

Hybridization–Ionicity Mapping for Descriptor-Guided Design of Amorphous Ge–Sb–Se Selector-Only Memory

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Abstract

Quantitative relationships among composition, bonding, and functional properties are essential for the rational design of amorphous chalcogenides. Here, we examine whether hybridization and ionicity, established composition-derived bonding descriptors, can guide selector-only memory (SOM) design. Mapping of reported SOM compositions reveals systematic correlations with the read-window margin (RWM) and identifies a favorable region for threshold-state differentiation. Guided by these trends, amorphous Ge–Sb–Se compositions with increasing Sb content were fabricated and evaluated, and all exhibited programmable SOM behavior with nonmonotonic electrical and reliability trends. Up to an intermediate Sb content, higher ionicity within an appropriate hybridization range increased polar heteropolar bonding, enlarged trap-energy separation and RWM, and improved threshold-voltage stability and endurance. Further Sb incorporation increased hybridization beyond the favorable range and promoted Sb–Sb-rich homopolar bonding, reducing trap-state differentiation and memory performance. X-ray photoelectron and Raman spectroscopy confirmed the corresponding bonding evolution, while temperature-dependent transport analyses linked these changes to trap energetics. These results establish a composition–bonding–trap–property relationship and show that hybridization–ionicity mapping can narrow candidate compositions before extensive fabrication and characterization.

1 Introduction

The continued expansion of artificial intelligence (AI), high-performance computing, and data-intensive applications is placing increasingly demanding requirements on memory systems in terms of access speed, storage capacity, energy efficiency, and scalability. Current memory hierarchies largely rely on dynamic random-access memory (DRAM) for rapid data access and NAND flash memory for high-density nonvolatile storage. Despite their respective advantages, the substantial difference in performance and functionality between these memory technologies has motivated the development of storage-class memory (SCM), which is intended to provide an intermediate memory hierarchy combining fast access with nonvolatile data retention [1–4]. This need is becoming increasingly relevant with the development of Compute Express Link (CXL)-based computing architectures, where memory expansion and sharing across heterogeneous computing resources place additional demands on both memory capacity and data-access efficiency [5–7]. In this context, several emerging nonvolatile memory technologies have been investigated as potential SCM candidates, among which selector-only memory (SOM) has recently received growing attention [8, 9]. SOM utilizes the rapid threshold switching (TS) response of amorphous chalcogenides while retaining electrically programmed information through distinct threshold voltage (V_{th}) states. Accordingly, SOM has shown the potential to combine some of the desirable characteristics associated with conventional memory technologies, particularly fast electrical operation and nonvolatile information storage, while retaining a simple two-terminal device configuration. Although further improvements in device performance and reliability are still required for practical implementation, these characteristics make SOM a promising platform for exploring high-density nonvolatile memory architectures.

An additional feature of SOM is its ability to integrate the electrical functions required for both cell selection and information storage within a single active element. This characteristic is particularly relevant to crossbar arrays, in which cells are arranged at the intersections of word and bit lines to enable high-density integration and vertical stacking. In conventional cross-point architectures, unintended conduction through unselected cells can form sneak-current paths and interfere with reliable cell access [10–14]. A one-selector–one-memory (1S1M) configuration is therefore commonly employed, where a highly nonlinear selector is connected in series with a separate memory element to provide the required cell selectivity. While this configuration effectively suppresses unwanted current paths, integrating two functional elements within each cell introduces additional considerations in terms of stack design, material compatibility, fabrication complexity, and cell footprint. SOM provides an alternative approach in which nonlinear TS behavior and memory functionality originate from a single amorphous chalcogenide layer, thereby potentially simplifying the device stack and fabrication process while reducing the cell footprint [8, 15, 16]. The memory state is represented by two electrically programmable V_{th} states rather than conventional high- and low-resistance states. In this study, the lower threshold state, V_{th1} , is established by a positive write pulse, whereas the higher threshold state, V_{th2} , is established by a negative write pulse. A read voltage (V_{read}) positioned between the two thresholds induces TS and a high-current response in the V_{th1} state, while the V_{th2} state remains in the low-current off-state. The separation between these thresholds, defined as the read window margin (RWM, $\Delta V_{th} = V_{th2} - V_{th1}$), represents the voltage margin available for reliable state discrimination. Through this threshold-state-based operation, a single SOM element can provide both the nonlinear selectivity required to suppress sneak currents and the nonvolatile functionality required for information storage.

The operation of SOM is inherently associated with the electronic and structural characteristics of the amorphous chalcogenide network, which are sensitively influenced by elemental composition and local chemical bonding. Previous studies have suggested that the relative contributions of heteropolar and homopolar bonds can influence the localized electronic states underlying TS and the structural stability of the amorphous network, thereby affecting the RWM and reliability of SOM devices [17–20]. Although the effects of individual bonds depend on their chemical identity and local environment, these findings indicate that an appropriate heteropolar–homopolar bonding balance is an important consideration for SOM material design. However, SOM compositions have largely been investigated through composition-specific experimental approaches, in which candidate materials are fabricated and their SOM characteristics are subsequently evaluated. Consequently, favorable compositional information has been accumulated primarily on a material-by-material basis, while quantitative guidance for systematically directing composition selection at the initial stage of SOM development remains limited. Such guidance could reduce reliance on iterative composition screening and provide a more rational basis for exploring new SOM materials.

To address this limitation, we considered ionicity and hybridization as complementary composition-derived descriptors of the overall bonding tendencies of chalcogenide materials. Ionicity is associated

with charge polarization and is therefore relevant to polar heteropolar bonding environments, whereas hybridization represents the tendency toward s – p orbital mixing and saturated covalent coordination and provides complementary information related to the evolution of the heteropolar–homopolar bonding balance. These descriptors have previously been employed as bond-orbital coordinates for mapping characteristic material regions of phase-change memory (PCM) and ovonic threshold switching (OTS) chalcogenides [21–25]. Here, we extend this framework to previously reported SOM compositions not simply to identify their compositional region, but to examine how the emergence and characteristics of SOM correlate with ionicity, hybridization, and the associated bonding tendencies. By placing previously reported SOM compositions within a common quantitative materials space, the mapping enables compositional trends associated with favorable SOM characteristics to be identified and subsequently applied to material design. To evaluate whether these mapping-derived trends can guide prospective composition design, four Ge–Sb–Se compositions with systematically increasing Sb concentrations were selected along a compositional direction expected to favor SOM operation and performance. The resulting materials were fabricated into SOM devices and evaluated through electrical and reliability measurements together with analyses of their bonding evolution. By correlating the hybridization–ionicity descriptors with experimentally observed bonding configurations and device characteristics, this work demonstrates the applicability of the mapping as a systematic, quantitative approach for guiding composition selection at the initial stage of SOM development, complementing conventional composition-by-composition experimental screening.

2 Experimental methods

2.1 Device fabrication

Four SOM devices with different chalcogenide compositions were prepared on Si/SiO₂ substrates. Tungsten (W) with a thickness of 30 nm was first deposited as the bottom electrode (BE) by physical vapor deposition (PVD). The W BE pattern was defined by photolithography and subsequently transferred by inductively coupled plasma reactive-ion etching (ICP-RIE). The etching was carried out at a chamber pressure of 5 mTorr using Ar and Cl₂ flow rates of 4 and 30 standard cubic centimeters per minute (sccm), respectively, resulting in an etch rate of approximately 1 nm/min. The amorphous chalcogenide active layers were subsequently formed on the patterned BE by radio frequency (RF) co-sputtering. The Sb-free Ge–Se (GS) layer was prepared by simultaneously sputtering GeSe and Ge targets, each operated at RF power of 30 W. For the Sb-containing Ge–Sb–Se (GSS) layers, a GeSbSe composite target was co-sputtered with an elemental Sb target. The RF power of the GeSbSe target was maintained at 35 W, whereas the Sb-target power was systematically adjusted to 5, 10, and 15 W to modulate the Sb concentration. During deposition of the chalcogenide layers, the chamber was maintained at a base pressure of 7×10^{-7} Torr and a working pressure of 3.3 mTorr with an Ar flow rate of 20 sccm. Following formation of the active layer, photolithography was employed to define the top electrode (TE) region. Before W TE deposition, a 5-nm-thick carbon (C) interlayer was introduced between the chalcogenide layer and the TE to mitigate interfacial diffusion. The C layer was deposited by direct current (DC)

magnetron sputtering at 140 W using an Ar flow rate of 50 sccm, with base and working pressures of 8×10^{-7} and 2.3 mTorr, respectively. A 50-nm-thick W TE was then deposited by DC magnetron sputtering at 140 W under a base pressure of 9×10^{-7} Torr and a working pressure of 2.1 mTorr, while maintaining an Ar flow rate of 15 sccm. Device fabrication was finalized by a lift-off process. Accordingly, the completed device structures consisted of W/C/active layer/W/SiO₂/Si.

Additionally, as shown in Fig. S1, five GeSbSeSn device compositions were fabricated to further explore the Sb-rich region of the hybridization–ionicity map. The GeSbSeSn active layers were deposited by RF co-sputtering using GeSbSe, Sb, and Sn targets. The RF power applied to the GeSbSe target was fixed at 35 W, while those applied to the Sb and Sn targets were varied in different combinations to tune the resulting compositions. All other fabrication parameters and process conditions were maintained identical to those used for the GS and GSS1–3 devices.

2.2 Material analysis

The structural and compositional characteristics of the fabricated SOM devices were examined using complementary material characterization techniques. Cross-sectional microstructures of the devices were characterized by high-resolution transmission electron microscopy (HR-TEM; JEM-ARM200F NEOARM, JEOL), with TEM specimens prepared using focused ion beam (FIB; Crossbeam 350, ZEISS) milling. Energy-dispersive X-ray spectroscopy (EDS) mapping was performed in conjunction with HR-TEM to visualize the spatial distributions of Ge, Sb, and Se across the GS and GSS1–3 device structures. The atomic compositions of the chalcogenide layers were quantitatively determined by Rutherford backscattering spectroscopy (RBS). The chemical bonding configurations of the chalcogenide layers were investigated by X-ray photoelectron spectroscopy (XPS; Thermo K-Alpha) and Raman spectroscopy (XPER RF, Nanobase). These measurements were used to evaluate the evolution of the local bonding environment, including changes in homopolar and heteropolar bonding configurations, as a function of Sb concentration. Ultraviolet photoelectron spectroscopy (UPS; NEXSA G2, Thermo Scientific) was further employed to determine the work function and valence-band-edge position of each chalcogenide composition. The optical properties were characterized by ultraviolet–visible–near-infrared (UV–vis–NIR) spectroscopy (V-650, JASCO), from which the optical bandgap (E_g) was extracted using the measured transmittance and reflectance spectra. The combined UPS and UV–vis–NIR results were subsequently used to establish the energy-band structures of the chalcogenide layers. For the five additional GeSbSeSn devices presented in Fig. S1, the elemental compositions were independently determined by Auger electron spectroscopy (AES; PHI-710, ULVAC-PHI).

2.3 Electrical characterization

The electrical characteristics of SOM devices were evaluated under both direct current (DC) and pulse operation. DC current–voltage (I – V) characteristics were measured in voltage-sweep mode using an HP4155B semiconductor parameter analyzer to assess the TS behavior of each device. Pulse-based measurements were performed using an HP4155B semiconductor parameter analyzer in combination with an arbitrary function generator (AFG; Agilent 81150A), an oscilloscope (OSC; MSOX3024T,

Tektronix), and an RF electrical circuit switch box. The pulse measurement configuration is illustrated in Fig. S2. Unless otherwise specified, bipolar write pulses with amplitudes of + 5 and – 5 V, a pulse width of 50 ns, and rise/fall times of 6/50 ns were employed. V_{th} drift was characterized by controlling the delay between the write and subsequent read operations over a time range from 10^{-6} to 10^2 s. Endurance characteristics were assessed by repeatedly applying alternating + 5 and – 5 V write pulses, while read pulses were periodically introduced to monitor the evolution of V_{th} throughout cycling. Temperature-dependent DC I – V measurements were conducted at 25, 45, 65, and 85°C using a hot stage equipped with a precision temperature controller to investigate the charge-transport characteristics of the devices. The measured data were analyzed within the Poole–Frenkel (PF) conduction framework by plotting $\ln(J/E)$ as a function of $E^{1/2}$, where J and E denote the current density and applied electric field, respectively. The linearity of the resulting plots was examined at each temperature to evaluate the applicability of PF-type transport. The trap depth of the active layer was further extracted from the temperature dependence of the PF fitting intercept using its relationship with $1/k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature. In addition, the activation energy (E_a) associated with thermally activated carrier transport was independently evaluated for each device using the Arrhenius relation. For this analysis, $\ln(J/E)$ was plotted against $1/k_B T$ at a fixed electric field, and E_a was determined from the slope of the corresponding linear fit.

3 Results and discussion

3.1 Hybridization–Ionicity Mapping for SOM Material Design

The hybridization–ionicity mapping employed in this study is based on two quantitative bond-orbital descriptors that represent complementary aspects of composition-dependent bonding tendencies. These descriptors translate the elemental composition of a material into quantitative coordinates, enabling chemically diverse chalcogenide compositions to be compared within a common materials space. In their conventional chemical meanings, ionicity generally refers to the degree of charge separation between bonded atoms arising from differences in their electronic characteristics, whereas hybridization describes the mixing of atomic orbitals, particularly s or p states, involved in the formation of directional covalent bonds. The quantitative description of such bonding characteristics using atomic electronic parameters was established through earlier bond-orbital and quantum-defect approaches, including the framework developed by Phillips and related studies. In this framework, characteristic orbital parameters of the constituent elements were related to their electronic dissimilarity and chemical bonding tendencies, providing a basis for describing structural and bonding characteristics from elemental properties rather than solely from experimentally determined bond configurations [21–23]. Building on this theoretical foundation, Lencer et al. introduced a bond-orbital mapping framework for PCMs in which ionicity and hybridization were formulated as quantitative, composition-derived coordinates based on the orbital radii of the constituent elements [24]. Using these coordinates, PCM

compositions were shown to occupy a characteristic region of the hybridization–ionicity map, and the framework was subsequently extended to OTS materials [25]. Accordingly, throughout this work, the terms “ionicity” and “hybridization” specifically refer to these quantitative bond-orbital coordinates, which are used as compositional descriptors representing the relative tendency or likelihood of a material toward ionic and hybridized bonding characteristics, respectively, rather than as direct measures of the ionic character of an individual bond or the literal degree of orbital hybridization at a specific atomic site. The ionicity coordinate, r'_σ , is the absolute difference between the p -orbital radii of the constituent species. For a binary compound AB, A and B denote cation-like and anion-like species, respectively, as in Eq. (1). For multicomponent materials, the individual radii are replaced by separately normalized composition-weighted averages for the two groups, as in Eq. (2):

$$r'_\sigma = |r_p^A - r_p^B|$$

1

$$r'_\sigma = \left| \left(\frac{\sum_i n_i r_{p,i}}{\sum_i n_i} \right) - \left(\frac{\sum_j n_j r_{p,j}}{\sum_j n_j} \right) \right|$$

2

where r_p is the p -orbital radius, n is the atomic fraction or stoichiometric coefficient, and i and j denote the anion-like and cation-like species, respectively. The difference in p -orbital radii reflects the electronic dissimilarity of the p states participating in bonding and therefore provides an orbital-based descriptor of the tendency toward charge localization and ionic character. A larger r'_σ represents a greater compositional tendency toward asymmetric charge distribution between chemically distinct species. Although this concept is related to electronegativity difference and bond polarization, r'_σ is not itself an electronegativity difference because it is quantitatively defined from orbital radii. Thus, the “ionicity” discussed throughout this study refers specifically to this orbital-radius-based tendency toward charge-polarized bonding rather than to the experimentally measured fraction of ionic or heteropolar bonds.

The hybridization coordinate, r_π^{-1} , is defined using the difference between the p - and s -orbital radii of the constituent species. For a binary compound AB as shown in Eq. (3), the contributions from the two constituent species are summed, whereas for a multicomponent material, the corresponding $r_p - r_s$ values are composition-weighted separately for the cation-like and anion-like species shown in Eq. (4):

$$r_\pi^{-1} = [(r_p^A - r_s^A) + (r_p^B - r_s^B)]^{-1}$$

3

$$r_\pi^{-1} = \left[\left(\frac{\sum_i n_i (r_{p,i} - r_{s,i})}{\sum_i n_i} \right) + \left(\frac{\sum_j n_j (r_{p,j} - r_{s,j})}{\sum_j n_j} \right) \right]^{-1}$$

where r_s and r_p denote the s - and p -orbital radii, respectively. The differences between the s - and p -orbital radii are related to the energetic separation of the corresponding electronic states and therefore provide an orbital-based measure of the tendency toward s - p hybridization. Within the original bond-orbital framework, increasing r_{π}^{-1} corresponds to a greater tendency toward orbital hybridization and the formation of more saturated covalent bonds, accompanied by a departure from pure p -bonding. Thus, the “hybridization” discussed throughout this study represents a composition-derived tendency toward s - p orbital mixing and saturated covalent bonding rather than the literal degree of orbital hybridization at individual atomic sites or a direct measure of the fraction of covalent bonds.

To examine whether these quantitative bond-orbital descriptors can also provide a meaningful compositional perspective for SOM materials, we extended the hybridization–ionicity framework to previously reported SOM compositions. As shown in Fig. 1a, these SOM compositions were plotted together with representative PCM and OTS materials to compare their relative distributions within the same bond-orbital space. The PCM dataset was adopted from the materials map originally established by Lencer et al., which included group-V elements, binary compounds, and ternary, $A_2^{IV}B_2^{VC_5^{VI}}$, $A^{IV}B_2^{VC_4^{VI}}$, and $A^{IV}B_4^{VC_7^{VI}}$ alloys [24]. The OTS dataset was adopted from the subsequent work of Velea et al., in which bond-orbital coordinates were calculated for Te-based OTS compositions reported in the literature, encompassing Ge–Te, Si–Te, Ge–Sb–Te, Ge–In–Te, Si–Sb–Te, Si–Ge–Te, Si–As–Te, Sb–As–Te, and Ge–As–Te-related systems [25]. For the SOM dataset, previously reported SOM materials were surveyed, and their ionicity and hybridization coordinates were calculated from the constituent elements and compositions reported in the corresponding studies, as summarized in Table S1 [17–19, 26–34]. The resulting map shows that the PCM compositions are primarily distributed in Zone (1), indicated by the gray region in Fig. 1a, corresponding approximately to ionicity values of 0–0.1 and hybridization values of 2.0–2.3. This distribution is consistent with the original PCM materials map, where relatively low ionicity and hybridization were associated with the p -bonding and resonance-bonding characteristics of crystalline PCMs [24, 35]. Increasing ionicity promotes charge localization, whereas increasing hybridization favors more saturated covalent bonding, both of which reduce the conditions favorable for resonance bonding. In contrast, the Te-based OTS compositions reported by Velea et al. occupy Zone (2), characterized by lower ionicity of approximately 0–0.05 and higher hybridization of approximately 2.1–2.45 [25]. Compared with PCMs, this distribution represents a bonding regime with reduced charge-localization tendency and stronger directional covalent character. This distribution is consistent with a more directional covalent network that retains amorphous stability while supporting field-responsive electronic transport [25, 36–39]. These datasets provide reference regions for SOM analysis rather than strict boundaries between material functionalities.

Interestingly, the SOM compositions also exhibit discernible compositional distributions within the same map, as indicated by Zones (3)–(5) in Fig. 1a. Although the boundaries between these regions should not be regarded as strict material-class limits, the mapped compositions show a tendency to group

according to their constituent elements. Zone (3) contains predominantly Se-based compositions, Zone (4) mainly Te-containing materials, and Zone (5) Ge–Se binary and several Sb-containing systems. The overlap and spread of these regions emphasize that the map is a compositional representation, not a categorical classifier. Nevertheless, SOM compositions tend to extend toward higher ionicity than the surveyed PCM and OTS materials. This distinction becomes particularly apparent when chemically related OTS and SOM systems are compared. For example, the Te-based OTS compositions in Zone (2) are mainly distributed at ionicity values of approximately 0–0.05, whereas the Te-based SOM compositions in Zone (4) extend to approximately 0.08–0.12. Although this difference alone is insufficient to establish a causal relationship between ionicity and SOM operation, it raises an important question regarding the bonding characteristics required to introduce memory functionality into a TS material.

OTS and SOM both exhibit TS, and reported devices can have broadly comparable orders of magnitude in leakage, V_{th} drift, and endurance, depending on composition, geometry, and measurement conditions [10, 39–41]. The distinguishing requirement for SOM is a threshold response that retains the influence of the preceding electrical stimulus, yielding reproducibly separable programmed states [32, 42]. Accordingly, the RWM is relevant not only as the operating voltage margin for reliable state discrimination, but also as a quantitative measure of the extent to which the threshold response is differentiated into distinct programmable states. This interpretation is particularly useful for the present materials mapping because it provides a device-level metric for evaluating compositional evolution from conventional OTS-like TS toward the programmable threshold-state behavior required for SOM memory operation. From a materials-engineering perspective, a compositional direction that enlarges the RWM can therefore be regarded as favorable for strengthening the tendency toward SOM characteristics. Previous SOM studies have shown that polar heteropolar configurations, such as Ge–Se, can modify the local electronic environment and trap-related states involved in TS, thereby affecting the RWM [17, 36, 43]. This provides physical motivation for comparing RWM with ionicity, while recognizing that the descriptor does not identify the responsible microscopic defects.

Figure 1b shows the reported RWM values as a function of ionicity over approximately 0.05–0.2, the range occupied by most surveyed SOM compositions. The data show a positive overall trend, with higher-ionicity compositions generally exhibiting larger RWM. This correlation indicates that compositions with higher ionicity within the predominantly polar covalent regime tend to exhibit a wider RWM. When considered together with previous reports associating polar heteropolar bonding environments with the localized electronic states involved in SOM operation, the observed ionicity–RWM relationship supports the relevance of ionicity as a quantitative compositional descriptor for SOM materials. Accordingly, increasing ionicity within an appropriate covalent range may provide a meaningful materials-engineering direction for promoting threshold-state differentiation and improving the RWM.

The significance of this bonding tendency may also extend to SOM reliability, particularly V_{th} drift and endurance. V_{th} drift refers to the time-dependent shift of a programmed threshold state and is generally

associated with structural relaxation of the metastable amorphous network, which modifies the local bonding environment and redistributes localized trap states over time [44]. Therefore, a more structurally stable bonding network that suppresses such time-dependent atomic rearrangement and trap-state evolution is expected to reduce the magnitude of V_{th} drift. Endurance represents the ability to maintain distinguishable and reproducible threshold states during repeated write/read cycling, and its degradation can arise from cumulative structural and bonding rearrangements induced by repeated electrical excitation. Previous SOM studies have reported improved reliability when unfavorable homopolar configurations are suppressed, and the amorphous network is reinforced by more stable bonding configurations [19, 42, 45, 46]. Accordingly, if an increase in ionicity within an appropriate covalent range is accompanied by the formation of a more favorable polar heteropolar bonding environment, it may also contribute to improved V_{th} stability and endurance. Because ionicity describes an overall compositional bonding tendency rather than individual bond configurations, this relationship should be experimentally examined through direct comparison with bonding and reliability measurements.

Hybridization provides a complementary perspective. In contrast to the relatively clear displacement of SOM compositions toward higher ionicity, their hybridization values span a broader range depending on elemental constituents and stoichiometry, with most of the surveyed SOM materials located between approximately 2.0 and 2.5, as shown in Fig. 1a. A more distinct trend emerges when hybridization is directly compared with the reported RWM in Fig. 1c: RWM generally increases as hybridization approaches approximately 2.22–2.3, whereas compositions beyond this range tend to exhibit reduced RWM. This nonmonotonic relationship suggests that favorable SOM characteristics are associated with an appropriate hybridization range rather than a monotonic increase in this descriptor. From a bonding perspective, increasing hybridization reflects a greater tendency toward s – p orbital mixing and saturated covalent bonding. However, within a given compositional system, further progression toward a high-hybridization regime can alter the available local coordination and, depending on elemental stoichiometry, increase homopolar configurations when favorable heteropolar coordination becomes limited. Such an increase in unfavorable homopolar bonding may not only reduce RWM but also destabilize the bonding network and associated trap landscape, potentially leading to increased V_{th} drift and degraded endurance. Hybridization therefore does not directly represent the homopolar-bond fraction; rather, the trend observed in Fig. 1c suggests that it can provide a quantitative indication of a compositional range within which a favorable heteropolar–homopolar bonding balance is maintained. Accordingly, hybridization is more appropriately considered as a descriptor for identifying a favorable compositional window for SOM operation rather than one that should simply be maximized or minimized.

Taken together, Fig. 1b, c motivate considering the two descriptors jointly. A composition may move toward higher ionicity while also leaving the hybridization range associated with larger RWM. Such a trajectory provides a useful test of whether a favorable bonding balance, rather than maximizing either coordinate independently, is associated with SOM properties. Because both descriptors are calculated

from composition, their separate effects cannot be established simply by changing one constituent along a single compositional trajectory.

For experimental evaluation, we focused on Zone (5), which contains Ge–Se- and Sb-based SOM compositions. The literature-derived selection direction was increasing ionicity below approximately 0.2 while examining hybridization within and slightly beyond the favorable interval of approximately 2.22–2.3. These values are empirical coordinates for the present screening exercise, not universal boundaries separating covalent and ionic materials or SOM and non-SOM behavior. Four compositions with progressively increasing Sb content, indicated by the purple stars in Fig. 1a, were selected to sample this trajectory.

The experimental comparison was designed to address two questions: whether the selected materials exhibit programmable threshold states, and whether their RWM and reliability follow the bonding evolution associated with the descriptor trajectory. Temperature-dependent transport, XPS, and Raman analyses were used to connect switching characteristics with effective trap-related energies and local bonding environments. This comparison tests the practical value and limitations of the map as an initial selection guide; observing SOM in the selected compositions does not by itself establish its ability to exclude all non-SOM materials.

3.2 Experimental Realization of SOM Based on Hybridization–Ionicity Mapping

The four compositions are denoted GS, GSS1, GSS2, and GSS3 in order of increasing Sb concentration. They span the descriptor trajectory identified in Section 3.1, including a highest-Sb composition slightly beyond the favorable hybridization range, allowing the corresponding switching trends to be examined under comparable fabrication and measurement conditions.

The cross-sectional structures of the four devices were examined by HR-TEM, as shown in Fig. 2a–d. All devices exhibited W/C/chalcogenide/W stacks, with continuous active layers formed between the BE and the C interlayer. The active-layer thicknesses were approximately 65 nm for GS–GSS3 indicating comparable thicknesses among the four devices. Because the electric field across the active layer depends on its thickness, maintaining similar thickness reduces its influence when comparing the electrical characteristics of devices with different compositions. Fast Fourier transform (FFT) patterns obtained from the HR-TEM images of the active layers, shown in the upper right insets of Fig. 2a–d, exhibited diffuse halo patterns without distinct diffraction spots, confirming the amorphous nature of all four chalcogenide layers. EDS elemental mapping further confirmed the successful incorporation of Ge, Sb, and Se throughout the corresponding active layers, as shown in the lower insets of Fig. 2a–d. With increasing Sb concentration, the Sb distribution became progressively more pronounced across the active layer, consistent with the intended compositional variation among the devices. RBS was used to determine the elemental compositions of the four chalcogenide layers, as shown in Fig. 2e–h. The compositions obtained from the RBS analysis were $\text{Ge}_{55}\text{Se}_{45}$ for GS, $\text{Ge}_{40}\text{Sb}_{10}\text{Se}_{50}$ for GSS1,

$\text{Ge}_{34}\text{Sb}_{21}\text{Se}_{45}$ for GSS2, and $\text{Ge}_{29}\text{Sb}_{31}\text{Se}_{40}$ for GSS3. The Sb concentration increased from 0 at.% in GS to 10, 21, and 31 at.% in GSS1, GSS2, and GSS3, respectively, corresponding to an increase of approximately 10 at.% between adjacent compositions. These results confirm that the intended variation in Sb concentration was achieved while maintaining comparable active-layer thicknesses.

DC and pulsed current–voltage (PIV) measurements were used to resolve the threshold response after positive and negative write pulses (Fig. S2). The lower and higher programmed thresholds are denoted V_{th1} and V_{th2} , respectively, with $\text{RWM} = V_{\text{th2}} - V_{\text{th1}}$. For DC characterization, each ± 5 V, 50 ns write pulse was followed by a positive-voltage sweep. The pulse rise/fall times were 6/50 ns, and an 80 μA compliance limited the current after TS. V_{th} was identified from the abrupt current increase during the subsequent sweep.

PIV measurements evaluated the programmed states using pulsed readout. As shown in Fig. S2b, the circuit consisted of an AFG, the device, a 70 k Ω series load resistor, and an oscilloscope. Two oscilloscope channels monitored the input waveform and the voltage across the resistor; the latter was converted to current using the load resistance. A triangular read pulse with an amplitude of 7 V, a width of 10 μs , and rise/fall times of 8 μs was applied after each write pulse. The write conditions were identical to those used for DC characterization. The write–delay–read and cycling sequences used for drift and endurance measurements are shown in Fig. S2c, d, respectively.

Figure 3a–d present the DC I – V characteristics of the GS, GSS1, GSS2, and GSS3 devices. In each device, the V_{th} depended on the polarity of the preceding write pulse, resulting in distinguishable V_{th1} and V_{th2} states. The extracted V_{th1} and V_{th2} values were 3.5 and 5.3 V for GS, 3 and 5.1 V for GSS1, 1.9 and 4.2 V for GSS2, and 1.6 and 3 V for GSS3, respectively. The corresponding RWM values were 1.8, 2.1, 2.3, and 1.4 V. Thus, all four compositions selected on the basis of the hybridization–ionicity mapping exhibited the V_{th} modulation required for SOM operation, while the magnitude of the RWM varied with the active-layer composition.

Leakage was evaluated at half of the midpoint read voltage, $1/2 V_{\text{read}} = (V_{\text{th1}} + V_{\text{th2}})/4$, for each device. The currents in the V_{th1} and V_{th2} states were 5.34 and 0.32 nA for GS, 47.6 and 0.92 nA for GSS1, 78 and 17.9 nA for GSS2, and 351.9 and 21.2 nA for GSS3, respectively. These operating-point measurements compare leakage under a device-specific half-bias condition; they are not measurements at a common absolute voltage.

The SOM characteristics identified from the DC measurements were subsequently examined under pulse-based read operation. Figure 3e–h show the PIV characteristics of GS, GSS1, GSS2, and GSS3 obtained using the pulse sequence described above. Following positive and negative write pulses, distinct V_{th1} and V_{th2} switching distributions were observed for all four compositions. The V_{th1} , V_{th2} , and corresponding RWM values obtained from the PIV measurements were consistent with those extracted from the preceding DC measurements, exhibiting similar values and compositional trends. The observation of two distinguishable threshold states under both DC and pulsed read conditions therefore

confirms that the four compositions selected based on the hybridization–ionicity mapping consistently exhibit the predicted SOM behavior under the measurement conditions used in this study.

The RWM also showed a systematic dependence on the hybridization and ionicity parameters discussed in the preceding section. As the Sb concentration increased from the Sb-free GS composition to GSS1 and GSS2, the RWM increased from approximately 1.8 to 2.1 and 2.3 V, respectively. Over this compositional range, the ionicity increased while remaining below 0.2, whereas the hybridization remained within the range of approximately 2.22–2.3 identified as favorable for SOM operation. This behavior is consistent with the previously established relationship in which increasing ionicity is associated with a wider RWM within an appropriate hybridization range.

GSS3, however, exhibited a different trend. Despite its higher ionicity, its RWM decreased to approximately 1.4 V, compared with 2.3 V for GSS2, while its hybridization exceeded approximately 2.3. To further evaluate this behavior, the RWM values of the four devices were added to the previously established correlations between RWM and ionicity and hybridization, as shown in Fig. 3i, j, respectively. In Fig. 3i, the RWM increased approximately linearly with ionicity from GS to GSS2, whereas GSS3 deviated from this trend. This deviation is consistent with the hybridization dependence shown in Fig. 3j: RWM increased with hybridization within the range of 2.22–2.3 but decreased once the hybridization exceeded approximately 2.3, following the opposite trend identified beyond this range.

Taken together, these results indicate that the SOM characteristics are governed by the combined influence of ionicity and hybridization rather than by ionicity alone. Increasing the Sb concentration from GS to GSS2 enhances the ionicity while maintaining the hybridization within a favorable range, thereby widening the RWM. Further Sb incorporation in GSS3, however, increases the hybridization beyond this range and may introduce competing effects associated with changes in the bonding configuration, including an increased contribution of homopolar bonds. The experimentally observed compositional dependence therefore agrees with the tendency predicted from the hybridization–ionicity mapping and suggests that an appropriate range of Sb concentration and corresponding mapping parameters is important for achieving a wider RWM. The relationship between these mapping parameters, the underlying bonding configuration, and other reliability characteristics, including V_{th} drift and endurance, is examined in the following sections.

3.3 Trap-mediated SOM Mechanism and Bandgap Evolution with Sb Incorporation

To further clarify the compositional dependence of the electrical characteristics, the V_{th} ranges and off-state currents of GS and GSS1–3 were compared, as summarized in Fig. 4. As shown in Fig. 4a, both V_{th1} and V_{th2} progressively shift toward lower voltages with increasing Sb concentration, while the off-state current increases monotonically from GS to GSS3 (Fig. 4b). Previous studies on amorphous chalcogenide selectors and SOM devices have widely described subthreshold transport in terms of trap-mediated conduction, in which carrier transport is governed by the thermal and field-assisted release of

carriers from localized states [26, 28, 29, 37]. Based on this established transport picture, temperature-dependent electrical analyses were performed using the Arrhenius and PF approaches to examine the trap-related energetics underlying the observed compositional trends. These two analyses provide complementary information on thermally activated carrier transport and field-assisted carrier emission, respectively.

The thermal activation of carrier transport was first examined using the Arrhenius relation. In an amorphous chalcogenide, structural disorder and local defects can introduce localized electronic states within E_g . Carriers occupying these states require sufficient thermal energy to participate in transport, and the corresponding energy barrier can be represented by E_a . At a fixed electric field, the temperature dependence of the current can be expressed as Eq. (5)

$$\ln \left(\frac{J}{E} \right) = \ln (C) - \frac{qE_a}{k_B T}$$

5

where J is the current density, E is the applied electric field, C is a proportionality constant, q is the elementary charge, k_B is the Boltzmann constant, T is the absolute temperature, and E_a is the activation energy [25]. Accordingly, E_a was determined from the slope of the linear relationship between $\ln(J/E)$ and $1/(k_B T)$. To reduce the influence of a particular bias condition on the extracted value, the analysis was performed at several fixed DC biases ranging from 0.3 to 0.8 V. Linear fitting was carried out independently at each bias, and the resulting values were used to determine the representative E_a for each programmed state. The corresponding Arrhenius plots for the V_{th1} and V_{th2} states of GS, GSS1, GSS2, and GSS3 are presented in Fig. S3.

Unlike the E_a extracted from the Arrhenius analysis, the trap-state depth was determined using the PF model. The PF mechanism describes field-assisted thermal emission of a carrier from a localized coulombic trap. When an external electric field is applied, the potential barrier confining the trapped carrier is lowered, thereby reducing the energy required for carrier emission. The probability of detrapping therefore increases with electric field, resulting in an exponential increase in current. The PF relation used in this analysis can be written as Eq. (6)

$$\ln \left(\frac{J}{E} \right) = \frac{q}{k_B T} \sqrt{\frac{qE}{\pi \epsilon}} - \frac{q\Phi_t}{k_B T} + \ln (C)$$

6

where ϵ is the dielectric permittivity of the active layer and Φ_t represents the zero-field trap barrier, hereafter referred to as the trap depth [47]. The equation predicts a linear dependence of $\ln(J/E)$ on $E^{1/2}$ at a fixed temperature, while the intercept of the fitted line contains information on Φ_t according to Eq. (7).

$$y - \text{intercept} = - \frac{q\Phi_t}{k_B T} + \ln(C)$$

7

Temperature-dependent DC I - V characteristics were measured at 25, 45, 65, and 85°C for both programmed states of each device, as shown in Fig. S4. The subthreshold current increased with increasing temperature for all compositions, consistent with an increased probability of thermally assisted carrier emission. For each temperature, the measured data were transformed into $\ln(J/E)$ versus $E^{1/2}$ plots and fitted within the selected subthreshold electric-field range. Approximately linear relationships were obtained for the V_{th1} and V_{th2} states of all four devices, as shown in Fig. S4. Because the PF intercept contains both the trap-barrier and temperature terms, the y -intercepts extracted at the four temperatures were subsequently plotted as a function of $1/(k_B T)$. The slope of this secondary linear fit was then used to determine Φ_t . This sequential analysis incorporates both the electric-field and temperature dependences of the subthreshold current in the estimation of the trap depth [47].

The Arrhenius analysis-derived E_a values and the PF model-derived trap depth values are summarized in Fig. 4c. The E_a values for the V_{th1} and V_{th2} states were 0.446 and 0.648 eV for GS, 0.411 and 0.634 eV for GSS1, 0.322 and 0.550 eV for GSS2, 0.183 and 0.284 eV for GSS3, respectively. Independently, PF fitting yielded trap depths of 0.469 and 0.660 eV for GS, 0.430 and 0.652 eV for GSS1, 0.335 and 0.573 eV for GSS2, and 0.194 and 0.303 eV for GSS3. Although E_a and Φ_t describe different aspects of thermally activated and field-assisted transport, both analyses exhibit comparable state- and composition-dependent trends, supporting a trap-mediated conduction picture for the subthreshold regime. For all four compositions, the V_{th1} state consistently exhibits lower E_a and Φ_t values than the corresponding V_{th2} state. The lower characteristic energies indicate that carriers associated with the V_{th1} state require less thermal or field-assisted energy to participate in conduction, consistent with the lower switching voltage of this state. In contrast, the higher E_a and Φ_t values of the V_{th2} state reflect a larger energetic barrier to carrier activation or emission, requiring a higher applied field to induce TS. Furthermore, both E_a and Φ_t progressively decrease with increasing Sb concentration for the two programmed states. This evolution indicates a gradual reduction in the energetic barriers associated with subthreshold carrier transport, facilitating carrier activation and shifting the onset of TS toward lower voltages due to the incorporation of Sb. Accordingly, the decrease in the independently extracted trap-related energies closely follows the downward shift of both V_{th1} and V_{th2} from GS to GSS3, indicating a close relationship between trap energetics and the composition-dependent threshold behavior of SOM devices.

The evolution of the off-state current was further examined in relation to the electronic band structure. The cutoff energy ($E_{\text{cut-off}}$), valence-band maximum (E_{VBM}), and E_g were obtained from UPS and UV-vis measurements (Fig. S5) and used together with the extracted trap-related energies to construct the band diagrams in Fig. 4d–g. The E_g decreased progressively from 2.41 eV for GS to 2.33, 2.20, and 2.02 eV for GSS1, GSS2, and GSS3, respectively, consistent with previous reports of Sb-induced E_g narrowing in

amorphous Ge–Sb–Se materials [48, 49]. The simultaneous narrowing of the E_g and reduction in trap-related energies facilitate carrier excitation and emission, respectively, consistent with the increased off-state current and lower switching voltages observed with increasing Sb concentration.

Finally, the RWM trend was examined in relation to the energetic separation between the two programmed states. The energy difference between the V_{th1} and V_{th2} states showed a compositional trend comparable to the experimentally measured RWM, with PF values of 0.191 (0.660–0.469), 0.222 (0.652–0.430), 0.238 (0.573–0.335), and 0.109 (0.303–0.194) eV for GS, GSS1, GSS2, and GSS3, respectively. In terms of E_a , they showed 0.202 (0.648–0.446), 0.223 (0.634–0.411), 0.228 (0.550–0.322), and 0.101 (0.284–0.183) eV for GS, GSS1, GSS2, and GSS3 as well. Thus, while the absolute trap-related energies progressively decrease with increasing Sb concentration, their separation evolves differently and closely corresponds to RWM. This distinction indicates that the RWM is more closely associated with the energetic differentiation between the two programmed states than with their absolute trap-related energies alone. The distinct evolution of the absolute trap-related energies and their energetic separation suggests that Sb incorporation modifies the trap landscape in more than a simple uniform energy shift. Because localized electronic states in amorphous chalcogenides are strongly influenced by the local chemical environment, this behavior is expected to be associated with composition-dependent changes in the bonding configuration.

These trends suggest that the Sb-dependent trap-energy evolution is closely associated with changes in the local bonding environment. Previous SOM studies have shown that polar heteropolar configurations, including Ge–Se- and Sb–Se-related bonding environments, can modify the localized electronic states involved in TS, whereas excessive Sb incorporation can promote Sb-related homopolar configurations, particularly Sb–Sb, and alter the corresponding localized-state distribution [18, 50, 51]. Importantly, different homopolar configurations do not necessarily generate equivalent trap states, because their energetic characteristics depend on the chemical identity and electronic structure of the constituent bonds. Thus, the continued reduction in the absolute trap-related energies with increasing Sb content and the nonmonotonic evolution of their energetic separation may originate from different aspects of the underlying bonding evolution: the former can be influenced by the specific chemical nature of the constituent bonds, whereas the latter may be more closely associated with changes in the heteropolar–homopolar bonding balance. Direct characterization of the local bonding configuration is therefore required to clarify the material origin of the observed trap modulation. In the following section, the Sb-dependent bonding evolution is examined by XPS and Raman spectroscopy together with the V_{th} drift and endurance characteristics of the four SOM devices.

3.4 Reliability Characteristics and Sb-Dependent Bonding Evolution

To assess the reliability of the GS and GSS1–3 SOM devices, V_{th} drift and endurance measurements were performed, as summarized in Fig. 5. Accordingly, the V_{th} drift measurements were performed by varying the time interval between the write pulse and the subsequent read verification pulse. As

illustrated by the pulse scheme in Fig. S2c, the time interval was varied from 10^{-6} to 10^2 s, and the corresponding evolution of the V_{th1} and V_{th2} states was monitored over this time range. The drift coefficient was expressed in mV/dec, where a smaller drift coefficient indicates greater temporal stability of the programmed threshold state. As shown in Fig. 5a–d, the drift coefficients of the V_{th1} and V_{th2} states were 129.4 and 403.6 mV/dec for GS, 66.4 and 367 mV/dec for GSS1, 8.2 and 9.2 mV/dec for GSS2, and 23.2 and 83.4 mV/dec for GSS3, respectively. The drift coefficients decreased from GS to GSS1 and further to GSS2, indicating improved temporal stability with Sb incorporation over this compositional range. However, an obvious increase was observed for GSS3 compared with GSS2, suggesting that further Sb incorporation does not continuously improve the V_{th} stability.

Endurance measurements were subsequently performed to evaluate the ability of each device to retain distinguishable V_{th1} and V_{th2} states under repeated write operations. Alternating positive and negative write pulses were applied using the pulse scheme shown in Fig. S2d, and the programmed threshold states were periodically monitored by read pulses. As shown in Fig. 5e–h, GS maintained distinguishable V_{th} states up to approximately 10^2 cycles, whereas GSS1, GSS2, and GSS3 exhibited endurance of approximately 10^3 , 10^7 , and 10^5 cycles, respectively. Similar to the V_{th} drift results, the endurance characteristics improved from GS to GSS1 and GSS2, while GSS3 showed a slight degradation relative to GSS2. The V_{th} drift coefficients of the four splits are summarized and compared in Fig. 5i, while their endurance characteristics are presented in Fig. 5j. The summarized results in Fig. 5i, j therefore show that both V_{th} stability and endurance improve toward GSS2 and partially deteriorate in GSS3. This nonmonotonic reliability trend, which follows the compositional dependence of the RWM, suggests that the stability of the programmed threshold states is closely related to changes in the local bonding environment induced by increasing Sb concentration. The corresponding Sb-dependent bonding evolution was therefore examined using XPS and Raman spectroscopy.

The XPS core-level spectra exhibited comparable binding energies across the four compositions, with no noticeable shifts upon increasing Sb concentration. As shown in Fig. S6, the Ge 3d spectra were deconvoluted into components centered at approximately 30.4 and 31.2 eV, assigned to Ge–Ge and Ge–Se bonds, respectively [52, 53]. In Fig. 6a–d, the Se 3d spectra were resolved into Se–Ge, Se–Sb, and Se–Se doublets, with the corresponding $3d_{3/2}$ and $3d_{5/2}$ components located at approximately 54.36/53.5, 54.66/53.8, and 54.96/54.1 eV, respectively [54–57]. For the Sb-containing GSS1–3 films shown in Fig. 6e–g, the Sb 3d spectra were further deconvoluted into Sb–Se and Sb–Sb components at approximately 540.2/530.86 and 538.34/529.0 eV for the $3d_{3/2}$ and $3d_{5/2}$ states, respectively [50, 51, 58].

The relative contributions of the fitted bonding components were quantified from their normalized peak areas, as summarized in Table S2. In the Se 3d spectra, the combined Se-centered heteropolar contribution (Se–Ge + Se–Sb) increased from 71.97% in GS to 73.49% in GSS1 and 83.21% in GSS2, while the Se–Se homopolar contribution decreased from 28.03% to 26.51% and 16.78%, respectively. This trend partially reversed in GSS3, where the heteropolar contribution decreased to 81.72% and Se–Se increased to 18.28%. A more pronounced reversal was observed in the Sb 3d spectra: the Sb–Se

contribution increased from 10.85% in GSS1 to 28.97% in GSS2, accompanied by a decrease in Sb–Sb from 69.04% to 60.27%, whereas GSS3 exhibited a reduced Sb–Se contribution of 19.09% and an increased Sb–Sb contribution of 71.37%. Thus, Sb incorporation up to GSS2 favors a more heteropolar local bonding environment, whereas further Sb enrichment in GSS3 is accompanied by a recovery of homopolar bonding, most prominently through Sb–Sb configurations.

Raman spectroscopy was further employed to examine the Sb-dependent bonding evolution, as shown in Fig. 6h. Three characteristic spectral regions were considered based on vibrational modes reported for amorphous Ge–Sb–Se materials [59–62]. The band at approximately $150\text{--}160\text{ cm}^{-1}$ is associated with overlapping Ge–Ge and Sb–Sb homopolar configurations, whereas the prominent band near 200 cm^{-1} contains contributions from heteropolar Ge–Se and Sb–Se bonds; the higher-wavenumber feature at approximately $260\text{--}280\text{ cm}^{-1}$ is primarily assigned to Se–Se-related modes. Because the Ge–Ge/Sb–Sb and Ge–Se/Sb–Se vibrations substantially overlap within their respective spectral regions, the Raman intensities were interpreted in terms of combined relative bonding contributions rather than quantitative populations of individual bonds. The $150\text{--}160\text{ cm}^{-1}$ band initially increased from GS to GSS1, decreased slightly in GSS2, and then increased markedly in GSS3. With increasing Sb concentration, the contribution to this region is expected to evolve from predominantly Ge–Ge-related configurations toward a greater Sb–Sb contribution; accordingly, the decrease from GSS1 to GSS2 and the pronounced increase in GSS3 are consistent with the XPS-derived suppression of homopolar bonding toward GSS2 followed by substantial Sb–Sb formation in GSS3. The Se–Se-related band at approximately $260\text{--}280\text{ cm}^{-1}$ progressively decreased from GS through GSS1 to GSS2 and slightly recovered in GSS3, in agreement with the Se–Se evolution obtained from the Se 3d XPS spectra. In contrast, the heteropolar-related band near 200 cm^{-1} progressively increased from GS to GSS1 and GSS2 before decreasing slightly in GSS3, closely following the XPS-derived heteropolar contribution, which was highest for GSS2. Thus, despite the overlap of individual vibrational modes, the overall Raman spectral evolution independently supports the nonmonotonic Sb-dependent bonding evolution identified by XPS.

The combined XPS and Raman results are summarized schematically in Fig. 6i. From GS to GSS2, the increase in ionicity within the relatively narrow hybridization range of approximately 2.2–2.3 coincides with an increasing contribution of polar heteropolar Ge–Se and Sb–Se configurations and a reduction in homopolar bonding. In GSS3, ionicity continues to increase, but the hybridization value exceeds approximately 2.3 and the preceding bonding trend is partially reversed, most notably through the pronounced increase in Sb–Sb configurations. These results experimentally demonstrate that the composition-derived descriptor trajectory is accompanied by a distinct evolution of the local bonding environment. The relationship of this bonding evolution to trap energetics, RWM, and reliability characteristics is discussed in the following section.

3.5 Correlation Between Materials Descriptors, Bonding Configuration, and SOM Characteristics

The combined electrical, trap-related, reliability, and bonding analyses reveal two distinct compositional regimes in the present Ge–Sb–Se series. From GS to GSS2, increasing Sb concentration is accompanied by an enhanced contribution of heteropolar bonding, an enlarged energetic separation between the two programmed states and RWM, and improved V_{th} stability and endurance. Further Sb incorporation in GSS3 produces a different response: although the absolute V_{th} values and corresponding trap-related energies continue to decrease, the energetic separation between the two programmed states and the RWM are reduced, together with degraded reliability and a pronounced increase in Sb–Sb-rich homopolar bonding. These contrasting trends indicate that the SOM characteristics are governed not simply by Sb concentration itself, but by composition-induced changes in the local bonding environment and the resulting trap-energy landscape.

From GS to GSS2, increasing ionicity is accompanied by a higher relative contribution of polar heteropolar Ge–Se and Sb–Se bonds, consistent with the greater charge-polarization tendency represented by the ionicity descriptor. Such changes are particularly relevant to amorphous chalcogenides, in which the energetic position and localization of electronic states are strongly influenced by the chemical identity and coordination of neighboring atoms. Previous studies on Se-based selectors and SOM devices have associated Se-containing heteropolar bonds with relatively shallow trap states, whereas Se–Se homopolar defects have been linked to deeper localized states [63]. Polar heteropolar bonding has also been reported to modify the local electronic environment and thereby affect the energetic differentiation between polarity-programmed threshold states [17, 32, 46, 51]. In the present series, the increasing contribution of Sb–Se bonding to the Ge–Se-based network from GS to GSS2 is accompanied by a progressive decrease in the trap-related energies of both V_{th1} and V_{th2} , consistent with the downward shift of the overall threshold-voltage range and the increase in off-state current. At the same time, the two programmed states shift by different amounts, resulting in a progressively larger energetic separation toward GSS2 that closely follows the widening of the RWM. Thus, the RWM is associated more directly with the energetic differentiation between the two programmed states than with their absolute trap-related energies alone.

The same bonding evolution is also consistent with the improvement in reliability from GS to GSS2. V_{th} drift is associated with structural relaxation of the metastable amorphous network, during which changes in the local bonding configuration and trap landscape progressively shift the programmed threshold voltage [19, 44]. Endurance degradation, in contrast, reflects the cumulative effects of electric-field-induced structural perturbation, bond rearrangement, and atomic redistribution during repeated write operations [17, 63, 64]. Accordingly, the increased relative contribution of heteropolar Ge–Se and Sb–Se configurations and the concurrent suppression of homopolar bonding toward GSS2 coincide with a pronounced reduction in V_{th} drift and improved endurance. This correspondence suggests that the bonding environment established near GSS2 more effectively preserves the local structural and electronic configurations against both temporal relaxation and repeated electrical excitation.

A different bonding regime emerges from GSS2 to GSS3. Although ionicity continues to increase, the hybridization coordinate exceeds approximately 2.3, moving beyond the range associated with favorable

SOM characteristics in the preceding compositions. Hybridization reflects the tendency toward s-p orbital mixing and directional, saturated covalent coordination, including the local coordination behavior commonly described by the 8 - N rule [24, 35]. In the present Ge-Sb-Se system, further Sb incorporation increasingly limits the availability of Se for additional Sb-Se heteropolar coordination, such that a larger fraction of Sb is accommodated through Sb-Sb configurations. Consistent with this interpretation, XPS and Raman analyses show a pronounced increase in Sb-Sb homopolar bonding and a decrease in the relative Sb-Se contribution in GSS3 compared with GSS2. This shift disrupts the heteropolar-homopolar balance established toward GSS2 and coincides with a marked decrease in the energetic separation between the V_{th1} - and V_{th2} -related states, a narrower RWM, increased V_{th} drift, and reduced endurance. The hybridization value of approximately 2.3 should not, however, be regarded as a universal boundary for homopolar-bond formation or SOM degradation; rather, it represents an empirical, material-specific range within the present Ge-Sb-Se compositional space.

The continued decrease in the absolute V_{th} values and trap-related energies from GSS2 to GSS3 requires separate consideration. Although homopolar configurations are generally associated with relatively deep localized states, their energetic characteristics depend on the chemical identity and electronic structure of the specific bonds. From GSS2 to GSS3, the Se-Se contribution increases only from 16.78% to 18.28% (1.50 percentage points), whereas the Sb-Sb contribution increases from 60.27% to 71.37% (11.10 percentage points), indicating that the dominant change is the formation of Sb-Sb-rich local environments. The reported bond energies of Se-Se and Sb-Sb are approximately 44.0 and 30.2 kcal/mol, respectively [65, 66], suggesting that the increased Sb-Sb contribution introduces a relatively weak bonding environment. Such configurations can facilitate local bond distortion and reconfiguration, increase structural disorder, and broaden the distribution of localized electronic states near the band edges. Sb-related bonding configurations in Ge-Se systems have also been associated with localized antibonding and band-tail states and with bandgap narrowing [36, 44, 50, 67]. Together with the experimentally observed decrease in E_g , this bond-specific evolution provides a plausible explanation for the continued reduction in the absolute trap-related energies and V_{th} values in GSS3, despite the simultaneous deterioration in the energetic separation between the two programmed states.

These results clarify the complementary roles of ionicity and hybridization in relation to bonding configuration and SOM characteristics. Ionicity primarily represents the compositional tendency toward bond polarization and, within the present compositional range, is associated with the increased relative contribution of polar heteropolar bonding. Hybridization, in contrast, provides complementary information on changes in local covalent coordination and can indicate when further compositional modification begins to disrupt the heteropolar-homopolar balance favorable for SOM operation. It does not directly quantify the homopolar-bond fraction, nor should either descriptor be interpreted as an independent causal parameter. Rather, the present results show that favorable SOM characteristics emerge when increasing ionicity is accompanied by a bonding configuration that remains within an appropriate hybridization regime. In the present Ge-Sb-Se series, this condition is approached toward GSS2, whereas further Sb enrichment in GSS3 shifts the system into a higher-hybridization, Sb-Sb-rich

regime accompanied by reduced trap-state differentiation, RWM, and reliability. Favorable SOM characteristics therefore require an appropriate balance between ionicity and hybridization rather than the independent maximization of either descriptor.

4 Conclusions

In this study, we investigated the applicability of hybridization–ionicity mapping as a materials-design framework for SOM devices and experimentally examined its relationship with the electrical, trap-related, bonding, and reliability characteristics of Sb-based amorphous chalcogenides. The compositions selected within the targeted mapping region exhibited SOM operation with two distinguishable V_{th} states, supporting the potential of ionicity and hybridization as initial descriptors for identifying compositions likely to exhibit SOM behavior. Furthermore, the compositional evolution of the Ge–Sb–Se devices indicated that favorable SOM characteristics are associated with an appropriate balance between the two descriptors rather than the independent maximization of either parameter. For the Sb-based SOM devices investigated in this study, increasing ionicity while remaining within a predominantly covalent regime, together with maintaining hybridization within a favorable range of approximately 2.25–2.3, was associated with an increased contribution of polar heteropolar bonding, enlarged trap-energy separation and RWM, and improved V_{th} stability and endurance. Further Sb incorporation beyond this range, despite the continued increase in ionicity, was accompanied by higher hybridization, an increased Sb–Sb-rich homopolar contribution, and deterioration of the RWM and reliability. These findings suggest that ionicity and hybridization may provide not only an initial means of identifying compositions likely to exhibit SOM behavior, but also quantitative guidance for estimating compositional ranges favorable for improved SOM characteristics at an early stage of material development.

Conventionally, the bonding characteristics governing SOM behavior are evaluated after material fabrication through experimental analyses such as XPS and Raman spectroscopy or computational approaches such as density functional theory (DFT). In contrast, hybridization and ionicity can be estimated from the constituent elements prior to extensive material characterization, providing the possibility of using these descriptors during the initial stage of composition selection. Accordingly, hybridization–ionicity mapping may complement conventional experimental and computational analyses by providing an initial basis for narrowing the candidate-composition space and guiding subsequent compositional optimization before detailed material evaluation. Although further validation across a broader range of materials and compositions is required, the experimental correlations observed in this study provide support for the potential use of this descriptor-based approach as a materials-selection framework for SOM development. Extending this framework to diverse constituent elements and compositional systems may further contribute to the development of a more generalized methodology for the design and optimization of amorphous chalcogenide SOM materials.

Authorship contribution I.O. wrote the original draft, developed the methodology and conceptualization, curated and formally analyzed the data, performed the investigation, and prepared the visualizations. W.H.J. contributed to resources and conceptualization. M.K.Y. contributed to the original draft,

methodology, and conceptualization. G.H.K. contributed to the original draft, acquired funding, administered and supervised the project, and validated the results. All authors reviewed and approved the final manuscript.

Declarations

Conflict of Interest

The authors declare no conflict of interest.

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Author Contribution

I.O. wrote the original draft, developed the methodology and conceptualization, curated and formally analyzed the data, performed the investigation, and prepared the visualizations. W.H.J. contributed to resources and conceptualization. M.K.Y. contributed to the original draft, methodology, and conceptualization. G.H.K. contributed to the original draft, acquired funding, administered and supervised the project, and validated the results. All authors reviewed and approved the final manuscript.

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Data availability

No datasets were generated or analysed during the current study.

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Figures

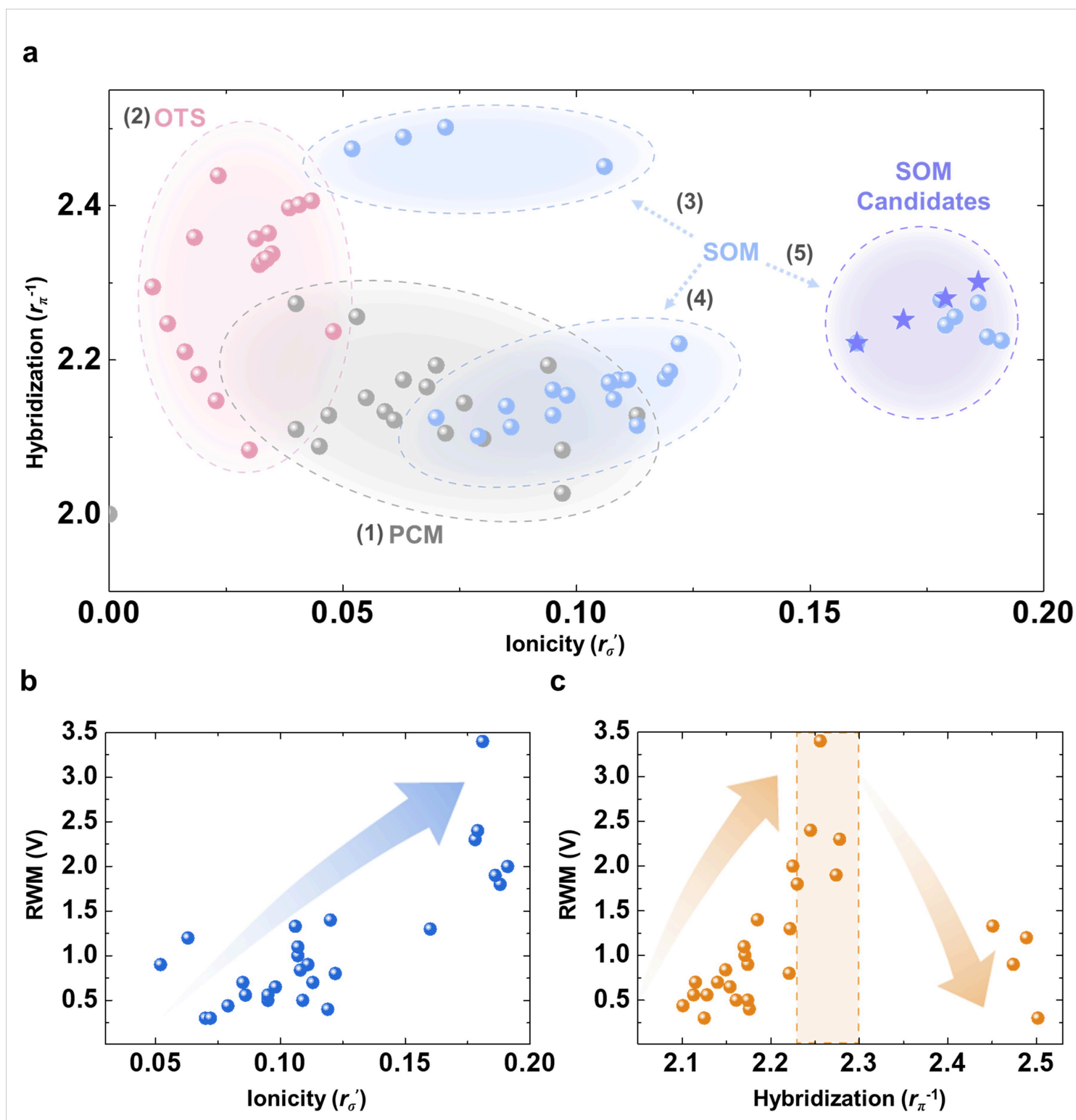


Figure 1

Hybridization–ionicity mapping and RWM trends for SOM material selection. **a** Hybridization–ionicity map of reported PCM, OTS, and SOM materials. Correlation of RWM with **b** ionicity and **c** hybridization.

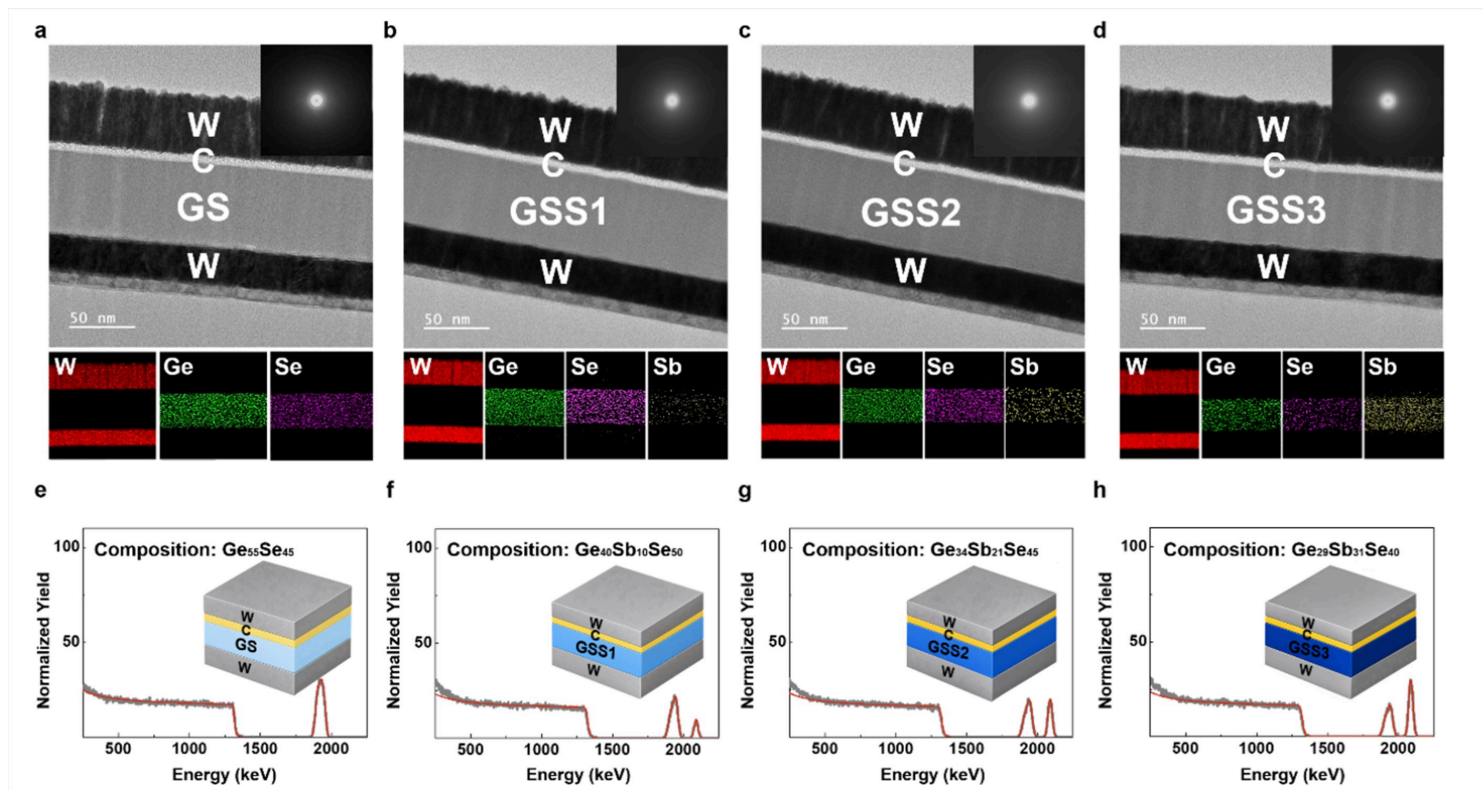


Figure 2

Structural and compositional characterization of GS and GSS1–3 SOM devices. Cross-sectional TEM images, EDS elemental maps, and corresponding FFT patterns of **a** GS, **b** GSS1, **c** GSS2, and **d** GSS3 devices. RBS spectra and corresponding device structures of **e** GS, **f** GSS1, **g** GSS2, and **h** GSS3.

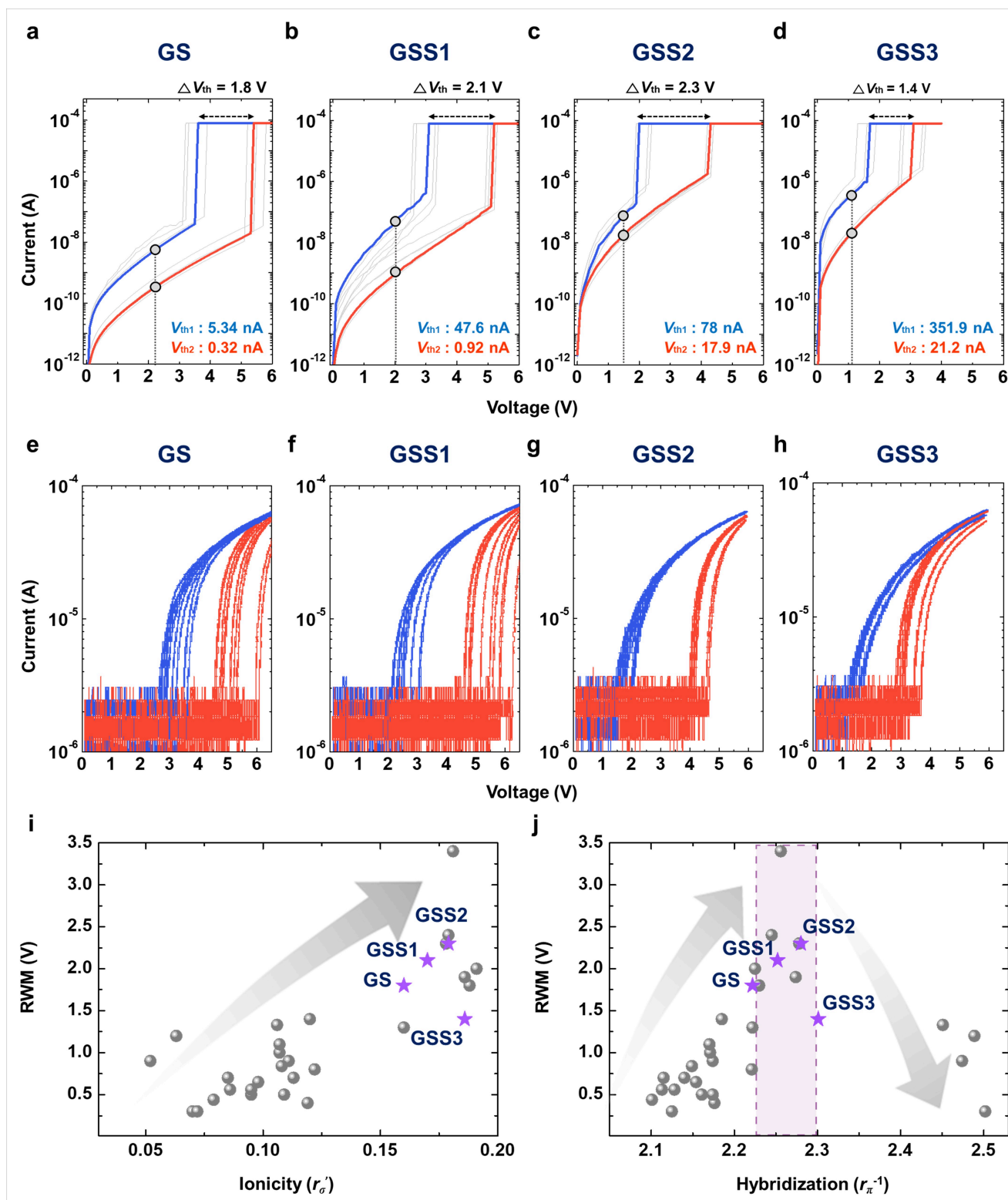


Figure 3

Electrical switching characteristics and descriptor-dependent RWM evolution of GS and GSS1–3 SOM devices. DC I - V characteristics of **a** GS, **b** GSS1, **c** GSS2, and **d** GSS3. PIV characteristics of **e** GS, **f** GSS1, **g** GSS2, and **h** GSS3. Experimentally obtained RWM values of the four devices plotted on the correlations between RWM and **i** ionicity and **j** hybridization introduced in **Fig. 1b, c**, respectively.

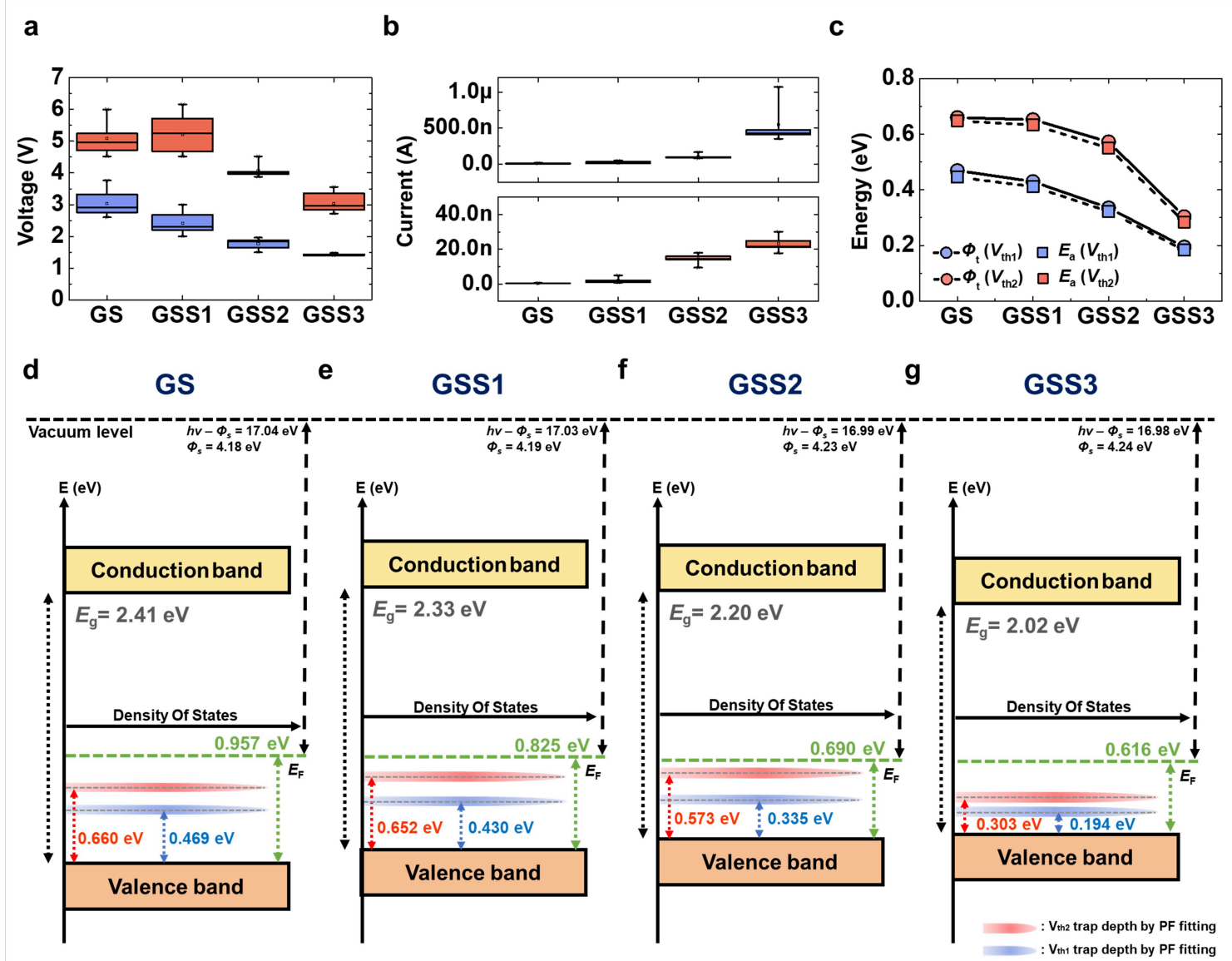


Figure 4

Trap-related energetics and band-structure evolution of GS and GSS1–3 SOM devices. **a** Distribution of V_{th1} and V_{th2} extracted from the PIV measurements. **b** Off-state currents obtained from the DC measurements. **c** Trap energies extracted from the PF and Arrhenius analyses for the V_{th1} and V_{th2} states. **d–g** Energy-band diagrams constructed from the UPS and UV–vis spectroscopy results.

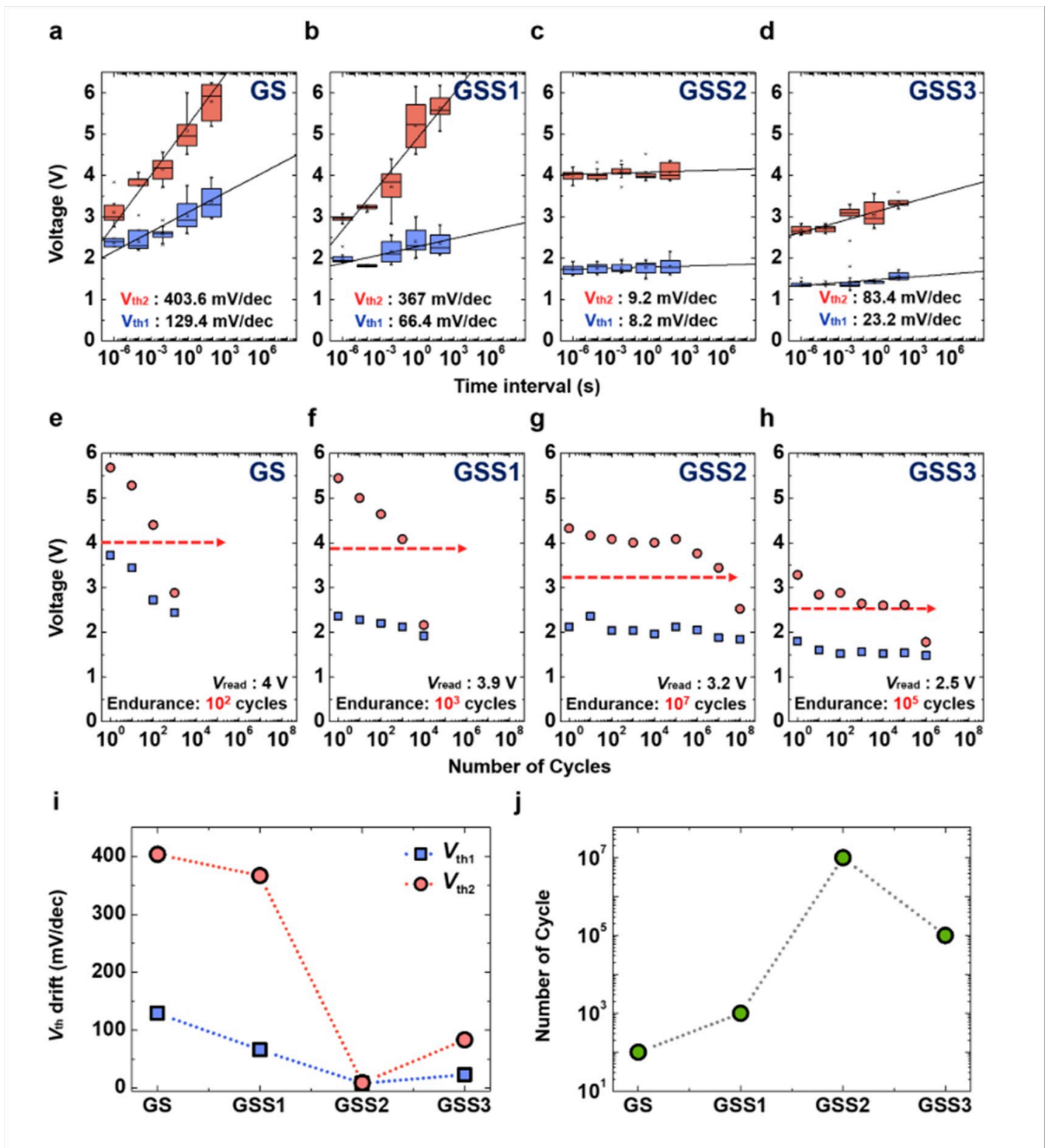


Figure 5

Reliability characteristics of GS and GSS1–3 SOM devices, including V_{th} drift and endurance behavior. V_{th} drift characteristics of **a** GS, **b** GSS1, **c** GSS2, and **d** GSS3. Endurance characteristics of **e** GS, **f** GSS1, **g** GSS2, and **h** GSS3. Comparison of **i** V_{th} drift and **j** endurance characteristics among the four SOM devices.

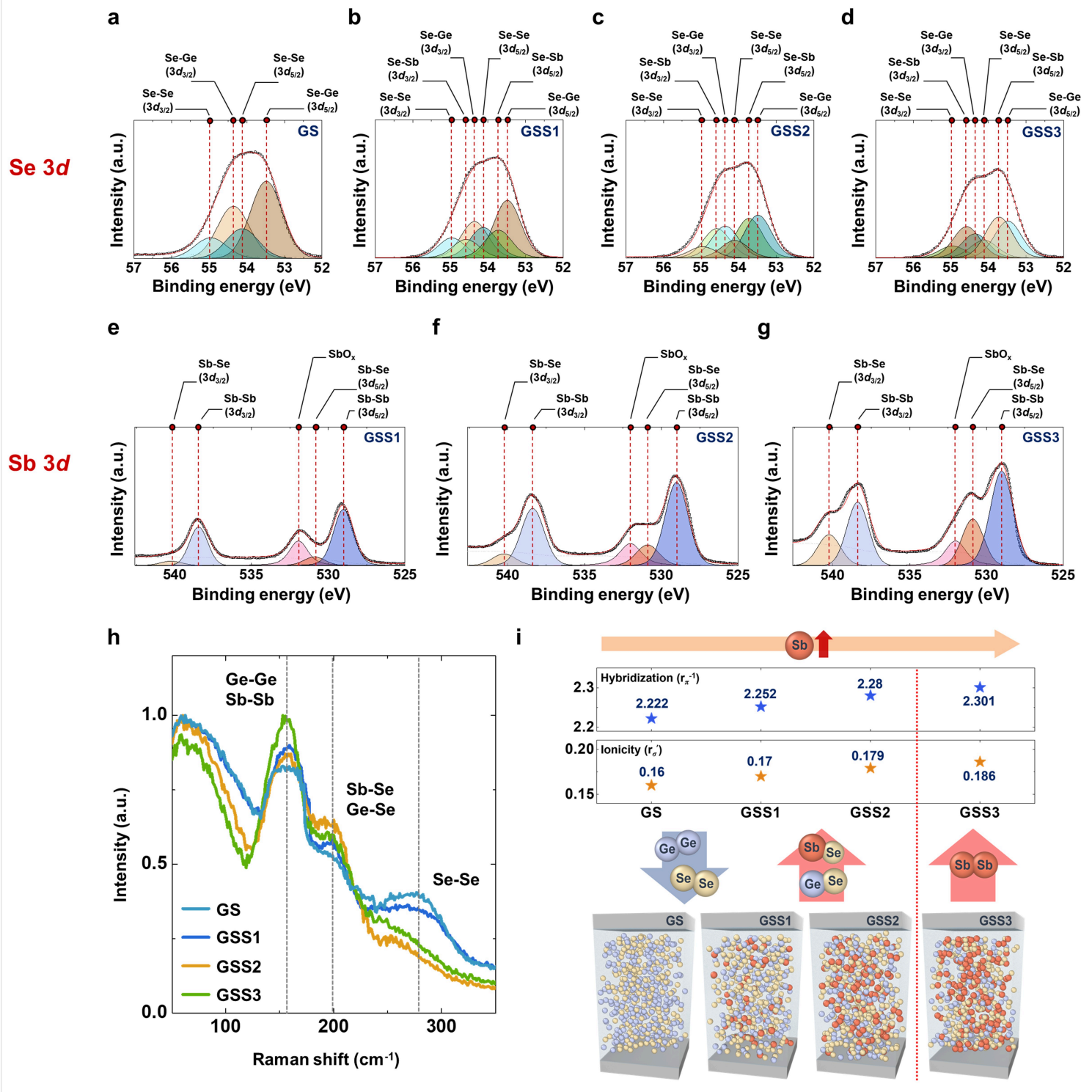


Figure 6

Sb-dependent bonding evolution revealed by XPS and Raman analyses in GS and GSS1–3 SOM devices. Se 3dXPS spectra of **a** GS, **b** GSS1, **c** GSS2, and **d** GSS3, and Sb 3d XPS spectra of **e** GSS1, **f** GSS2, and **g** GSS3. **h** Raman spectra of the four SOM devices. **i** Schematic summary of the evolution of chemical bonding configurations and the corresponding hybridization and ionicity descriptors with increasing Sb concentration.

Supplementary Files

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