Chemical Bonding Self-Organizations and Percolation Theory Applied to Minimization of Macroscopic Strain: Internal Interfaces in Non-Crystalline and Nano-Crystalline Thin Films*

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Integration of non-crystalline and nanocrystalline thin films and nanocrystalline/non-crystalline composites in devices generally requires isotropic properties, and minimization of macroscopic strain. A novel pathway for obtaining isotropic properties and strain reductions is identified. The microscopic mechanism is based on nanoscale chemical bonding self organizations such as those that occur in intermediate phases, IPs, of non-crystalline glasses and thin films. This article emphasizes the importance on internal interfacial properties and the critical role they play. This understanding has emerged from studies on qualitatively different thin film materials, such as (i) As-Se thin film photoreceptors for electro-photographic applications, (ii) thin film transistor dielectrics for liquid crystal displays, (iii) high-k replacement dielectrics for SiO$_2$ in aggressively-scaled field effect transistors, and (iv) passive thin films for optically switched memory cells. [DOI: 10.1380/ejssnt.2009.375]

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I. INTRODUCTION

The cost reductions for processing and storing information in integrated circuits have had a trickle-down effect in many other areas, including optical information storage in high density disc formats and the proliferation of lap-top computers. Many of the processing advances in Si electronics have also catalyzed similar advances in processing for other applications as well. It has long been understood that the densities of electronically active defects that limit performance, and defect precursors that limit reliability life-times in Si metal oxide semiconductor devices are directly correlated with macroscopic strain, and strain-gradients in the semiconductor substrates, and/or the dielectric film and metal films that are required for device integration. This understanding has carried over to other information storage devices. This article presents discussion of strain minimization mechanisms that are operative in thin films that go beyond the dielectrics, metals and polycrystalline semiconductor thin films of integrated circuits.

Recent research results have demonstrated that percolation processes and the application of semi-empirical bond-constraint theory provide a semi-empirical microscopic foundation for understanding relatively small ranges of compositions that exhibit low defect, and essentially strain-free intermediate phases (IPs), or IP windows in non-crystalline bulk oxide and chalcogenide glasses, and thin film oxides and chalcogenides that cannot be quenched from a liquid melt [1, 2]. One class of IP windows involves competitive double percolation in As$_2$Se$_{1-x}$ and Ge$_x$Se$_{1-x}$ binary alloys, and the pseudo-binary alloy, As$_x$Ge$_2$Se$_{1-2x}$ [1]. These IP window widths persist over an 8 to 12% composition range, and have been identified primarily by the reversible heat flow measurements of Boolchand and his coworkers [3]. The transitions for entering into, and remaining within the IP window in Ge$_x$Se$_{1-x}$ alloys involve competition between locally-compliant Se-Se dimer bonding in Ge-Se-Se-Ge groups, and locally-rigid monomer bonding in Ge-Se-Ge groups.

Thin film dielectrics and phase change memory materials are also addressed in this article, and compositions with minimal strain, and low defect densities have been identified by electrical measurements and spectroscopic techniques [6, 7], rather than the reversible heat flow approach of Boolchand and coworkers [3]. The conceptual framework developed by Lucovsky and Phillips to understand chemical bonding self-organizations (CBSOs) in chalcogenide and oxide glasses that result in macroscopic strain-reduction in IPs in bulk glasses is applied to strain-reduction in a broader range of thin film materials.

II. SEMI-EMPIRICAL BOND CONSTRAINT THEORY

References [8] and [9] have established important connections between (i) local and atom-specific chemical bonding bond-constraints and (ii) the formation of ideal defect or free bulk glasses and non-crystalline thin films. This seminal advance in glass science and technology was based on a semi-empirical bond constraint theory, SE BCT, that used a mean-field description of average atomic bond coordination, and bonding constraints. This theory explained the ease of glass formation in technologically important compounds such as As$_2$S$_3$ and SiO$_2$. SE BCT is mean-field approach that is based on the average atomic bonding coordination, $r_c$, and the average number of valence bond stretching and bending constraints/atom, $n_c$. It provides a simple quantitative criterion that separates

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chalcogenide and oxide compounds and/or binary alloys in general, into good, and poor glass formers.

A value of \( n_c \) equal to the network dimensionality of 3 provides a criterion for creating a continuous random network that allows relatively easy glass formation by quenching from a melt. This value of \( n_c = 3 \), also provides the basis for separating chalcogenide and oxide alloy compositions for into three different compositional regimes. Based on 2-body bond-stretching and 3-body bond-bending forces there is a linear relationship between \( r_c \) and \( n_c \), with a value of \( n_c = 3 \) corresponding to \( r_c = 2.4 \) [8, 9]. Alloy compositions with \( r_c < 2.4 \) and \( n_c < 3 \) are under-coordinated and designated as floppy. Alloys compositions with \( r_c > 2.4 \) and \( n_c > 3 \) are over-coordinated and designated as stressed-rigid. Ideal bulk glasses and thin films have values of \( r_c = 2.4 \) and \( n_c = 3 \). This simple description applies to several aspects of glass formation in Ge(Si)\(_2\)Se\(_{1-x}\) alloys [3]; however, instead of an abrupt transition between floppy and stressed-rigid bonding, there is an extended composition range in which mean-field theory does not apply, and in which glass formation persists and macroscopic strain is minimized. This regime has been identified by a reversible heat flow between alloy compositions, \( x_r(1) = 0.2 \), and \( x_r(2) = 0.26 \). This regime has been designated as an intermediate phase or IP by Boolchand [3].

Boolchand noted that a mean-field theory for constraint counting does not apply within an IP window, and that this region was instead characterized by unspecified chemical bonding self-organizations (CBSOs). SE BCT correctly identified the composition at which the IP began, but did not explain why the IP window terminated abruptly at \( x_r(2) = 0.26 \).

This article addresses these issues, providing a simple and elegant way to (i) understand the nature of the CBSOs that minimize macroscopic strain, and thereby (ii) predict the IP window boundaries and widths for a majority of the alloys studied by Boolchand and coworkers, as well as other IPs identified through electronic property studies [7]. The theory, as originally proposed is oversimplified, and requires (i) two modifications to constraint counting that go beyond the valence forces of Phillips in Refs. [8] and [9] [10, 11], and (ii) a specification of the chemical bonding self-organizations that give the IPs their interesting and unique properties, e.g., minimal strain, and low defect densities. The nano-scale for this CBSOs has been estimated from CBSOs that take place in Zr and Hf silicate thin films [12, 13]. Combined with the percolation theory criteria in Refs. [4] and [5] to these clusters, it can be shown that in fraction of atoms at the interfacial boundary between the locally-rigid ZrO\(_2\) or HfO\(_2\) in which locally-rigid ZrO\(_2\) or HfO\(_2\) nanocrystallites, approximately 2 nm grain size, that are encapsulated and completely separated by locally-compliant and connected SiO\(_2\). At higher concentrations, >40-50% Zr(Hf)O\(_2\), there are increases in nano-grain size, and insufficient SiO\(_2\) to encapsulate completely these larger nano-grains. As a result, these CPS compositions are no longer within an IP window analogue. There is an inversion of the two materials for alloys with concentrations of Zr and Hf ~75%, and this will be addressed later on in the text. By applying the percolation criteria in Refs. [4] and [5] to these clusters, it can be shown that in fraction of atoms at the interfacial boundary between the locally-rigid ZrO\(_2\) or HfO\(_2\) and locally-compliant SiO\(_2\) meets a percolation criterion for a compliant interface. For example, it we take a cube of ZrO\(_2\) or HfO\(_2\) 2.5 nm on edge, and fill it will 0.25 nm smaller cubes representing individual ZrO\(_2\)/HfO\(_2\) primitive units, then ∼50% of the these cubes are on the surface of this cube. These cubes are bounded on one or more faces to the constrained bonding within the cube, and on the remaining faces by the compliant bonding of the network they are surrounded by so that the resulting interface is compliant. Smaller, and larger cubes comprised of the same primitive units do not meet the percolation criterion, leading to a natural length scale of 2.5 nm.

A model that includes this type of CBSO is now developed and applied to representative IP phases identified by Boolchand et al. [3], as well as others that have been identified in electronic chalcogenide, oxide, and nitride materials [7, 11]. This model correctly describes and predicts IP window widths in chalcogenide binary, and pseudo-binary alloys addressed below, as well as IP windows in the thin film electronic materials.
IV. APPLICATION TO $\text{Ge}_x\text{Se}_{1-x}$ BULK GLASSES

The IP window for $\text{Ge}_x\text{Se}_{1-x}$ extends from a first transition at $x_c(1) = 0.20$ to a second transition at $x_c(2) = 0.26$ [3]. *Looking into the IP window* from the respective floppy and stressed rigid alloy regimes wherein mean-field theory applies, the first transition threshold is at $x_c(1) = 2.4$ bonds/atom, and $n_c(1) = 3.0$ constraints/atom, and the second transition threshold is at $x_c(2) = 2.52$ and $n_c(2) = 3.34$. The $n_c(2)$ value takes into account both corner sharing (CS) and edge sharing (ES) $\text{GeSe}_4/2$/tetrahedra [3]. Since $n_c$ is larger than 3 throughout the IP regime, mean-field theory cannot be applied and must be replaced by a non-mean field approach based on CBSOs [1, 2].

There are two conditions that must be satisfied for entrance in an IP window. As noted above, the mean-field criterion of $n_c = 3$ at the first transition has no meaning within the IP regime in which strain reducing CBSOs take place; it simply heralds the entrance into the IP window. The additional condition that must apply within the IP is that either site and/or volume percolation of a compliant bonding arrangement, or a larger molecular bonding arrangement must be present to eliminate macroscopic strain [4, 5].

The compliant local bonding arrangement in $\text{Ge}_x\text{Se}_{1-x}$ alloys is $1/4\text{Ge-Se-Ge}_1/4$, and the rigid local bonding arrangement is $1/4\text{Ge-Se-Ge}_1/4$ [1]. These arrangements correspond respectively to $\text{GeSe}_4/2\text{Ge}_2\text{Se}_8$, and $\text{GeSe}_2/2\text{Ge}_2\text{Se}_{33}\text{Se}_{67}$. The first issue is to establish the $\text{GeSe}_4$ concentration at the entrance into the IP is above a site percolation limit of 0.428 that applies for a 3-dimensional lattice, or network of tetrahedrally-bonded Ge-atoms [5]. If the bonding at the entrance to the IP is statistical, including $1/4\text{Ge-Se-Ge}_1/4$, $1/4\text{Ge-Se-Ge}_1/4$, then the compositional weighting factors are 1, 2 and 1 respectively, and the fraction of $1/4\text{Ge-Se-Ge}_1/4$ is 0.5 and above the site percolation limit. Paralleling the CPS in Zr and Hf silicates [9, 10], we assume that CBSO in this alloy is into local rigid clusters with a $\text{GeSe}_2$ composition, and with a nano-scale dimension of 2-3 nm, and these are encapsulated by a continuous, or connected network with a $\text{GeSe}_4$ compositions. The scale for this separation is assumed on the basis of analogy with bonding and CPS in Zr and Hf silicates as discussed above. Nano-scale phase separation would then provide the strain-reducing compliant interfaces required to explain the unique properties of the IP regime.

If the bonding is statistical upon entrance into the IP, then as the Ge content is increased the $1/4\text{Ge-Se-Ge}_1/4$ bonding environments will be depleted initially. This will be followed by *competitive double percolation* between $1/4\text{Ge-Se-Ge}_1/4$ and $1/4\text{Ge-Se-Ge}_1/4$ bonding, or equivalently, $\text{GeSe}_2$ and $\text{GeSe}_4$ groups [8]. This competition persists, with the alloy remaining macroscopically compliant until the concentration of the compliant bonding drops below the percolation limit of 0.428 [4]. This occurs at a value of $x_c(2) = 0.259$, and is in excellent agreement with Boolchand measurements [3]. A test of the universality of this model has been to demonstrate that it also applies to $\text{As}_2\text{Se}_{1-x}$ where additional constraints must be considered. This is indeed the case as addressed in Ref. [1].

V. IP WINDOWS IN REPRESENTATIVE THIN FILMS

The discussion in Section 4 was based on results for bulk-quenched glasses, all of which passed through their respective glass transition temperatures. This is crucial in the identification of IP windows, as well as the floppy and stressed-rigid alloy regimes that bracket them [3]. The situation is qualitatively different for thin films deposited at temperatures at which there may be insufficient mobility of the constituent atoms to self-organize in the lowest strain state since this state will generally require CBSOs with nano-scale clusters with ~2 nm dimensions. Therefore, the concept of a Boolchand IP may therefore have validity for films that have received a post-deposition anneal at, or close to a glass transition temperature. This constraint is well understood in thin film device technology, and generally properties of thin films required for a particular device functionality are qualitatively different from those as-deposited at lower temperatures.

Two qualitatively different changes can take place on thermal annealing: i) changes in the chemical composition of the film, e.g., loss of hydrogen from hydrogenated amorphous Si deposited at room temperature and annealed at 400°C, and/or ii) chemical bonding self-organizations that mandates CPS that involves clustering at a nm-scale. These concepts are applied to chalcogenide and nitride alloys. Similar considerations also apply to oxide and oxyxinitride alloys, including quaternary as well as ternary alloys as addressed in Ref. [6].

The first example is anecdotal and included for historical perspective since one of the authors (GL) was at the Xerox Corporate Research Center in Webster, NY, when this research was performed. It is based on the use of As-Se alloy photoreceptors for copying, i.e., xerography [16]. These alloys extend the spectral response from the *green* (∼540 nm) for a-Se, into the *red* (∼628 nm) region of the visible spectrum, as well as improving the resistance to crystallization by raising the glass transition temperature [17, 18]. Low As-concentration alloys up to at least 10% As in Se could be deposited at room temperature, and annealed close to their respective glass transition temperatures, $T_g$, to give photoconductivity levels adequate for commercialization. Alloys with 25 to 30% As showed some photoconductivity as-deposited at room temperature, but depositions, or annealing at temperatures close to $T_g$ resulted in significantly decreased in photo-response. The situation was qualitatively different when the alloys compositions extended to the stoichiometric composition of 40% As or As$_2$Se$_3$. These alloys showed excellent photo-response and have been commercialized. Why were the alloys dead within the 25-30% As alloy regime, and not at 40% As? The ∼30% compositions were chosen because they corresponded to a region in which $T_g$ and red response were expected to increase; this was deemed ideal for xerographic applications [16].

After 40 years, this issue is finally resolved by the results presented above. The IP window in the As$_2$Se$_{1-x}$ alloy system extends from $x_c$ ∼0.29 to 0.33, and in this IP window there is CPS into a locally-rigid As$_2$Se$_3$ compo-
The next alloys considered are thin film a-Si:N:H gate dielectrics as-deposited at 300°C for thin film transistors (TFTs) in liquid crystal displays [7, 19], and after high temperature annealing at 900°C for Si field effect transistors (FETs) for CMOS applications [19]. For a-Si:N:H alloys plasma-deposited at low temperature, 300°C, the source gas ratio, \( R = \text{NH}_3/\text{SiH}_4 \) determines the relative concentrations of Si, N, and H in the deposited thin films at that substrate temperature. \( R = 2-7 \) gives sub-nitride films with Si-Si bonds with N-Si ratios < 1.3, and H bonded predominantly in Si-H groups [19]. A higher source gas ratio, \( R = 12-15 \) gives films with N-Si ratios > 1.6 no detectable Si-Si bonding, and with H bonded initially in Si-NH groups, and eventually in SiH groups as well. There is a narrow range of source gas ratios, \( R = 10 \pm 0.5 \), with N/Si ratios of \( \sim 1.5 \pm 0.05 \) in which the H atom incorporation is predominantly in Si-NH groups. It is in this narrow range of compositions that the current drive, and electron channel mobilities in TFT devices display their highest values, and provide switching speeds that are ideal for liquid crystal displays, as in laptop computers [20].

By calculating mean field values of \( n_c \) for a-Si:N:H films for source gas ratios between 2 and 13, a narrow regime of alloy compositions has been identified at which the 300°C deposition gives an IP. This occurs for 11 > \( R > 9 \), and is bracketed between a floppy regime for \( R > 11 \), and stressed-rigid regime for \( R < 9 \). Mean-field values of \( n_c \) and, and \( n_c \) confirm that local bonding is compliant at the entrance into the proposed IP. An alloy composition obtained for \( R \sim 10.5 \) has a composition ratio Si:N:H equal to \( \sim 0.30:0.40:0.30 \), with an uncertainty of \( \pm 0.02 \), and \( r_c = 2.7 \pm 0.05 \), and \( n_c = 3.05 \pm 0.1 \).

Infrared spectra indicate predominantly N-H bonding arrangements at this composition, and 75% of the N-atoms, or equivalently \( 0.3 \) N-H groups are functionally equivalent to bridging O-atoms in Si-O-Si arrangements in SiO\(_2\), and are incorporated in bridging arrangements as well. More importantly, these N-H groups are interconnected through H-bonding between N and H atoms of nearest neighbor Si-N-H bonding arrangements. This H-bonding gives rise to \( \sim 15-17 \% \) compliant bonding that satisfies the requirement for a volume-percolation fraction at the Scher-Zallen [4, 5], and hence, the stress-free condition that reduces defects and gives a strong peak in the mobility as a function of N-H content.

As demonstrated in Ref. [19], annealing films at 900°C prepared for the same range of source-gas ratios noted above, releases H from H-N bonds that are interconnected through H-bonding [21]. Bulk trapping levels are reduced in films with \( \sim 15-17 \% \) H to levels where defect densities are sufficiently low for applications as thin film dielectrics in CMOS devices [21, 22]. The concentrations of bonded-H in NH groups in these annealed films, \( \sim 15-17 \% \), and is at the volume-percolation threshold for stress relief. This is then first example wherein local stress relief in as-deposited films is sufficient for one technological application, e.g., gate dielectrics for TFTs, and a more extended stress relief, based on percolation by a larger strain reducing molecular structure, Si-NH bonds and the atoms that encapsulate these Si-NH bonding groups after 900°C annealing, is ideal for another application as well.

VI. COMPLIANT NANO-CRYSTALLINE FILMS WITH NONCRYSTALLINE EMBEDDED CLUSTERS

A. Passivation Layers optical Memories

The ReWritable (RW) requirement for optical memories for CDs and DVDs requires that ZnS-SiO\(_2\) protective layers encapsulate the optically switched non-crystalline Ge\(_2\)Sb\(_2\)Te\(_5\) alloy (see Fig. 1). The ZnS-SiO\(_2\) protective layers must be stable at temperatures for write and erase cycles, and the crystallization of a non-crystalline Ge\(_2\)Sb\(_2\)Te\(_5\) alloy be reversible and produce sufficiently large changes in reflectance between amorphous and crystalline states to give reliable binary coded information. ZnS-SiO\(_2\) layers with \( \sim 20 \% \) SiO\(_2\) have an index of refraction approximately equal to the square root of that of Ge\(_2\)Sb\(_2\)Te\(_5\), \( \sim 2 \) compared with 4. The optical thickness of the bottom layer is \( \sim 1/4 \) of the wavelength of the laser photons used for reading, providing good anti-reflecting properties. The thickness of the upper layer is \( \sim 1/2 \) of the wavelength of the same photon wavelength, providing a strong back reflectance. The protective ZnS-SiO\(_2\) layers are diphase mixtures of nano-grains of nanocrystalline ZnS with \( \sim 2 \) nm SiO\(_2\) inclusions [23]. The isotropic character of this film is a direct consequence of (i) the isotropic or average cubic properties of the nanocrystals, and (ii) the minimization of macroscopic strain by the volume fraction of SiO\(_2\) inclusions being above the critical concentration for percolation of a compliant elastic response. This diphase mixture minimizes local bonding and macroscopic strain within the ZnS layers, limiting the size of the ZnS nano-grains to \( \sim 2 \) nm, a length scale too small to form the stable wurzite phase with a larger unit cell to provide the c- to a-relationship for an optimized wurzite structure.
Wurtzite crystallites are intrinsic uniaxial, and this would scatter the laser light used to read and write optical disc. In addition, the ZnS-SiO$_2$ layers are stable to temperatures higher than those used in cycling, to at least $\sim$600-620°C, because the melting temperature of SiO$_2$ is $>1000$°C.

**B. Phase-separated high-K silicate Alloys**

The resonant O K$_1$ edge x-ray absorption spectra in Figs. 2(a) and 2(b) illustrate respectively that nano-grain size in transition metal elemental oxides, e.g., HfO$_2$, can be controlled by (i) deposition onto a non-crystalline interface thin ($\sim$0.6 nm) Si–O–N interface passivation layer on Si, followed by annealing at $>700$°C in Ar, with film thickness in the nano-scale regime of 0.15 to 3 nm providing a dimensional constraint to grain-growth, and (ii) deposition and annealing in Ar over a sufficiently wide temperature range to demonstrate a kinetic constraint [24]. Combined with high resolution transmission electron microscopy (HRTEM) imaging these measurements have identified two different regimes of nanocrystallinity separated by a gap in which mixed nano-crystallinity exists, i.e., a diphasic nano-grain size regime.

Length scale determinations are based on $\pi$-bond coupling of band-edge TM d-states; the threshold for this coupling is about 5–6 primitive unit cells (PUCs), or $\sim$3 to 3.5 nm [24]. This coupling is manifested in cooperative Jahn-Teller distortion which generates a larger unit cell, $\sim$5-6 nm, and requires from 5 to 7 cells to establish coherent $\pi$-bonding and thereby a qualitatively different nano-structure in which $\pi$-bonding coherence is suppressed.

There are direct correlations between a $\pi$-bonding coherence, and the pinning of O atom divacancies at grain boundaries; these have been detected spectroscopically and explain the electron and hole trapping that limit device applications. In contrast, smaller nano-grain sizes between about 1.5 and at most 2.5 nm, suppress $\pi$-bond coupling and thereby reduce grain-boundary divacancy defect density and offer one solution to device applications [24].

Figure 3 indicates second mechanism that suppresses the formation of compound unit cells in TM oxides. These include diphasic mixtures of TM oxide, in this case nanocrystalline HfO$_2$, and non-crystalline SiO$_2$ [24, 25]. For a 80%-20% HfO$_2$-SiO$_2$ mixture, there is no detectable J-T splitting of the HfO$_2$ band edge d-states, but rather a sharpening of the band edge spectral features as the film thickness is increased from 2 nm to 4 nm, consistent with the a length scale of $\sim$3 nm for $\pi$-bond coupling being constrained by the diphasic nature of the film. In the 80% HfO$_2$ alloy, The SiO$_2$ nano-clusters that limit HfO$_2$ grain size are inclusions are uniformly distributed and reduce strain, as well as band edge defect contributions to the total energy. In a 20% HfO$_2$ alloy, the nano-grains are encapsulated within a non-crystalline SiO$_2$ matrix, and their nano-grain size is $<3$ nm, suppressing coherent $\pi$-bonding, and thereby reducing the total energy as well. The 20% concentration is above the threshold Scher-Zallen concentration of 16%.

![X-ray absorption spectroscopy O K edge spectra for Hf silicate films with 80% HfO$_2$ deposited on SiON/Si(100) and phase-separated by annealing at 900°C.](http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/))
VII. SUMMARY

Integration of non-crystalline and nanocrystalline thin films in device heterostructures generally requires isotropic properties, and the minimization of macroscopic strain. This provides device functionality, and ensures device reliability as well. A novel pathway for obtaining isotropic properties and strain reductions has been identified and discussed. The microscopic mechanism is based on nanoscale chemical bonding self mechanisms such as those that occur in intermediate phases, IPs, of non-crystalline glasses and thin films. This article emphasizes the importance on internal interfacial properties and the critical role they play. This understanding has emerged from studies on qualitatively different thin film materials, such as (i) As-Se thin film photoresistors for Xerographic electrophotographic applications, (ii) thin film transistor dielectrics for liquid crystal displays, (iii) high-K replacement dielectrics for SiO2 in aggressively-scaled field effect transistors, and (iv) passive thin films for optically switched memory cells.

Note added in proof

Length scales for short and intermediate range order, and the phase-separated nano-structures of this paper differ by about an order of magnitude: from 0.15 to 0.3 nm to 2 to 3 nm, respectively [1, 2, 5, 26]. This note provides a theoretical understanding of these differences, by using ab initio quantum chemistry bonding symmetries to address the first sharp diffraction peak, FSDP, in SiO2, and chalcogenide glass alloys, GexSey. Interatomic atomic pair correlation distances identify length scales for diffraction features [5, 26]. Values of $Q(A^{-1})$ for SiO2 indicate coherent bonding length scales for intermediate range order of ~0.4 and 0.6 nm. It was noted in Ref. [27], that the value of ~1.52 $A^{-1}$ for SiO2 correlates with Si–O pair distances; however, no theoretical basis was presented for the narrowing of the FSDP. Coherent length scales for FSDP bonding correlations, based on calculations, require that Si and O atomic basis sets extend beyond the s and p valence states of the constituent atoms, and include Si d-state symmetries as well. Inclusion of d-state symmetries are crucial in identifying symmetry-driven constraints that narrow Si–atom/second neighbor O-atom pair correlations, predicting the same FSDF $Q(A^{-1})$ for SiO2, and the Na and Li silicates [1, 2, 26].

Values of $Q(A^{-1})$ for Ge, Si, and As chalcogenides are smaller, ~1.0 to 1.3 $A^{-1}$, and are also based in part on $\pi$-d$^*\sigma$ bonding coupled indium symmetries. Combining $\pi$-d$^*\sigma$ bonding symmetry, and minimal Se non-bonding pair overlap, the value of $Q(A^{-1}) = 1.2 A^{-1}$ for low Ge content alloys ($\chi$~0.15) is consistent with a Ge-Se-Se-Ge third nearest neighbor distance [28]. The approximately linear decrease of $Q(A^{-1})$ to 1.0 $A^{-1}$ for alloys at the compound composition Ge3Sc2 ($\chi$=0.33) is consistent with a symmetry-driven correlation length that increases on average to a Se-Ge-Se-Ge fourth neighbor distance. Minimization of overlap between Se non-bonding pairs on each Ge atom in a more dense network structure is the significant factor in increasing this coherent length.

Length scales for strain-reducing chemical bonding self-organizations in this paper for chalcogenides are qualitatively different. They are not associated with symmetry driven aspects of the electronic structure that rely on $\pi$–d$^*$ bonding, but instead that are associated with incoherent longer range bonding in larger clusters, and as such they do not give rise diffraction signatures.

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