharply increases to >20 MA/cm$^2$ as the device size scales down to 60 nm, higher than Ge-Se/Te-based OTSs (Fig. S3). Although $V_{th}$ is closely determined by the As content, the time spent in switching on and off seems to be As-independent, as shown in Fig. 1d and Fig. S4. The switching-speed test circuit is shown in Fig. S4a. We carried out speed tests on 30 different devices for each material composition, and obtained the results in Fig. S4d statistically. The on-speeds of all compositions lie between 7 ns and 12 ns, and off-speeds are between 5 ns and 15 ns. A composition-independent switching speed is mainly due to the pure electronic nature of the OTS behavior, in which atomic migration is barely involved$^{25,26}$.

Other benefits of As incorporation can be found in the drift of $V_{th}$ of devices with time (Fig. 1e), that is, $V_{th}$ spontaneously increases over time after the first-fire (FF) process. The $V_{th}$ drift could induce write/read failure in the high-density memory array, as well as degradation of the device lifetime$^{27}$. For pure GeS, the $V_{th}$ value of 1.8 V drifts to 2.19 V within 1 hour, and then further rises to 2.3 V after 1 day. In the same way, the $V_{th}$ value of GeSAs$_{20}$ starts from 2.42 V, then increases to 2.66 V, and stops at 3 V. The rising trend of $V_{th}$ was inhibited at 25 at. % As content, where $V_{th}$ was around 2.5 V for all four tests, that is 2.46 V @ 0 s, 2.54 V @ 1 min, 2.5 V @ 1 hour and 2.58 V @ 1 day, i.e., only slightly increasing, while $V_{th}$ increases from 2.28 V to 2.67 V and further to 2.8 V @ 1 day in GeSAs$_{43}$. Obviously, an appropriate As
content is sufficient to restrain the $V_{th}$ drift. For device endurance, all GeS and GeSAs devices can be successfully turned on and off for at least $10^8$ cycles, as shown in Figs. S5-S6 and Fig.1f.

OTS selectors must withstand a temperature of 450 °C for 30 minutes in the BEOL process, in which the metal wire is bonded and the insulator layer is deposited$^{28,29}$. Since only chalcogenide glasses exhibit threshold-switching behavior, if they transform into a crystal under this condition, the crystallized selector then fails to exhibit any OTS function and can no longer be recovered. We therefore studied the crystallization temperature of Ge-S-As films utilizing X-ray diffraction (XRD) in Fig. S7. After annealing at different temperatures, a crystalline peak emerges in the GeS diffractogram after undergoing a heat treatment at 400 °C for 10 minutes, whereas three other films containing As remained amorphous through annealing at 450 °C for 30 minutes and even at 500 °C for 10 minutes. That is to say, incorporation of 20 at. % As brings about a more than 100 °C increase in the crystallization temperature, directly indicating that the incorporation of As contributes to a strong reinforcement of thermal stability. The material morphology can be further confirmed by transmission electron microscopy (TEM) and the corresponding fast Fourier transform images of a GeSAs$_{43}$ device annealed at 450 °C for 30 minutes are shown in Fig. 2a. In addition, there was no observed segregation and diffusion of elements after high-temperature treatment on the basis of EDS mappings. We then applied 100 triangular electrical pulses to the annealed cells, and the corresponding $I-V$ results are shown in Fig. 2b. After 450 °C annealing, the pure GeS device fails, but GeSAs devices can still work normally and so do devices with different sizes, as shown in Fig. 2b (200 nm) and Fig. S8 (60 nm). In Fig.2b, $V_h$ hardly changes, but $V_{th}$ of annealed GeSAs$_{20}$ fluctuates between 2.1 and 2.9 V, while the function of As on performance uniformity is still effective after annealing, and the $V_{th}$ fluctuation value of GeSAs$_{43}$ is only 0.24 V (1.73-1.97 V). Moreover, the DC test circuit is consistent with that before annealing, and $V_{fire}$ of annealed GeSAs devices slightly increase to 4.3-4.4 V. After the FF process as described by dotted lines, $V_{th}$ of GeSAs$_{20}$ lies in the range of 3.2-3.8 V i(dashed lines), while a sudden transition of the current occurs in GeSAs$_{25}$ devices at 2.7-3.3 V. Furthermore, $V_{th}$ decreases to 2.2-2.6 V with 43 at.% As incorporation. $V_{th}$ decreases with increasing As content, as shown in Fig. S9. At the same time, the changing trend of $I_{off}$ in GeSAs devices is also similar to that before annealing, i.e., $I_{off}$ goes up with the As concentration from 20 to 43 at.%, as illustrated in Fig. 2c. $I_{off}$ of GeSAs$_{20}$ is still the smallest of the three components, reaching 3 nA, then rises up to 38 nA when the content of As is 25 at.%. and continues to 58 nA in GeSAs$_{43}$ devices, basically in line with the statistical law of $I_{off}$ and $I_{on}$ of different devices with As content shown in Fig. S9. As displayed in the figure, the average $I_{on}$ drops from 0.71 mA to 0.7 mA and further to 0.41 mA with 43 at.% As incorporation.

Furthermore, we compare the performance variations of Ge-S-As devices with different thicknesses of the functional layer, before and after annealing, as shown in Fig. 2e (taking GeSAs$_{43}$ devices as an example). The changing tendencies are shown in detail in Figs. S10-S13. In Fig. 2e, the solid lines represent the deposited devices, and the dotted lines correspond to the annealed ones. Obviously, $V_h$ is thickness-independent, yet $V_{fire}$ and $V_{th}$ seem to increase nonlinearly as the thickness is doubled, no matter whether
the devices are annealed or not. Although $I_{on}$ increases with thickness, $I_{off}$ decreases owing to the smaller conductance caused by increasing thickness for every As content, resulting in a larger selectivity ($I_{on}/I_{off}$). A large selectivity value of $>10^5$ can be achieved in 20 nm-thick GeSAs$_{43}$ devices. However, the value of $I_{on}$ after annealing is generally lower than that before annealing, which is probably due to oxidation of the top TiN electrode. After annealing at 450 °C, GeSAs$_{20}$ devices operate normally for each pulse after $10^7$ cycles (Fig. S14 and Fig. 2f). In the case of GeSAs$_{25}$ devices, repeated operations can reach $10^9$ cycles (Fig. S14), whereas the GeSAs$_{43}$ cell can be switched on and off by each pulse for a remarkable $9 \times 10^9$ cycles (Fig. S15 and Fig. 2f). These results prove that As incorporation effectively prolongs the device lifetime of the OTS selectors. Compared with reported OTSs, annealed GeSAs devices present a better overall performance, as shown in Fig. S16.

The experimental results demonstrate that moderate As incorporation could significantly reduce the leakage current and suppress the $V_{th}$ drift, and, most importantly, it strongly enhances the thermal stability of OTS materials, improving the switching repeatability and prolonging the device lifetime, therefore enabling a processing-line-compatible OTS selector with superior properties for 3D memory applications.

Yet, what are the hidden mechanisms for these performance enhancements upon As incorporation? In order to reveal the physics of OTS behavior and the important role played by As, we performed ab-initio molecular-dynamics (AIMD) simulations based on density-functional theory (DFT). Models of amorphous GeS (a-GeS) and GeSAs (a-GeSAs), as presented in Fig. 3a, were generated by using a melt-quench-relaxation method. We first analyzed the number of valence electrons and the charge transfer between different elements in those amorphous Ge-S-As systems using the Bader Charge code$^{30,31,32}$, as shown in Fig. 3b. The average charge transfer for these elements was found to be -0.72 (Ge) and +0.72 (S) in a-GeS, and -0.66 (Ge), +0.71 (S) and -0.09 (As) in a-GeSAs$_{20}$. These values do not change a lot in a-GeSAs$_{25}$ (Ge: -0.63, S: +0.70, As: -0.10) and in a-GeSAs$_{43}$ (Ge: -0.53, S: +0.65, As: -0.07) compared with those for a-GeSAs$_{20}$. Interestingly, the electron transfer of S atoms in a-GeS shows a bimodal distribution, e.g., S ions receive electrons with the numbers of either $\sim$0.4 or $\sim$0.8. These two models correspond to two major configurations of chemical environment, e.g., homopolar bonds and heteropolar bonds, as shown in Fig. S17. More interestingly, As atoms appear to be almost electroneutral, showing both positive and negative small values of charge transfer, which is because As can bond with all Ge/As/S, as listed in Fig. S17. This can be rationalized by the fact that As belongs to group VA in the periodic table, possessing five outer valence electrons, and lies exactly between groups IVA (where Ge resides) with four valence electrons and VIA (where the chalcogens S/Se/Te reside) with six valence electrons. This is quite different from other dopants in a-GeSe such as C$^{33,34}$, Si$^{35}$, N$^{34,36}$, B$^{37}$, I$^{10}$ et al., acting as either cations or anions, which may be responsible for serious side-effects, like high $I_{off}$ (C doping)$^{34}$, higher $V_{fire}$, $V_{th}$ (N doping)$^{36}$ or poor thermal stability (B doping)$^{37}$. 
We evaluated the extent of atomic migration by calculating the mean-square displacement (MSD) for the models to identify the effect of As incorporation on the kinetic properties, which is usually linked with the stability of glass. The calculated MSD at 600 K in Fig.3c shows that the total atomic movements in a-GeSAs\textsubscript{20}, a-GeSAs\textsubscript{25} and a-GeSAs\textsubscript{43} are about 50% slower than in a-GeS, and the As atoms are the slowest in all a-GeSAs models. These results indicate that As could slow down the total atomic mobility due to the presence of relatively strong As-S bonds (as confirmed by ICOHP, a bond-strength indicator shown in Fig. S18), namely, the incorporation of As hinders the atomic migration. It is noteworthy that the MSD is positively correlated with the diffusion coefficient \((D)\) of amorphous solids or glasses. Smaller values of MSD correspond to smaller values of \(D\) and larger activation energies \((E_a)\) since \(D \sim \exp(-E_a/k_B T)\), thereby accounting for the >100 °C increase in the crystallization temperature after As incorporation, as illustrated in Fig. 2a and Fig. S7. Together, the high crystallization temperature (> 500 °C) and the low atomic mobility in amorphous GeSAs make it possible to achieve \(\sim 10^{10}\) cycling endurance, as shown in Fig. 2f.

Normally, due to the stronger electronegativity of sulfur atoms, it is more likely to form Ge-S heteropolar bonds than Ge-Ge homopolar bonds, which is demonstrated by different intensities of peaks in the PDF located at \(\sim 2.38\) Å and \(\sim 2.61\) Å in the a-GeS models, as shown in Fig. 3d. The dominance of Ge-S bonds in a-GeS can also be confirmed by the presence of the major peaks at 209 and 407 cm\(^{-1}\) in the Raman spectra (Fig. 3e), which are associated with Ge-S chains\(^{39}\). The vibrational modes of Ge-Ge bonds in the molecule \(\text{S}_3\text{Ge-GeS}_3\) and in edge-shared \(\text{GeS}_4\) tetrahedra are located at 291 and 366 cm\(^{-1}\), respectively.\(^{39}\) Nonetheless, owing to being surrounded by large numbers of Ge atoms (41.8% of the next-nearest neighbors, Fig. S19), Ge atoms could migrate and form Ge-Ge filaments\(^{40,41}\) triggered by high electric fields in the FF process\(^{17,42,43}\), leading to the delocalization of conduction state. Such paths dramatically increase the conductivity, resulting in a sharp increase in \(I_{\text{off}}\) by more than 140 times in the following switching operations (Fig. 1b and 2c). Yet, these Ge-Ge paths would be slowly dissolved due to their instability without external electric field after removal of the voltage\(^{17,21}\), \(V_{\text{th}}\) thereby spontaneously increases\(^{44}\), causing the so-called \(V_{\text{th}}\) drift, observed in Fig. 1e.

After the incorporation of As, Ge-As, As-S and As-As bonds emerge, and peaks in the PDF can be identified with such atom-atom correlations, located at 2.55 Å, 2.28 Å, and 2.51 Å, respectively (Fig. 3d)\(^{45,46}\). At the same time, the amplitudes of the Ge-Ge and Ge-S peaks in the PDF decrease as well, indicating that As atoms could bond with all Ge/S/As atoms. Similar conclusions can be drawn from experimental Raman results (Fig. 3e): intramolecular vibrational modes of \(\text{As}_4\text{S}_4\)\(^{47}\) and \(\text{AsS}_3\) rings in \(\text{As}_4\text{S}_3\) molecules\(^{48}\) appear at 218 and 270 cm\(^{-1}\), while peaks in the Raman spectra at 370 and 373 cm\(^{-1}\) can be attributed to edge-sharing \(\text{GeS}_4\) tetrahedra\(^{47}\), when there are still a great deal of Ge-S bonds at the point of As 20 at.%. With a further increase of As to 25 at.%, more As-S bonds arise and contribute to the Raman peak at 218 cm\(^{-1}\), while the 343 and 386 cm\(^{-1}\) Raman peaks have been ascribed to vibrations of \(\text{AsS}_3\) pyramidal units\(^{48–50}\). As a result, the proportion of Ge atoms which are next-nearest neighbors of other Ge atoms
significantly falls to 30.7% for GeSAs\textsubscript{20} and further to 20.3% for GeSAs\textsubscript{43} (Fig. S19), thereby decreasing the possibility of generating long Ge-Ge filaments through diffusion. These results, together with the slow atomic migration inhibited by As (Fig. 3c), account for the slower $V_{\text{th}}$ drift, as observed in Fig. 1e.

The electrical conduction in the sub-threshold region of OTSs is believed to be controlled by the Poole-Frenkel mechanism, that is, with charge carriers being thermally emitted from one trap to the conduction band and then captured by another trap\textsuperscript{25,26}. Thereby, the decrease at first and then an increase of $I_{\text{off}}$ with increasing As incorporation can be explained in terms of the size of the band gap and the density of trap states of amorphous Ge-S-As films, as can be characterized by photothermal deflection spectroscopy (PDS) experiments. As obtained from Tauc plots of such data (Fig. 4a), the band gap increases from 1.52 eV to 1.67 eV with an increase of the As content from 0 to 20 at. %, and then decreases to 1.62 eV, ending up at 1.5 eV for GeSAs\textsubscript{43}. This shows the same trend as for the variation of $I_{\text{off}}$ with different compositions (Fig. 1b and 1c), and which is also consistent with the compositional tendency of the conductivity activation energy (Fig. S20). The downward trend probably results from Mott delocalization caused by an increase in the concentration of As-As bonds\textsuperscript{51,52}, which have been evidenced in the theoretical PDFs from modelling studies (Fig. 3d) and further confirmed by experimental Raman results (Fig. 3e).

Since the excitation light absorbed by a sample in PDS measurements not only generates heat, but also produces a large number of electron-hole pairs, these non-equilibrium carriers can produce additional photo-absorption centres when they are trapped by defect states. Therefore, the trap-state positions shown in Fig. 4c can be obtained by Gaussian fitting of the absorption curves, from which we observed that trap states in a-GeS are located at 0.38 eV above the valence-band maximum. In samples with 20 and 25 at. % As contents, the trap states are located at 0.4 eV. However, two defect states appear in the GeSAs\textsubscript{43} sample; they occur at 0.36 eV and 0.42 eV respectively, presumably due to the formation of As clusters, as shown in Figs. 3d and 3e. It should be noted that more trap states in a-GeS were detected in a previous work\textsuperscript{17}, mainly due to the overlap of the absorption associated with the trap positions with the absorption of the deflection medium, as detailed in Fig. S21. The Urbach-tail energy ($E_u$) in Fig. 4b is obtained by a linear fitting of the absorption-coefficient data, $\alpha$, with photon energy, $h\nu$. Summing up all the information outlined above yields experimentally determined energy-band diagrams, as displayed in Fig. 4d. The trap densities can be calculated from the intensities of the absorption peaks, which are estimated to be $6.7 \times 10^{16}$ cm$^{-3}$eV$^{-1}$, $7.1 \times 10^{17}$ cm$^{-3}$eV$^{-1}$, and $4.5 \times 10^{17}$ cm$^{-3}$eV$^{-1}$ for trap D in pure GeS, GeSAs\textsubscript{20} and GeSAs\textsubscript{23}, respectively. The trap densities of D1 and D2 in GeSAs\textsubscript{43} are $1.4 \times 10^{17}$ cm$^{-3}$eV$^{-1}$ and $1.6 \times 10^{17}$ cm$^{-3}$eV$^{-1}$, respectively. The trap densities show a trend of firstly increasing and then decreasing, with increasing As concentration, while the turning point is situated at 20 at. % As, the same trend as observed for the band gap (Fig. 4b). According to the Poole-Frenkel mechanism\textsuperscript{25,26}, more traps imply that more carriers generated by an excitation signal would be captured. Moreover, a larger band gap also leads to a larger energy barrier ($E_C-E_D$) between the trap state and the conduction band\textsuperscript{25,26}. Both factors result in the increasing and decreasing trend for $I_{\text{off}}$, as shown in Figs. 1b and e.
The nature of these trap states can be identified from a further analysis of the DFT models, as presented in Fig. 5. The calculated electronic density of states (DOS) and corresponding normalized inverse participation ratio (IPR) of a-GeS, a-GeSAs$_{20}$, a-GeSAs$_{25}$ and a-GeSAs$_{43}$ are shown in Fig. 5a. In general, larger IPR values indicate more strongly localized electron states. We determine the mobility gap ($E_g$) of the amorphous models by calculating the energy separation between the mobility edges, defined by relatively lower IPR values of valence- and conduction-band states compared with the trap states in the band gap.$^{53}$ The values of $E_g$ for a-GeS, a-GeSAs$_{20}$, a-GeSAs$_{25}$ and a-GeSAs$_{43}$, calculated using hybrid potential functionals, are 1.55 eV, 1.70 eV, 1.59 eV and 1.48 eV, respectively, in line with the experimental results shown in Fig. 4d. All the DOSs for the models exhibit evident trap states, marked as A, B, C, D and E in the mobility gaps, which are located at 0.38 eV, 0.42 eV, 0.41 eV, 0.33 eV and 0.45 eV above the valence-band mobility edges, respectively, consistent with the experimental results shown in Fig. 4d. All the trap states show large IPR values, so that carriers trapped at these localized states will contribute little to the electrical conduction at room temperature because of their low mobility. However, the energy profile associated with the mobility gap could be tilted when a voltage bias is applied, leading to the tunneling of carriers from trap states to the valence bands. Besides in-gap states, the IPR values are usually large near the tail of the conduction band where the electronic states are strongly localized too (Anderson localization), as shown in Fig. 5a and Fig. S22$^{54,55}$. In order to find the origin of the trap states, we projected them onto real space by using the analytical tools for electron wave-functions in the VASPKit code$^{56}$, as shown in Figs. 5b-c. The trap states A, B, C and D in the a-GeSAs models are mainly found to be associated with structural motifs consisting of Ge-Ge bonds/chains$^{40,41,54,57}$, while the trap state E of a-GeSAs$_{43}$ is different from the others, and is dominantly associated with As-As bonds/chains. As the major sources of these traps, Ge-Ge bonds/chains therefore play a crucial role in OTS behavior, and As/S atoms also contribute to these in-gap states from the PDOS. Comparing with the trap A in a-GeS, As atoms participate in the contribution of trap states in the range of low As-doping contents, leading to an increased density of in-gap states from $6.7 \times 10^{16}$ cm$^{-3}$eV$^{-1}$ to $7.1 \times 10^{17}$ cm$^{-3}$eV$^{-1}$, as shown in Fig. 4. Interestingly, the contribution of Ge-Ge chains to the trap states appears to become saturated when the As content reaches 20 at. %, and thereafter the total density of in-gap states starts to decrease, even though the As-As bonds provide extra traps (Fig. 4). This exactly explains the non-monotonic effect of As incorporation on $I_{off}$ as the As content increases.

In conclusion, we have investigated OTS devices made of GeS, GeSAs$_{20}$, GeSAs$_{25}$, GeSAs$_{43}$ materials, and have studied the influence of As content on key OTS-performance parameters through electrical measurements. Annealing tests at 450 °C for 30 minutes, that mimic industrial BEOL processing, confirm that materials containing As show higher crystallization temperatures than pure GeS, and the devices can be still operated normally after such harsh heat treatment, indicating that the incorporation of As could remarkably enhance the thermal stability. A significantly slower drift of $V_{th}$ and a better device lifetime are also observed. This is because As atoms form strong bonds with both Ge and S, and also slow down the atomic migration, as confirmed by DFT-simulation calculations and experimental Raman spectra. In addition, the incorporation of As improves the OTS performance by modifying the band gap and defect
states. The trap states in the energy band gap, which are the key feature that leads to the OTS behavior, are enhanced due to the presence of Ge-As and As-S bonds. In particular, new trap states are found in GeSAs$_{43}$, mainly because the excess As atoms can form homopolar As-As bonds that generate extra free electrons. Interestingly, As atoms appear to be almost electroneutral, which is likely to be the reason that the serious side effects induced by other dopants can be avoided and therefore, this enables an excellent overall performance for practical selector switches in memory-array applications. Our work aims to understand the mechanism of As doping in the newly developed GeS selector, thereby paving the way for the optimization of 3D PCM products.

**Methods**

**Device preparation and measurement.** The 10 nm-GeSAs layers of all components were RF-sputtered, utilizing GeS, (GeS)$_{80}$As$_{20}$, (GeS)$_{75}$As$_{25}$ and (GeS)$_{57}$As$_{43}$ alloy targets using a power of 25 W. The 5nm C layers and top TiN electrodes were deposited by DC-sputtering using powers of 40 and 75 W, respectively. The device performances were characterized by a Keithley 4200A-SCS instrument.

**Structure and band-structure characterization.** All of the samples used for Raman scattering were 100 nm thick. A Renishaw inVia Qontor Raman microscope with a laser-excitation wavelength of 532 nm was utilized to obtain the Raman spectra, and the samples for PDS measurements were about 400 nm thick and deposited on fused quartz substrates. The Raman peaks may have some deviation from the literature results due to the different chemical environment, but the deviation is less than 3 cm$^{-1}$. Excitation light for the PDS measurements came from a 100W tungsten halogen lamp with a monochromator (CM110). The deflection signal was detected by a position-sensitive sensor (S3979, Hamamatsu Photonics). The samples were immersed in a liquid for the sake of signal enhancement. Tauc plots and the photothermal deflection spectra were obtained extending to a wavelength of 4000 nm. The Urbach-tail energy ($E_u$) in Fig. 4b was obtained by linear fitting of the absorption coefficient, $a$, to the photon energy, $h\nu$, using the equation $a = a_0 \exp(h\nu/E_u)$, where $E_0$ refers to the optical gap, and the resulting widths of the localized band tails were found to be 114, 115, 114 and 132 meV below the conduction-band minimum for As contents of 0, 20, 25 and 43 at%, respectively.

**Cs-corrected TEM characterization.** TEM samples were fabricated by focused ion beam (FIB) milling. The images for TEM and EDS analysis were taken using a JEOL JEM-ARM300F microscope.

**Atomic-model simulations.** The Vienna Ab initio Simulation Package (VASP) code was adopted to perform first-principles calculations$^{58,59}$. The projected augmented-wave (PAW) method was used and the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE)$^{60,61}$ or a hybrid (HSE06) functional$^{62-64}$ were employed to describe the exchange and correlation of the electrons. AIMD simulations based on DFT were performed to generate amorphous models by using a melt-quench-relaxation method. Each supercell contained 300 atoms, and the time step used was 3 fs and the cutoff energy of the plane-wave basis was set to 300 eV in the AIMD simulations. We initially built the Ge-S-As supercells by by randomly putting Ge, S and As atoms into boxes with the experimentally determined
density, and fully melting the cells at 3000 K. For 30 ps, the liquid phase was then cooled down to 300 K at a fast rate of 30 K per picosecond, and then equilibrated at 300 K for 30 ps. These models were further relaxed at 0 K to calculate the electronic structures. All atoms were relaxed with Γ-point sampling of the Brillouin zone until the atomic forces on each atom were smaller than 0.001 eV Å\(^{-1}\) and the energies were converged to \(1\times10^{-6}\) eV. The cutoff energy was set to 500 eV and the ionic and electronic convergence precisions were \(10^{-6}\) and \(10^{-7}\) eV, respectively. The cubic-box sizes of the relaxed amorphous models were 19.75 Å, 19.97 Å, 20.10 Å and 20.31 Å for a-GeS, a-GeS\(_{20}\), a-GeS\(_{25}\) and a-GeS\(_{43}\), respectively.

**Declarations**

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Competing Interests**

The authors declare that they have no competing interests.

**References**


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**Figures**

**Figure 1**

**Structure and electrical characteristics of Ge-S-As devices.**

*a.* Cross-sectional transmission electron microscope (TEM) image of a GeSAs$_{25}$ device, subjected to several triangular pulses, and energy-dispersive spectroscopy (EDS) mappings of Ti, C, Ge, S and As.  

*b.* DC *I-V* curves of devices with various As contents. The dotted lines refer to the first-fire (FF) process, and the solid lines refer to $I_{off}$. The inset shows a schematic of the DC testing circuit.  

*c.* *I-V* curves of Ge-S-As devices subjected to 100 consecutive triangular pulses.  

d. Input voltage and output current are integrated in the left panel, and the separate
pictures are shown in the right panel. The operating speed of each component reaches the nanosecond level. e. Drift of $V_{th}$ with time. Particular As contents can effectively diminish the spontaneous drift of $V_{th}$. f. Endurance performance in the as-deposited state for all compositions. The $I_{on}$ is very stable, whereas the $I_{off}$ fluctuates with an apparent upward drift, which may be due to the formation of Ge-Ge conductive filaments.

Figure 2

**Microstructure and electrical performance of Ge-S-As devices with different thicknesses after 450 °C annealing.** a. TEM picture of a GeSAs$_{43}$ device after 450°C annealing. FFT images, labelled I, II and III, represent left, middle and right areas marked on the Ge-S-As layer, revealing an amorphous nature. EDS mappings after heat treatment reveal no difference with those for the as-deposited state. b. $I$-$V$ curves of 450 °C annealed devices subject to 100 consecutive triangular pulses. The GeS device fails, whereas the GeSAs ones continue to work well. c. DC $I$-$V$ curves of 450 °C annealed devices. d. Different responses of GeSAs$_{43}$ devices with different thicknesses of the OTS layer, before and after annealing. e. Electrical performance for GeSAs$_{43}$ devices with different thicknesses, before and after heat treatment. $V_{fire}$, $V_{th}$, $V_{h}$ and $I_{on}$ of both states increase while $I_{off}$ monotonically decreases. f. Annealed devices demonstrate more superior endurance properties.
Figure 3

Structural models, electronic charge transfer, atomic-mobility properties, and Raman-scattering results for amorphous GeS, GeSAs_{20}, GeSAs_{25}, and GeSAs_{43}. a. Snapshots of the model atomic structures after full relaxation. b. The calculated charge transfer for the three elements, in which the +/- signs represent gain/loss of electrons, respectively. c. Mean-square displacement (MSD) of atoms in these models at 600 K for 6 ps. d. Partial PDFs, g(r), simulated at 300K. e. Experimental Raman spectra with Gaussian fitting of peaks.
Figure 4

Trap states and bandgaps of amorphous Ge-S-As films. 

a. Tauc plots of the optical-absorption coefficient, \((ahv)^{1/2}\) versus \(hv\), provide estimates for the bandgap. 

b. Semi-logarithmic plots of \(a\) versus \(hν\) characterize the Urbach tail, where \(a_0\) is independent of either thermal or structural disorder, while \(E_u\) is the Urbach-edge parameter.

c. In-gap trap states detected by PDS spectra; an extra one appears for 43 at.% As.

d. Experimentally determined energy band diagrams of amorphous Ge-S-As.
First-principles simulations of the trap states for a-GeSAs systems. a. Density of states (DOS) and normalized inverse participation ratio (IPR) of a-GeS, a-GeSAs$_{20}$, a-GeSAs$_{25}$ and a-GeSAs$_{43}$, which show the mobility gap and in-gap states. b. The trap states projected onto real space, in which the yellow areas, plotted with isovales of $1.3 \times 10^{-10}$ e$\times$bohr$^3$ encapsulate all the in-gap states and depict the molecular-orbital-charge density of the respective trap state. c. The atomic clusters associated with the trap states.

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