NON-CRYSTALLINE OXIDES AND CHALCOGENIDES: A NEW PARADIGM
BASED ON AB INITIO QUANTUM CHEMISTRY CALCULATIONS FOR
SHORT RANGE ORDER AND PROPERTIES, AND BOND-CONSTRAINT
THEORY FOR NETWORK CONNECTIVITY, NETWORK DISRUPTION
AND CHEMICAL PHASE SEPARATION

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The bonding and properties of non-crystalline chalcogenide glasses and thin films are compared with those of non-crystalline bulk glass and thin film oxides. This approach provides a methodology for understanding some of the more important applications of chalcogenides in the context of significant qualitative similarities and quantitative differences between these two classes of technologically important non-crystalline solids. The theoretical foundation for comparisons is two-fold: i) ab initio quantum chemistry calculations on small clusters to study short range order and properties dependent on this scale of order, and ii) bond constraint theory to identify the effects of network connectivity and bonding constraints. This approach is first applied to infrared effect charges and differences in the photo-structural network response between As$_2$S$_3$ and GeS$_2$. The methodology is then extended to comparisons between thin film silicate alloys, and their chalcogenide counter-parts, with emphasis on understanding the broader range of reversible memory and transport behaviors in the chalcogenide films and glasses. Finally, self-organization is addressed in oxide and chalcogenide thin films, providing the basis for device applications. These include ternary silicate alloys with irreversible self-organizations that are enabling for gate dielectrics, as well reversible self organizations in GeTe-Sb$_2$Se$_3$ alloys for information storage in read/write optical memories.

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1. Introduction

A major distinction and disconnect has evolved in the field of non-crystalline solids between experimental and theoretical studies of oxides and chalcogenides, primarily due to differences in the respective materials that have been exploited in important applications. Many of the more significant applications of oxides have been in bulk glass silicate alloys with control of the index of refraction for optical components being one of the more important areas addressed. The evolution of microelectronics has broadened the applications of oxides significantly, including thermally-grown SiO$_2$ as a gate dielectric, and thin film SiO$_2$ alloys with silicon nitride (Si$_3$N$_4$), P$_2$O$_5$ and B$_2$O$_3$ playing important roles in the evolution of integrated circuit technology. Advanced microelectronic applications have recently focused on transition metal (TM) and lanthanide rare earth (RE) atom oxides as replacement dielectrics for thermally grown SiO$_2$.

In marked contrast, many of the important applications of the chalcogenides have either been in thin film or thick film structures that involve photo-conducting or semiconducting properties, and more recently reversible bonding transitions that are important for information storage and manipulation.

This article will not attempt to provide a comprehensive survey of applications and

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2. Ab initio calculations: SiO₂ and transition metal oxides

The ab initio calculations highlighted in this article were first applied to SiO₂ [1], using the cluster in Fig. 1(a) that includes the Si-O, and Si-Si and O-O bond lengths (or equivalently the Si-O-Si and O-Si-O bond angles) obtained from diffraction studies [6,7]. This is an excellent test of the method since there is relatively new diffraction data with regard to bond-angle distributions that can be directly compared with the calculations [8,9]. These comparisons are a more stringent test of the theoretical approach than similar comparisons for the more covalent chalcogenide glasses and films such as As₂S₃ and GeS₂ that are the primary focus of the article.

The 9-atom Si-O clusters of Fig. 1(a) are terminated either by i) Si* pseudo-atoms that preserve Si and O core levels, and dipole moments, or ii) H-atoms with essentially equivalent results. The ab initio calculations give an average Si-O-Si bond angle of 148±2°, and a bond angle distribution of ~19°±2° in good agreement with recently published results [8,9]. This distribution is significantly different from the >30° bond angle spread of Mozz and Warren [6]. The same method, applied to GeO₂, BeF₂, GeS₂ and As₂S₃, gives values of ground state properties in excellent agreement with experiment, including i) the average bond angles and bond angle distributions, and ii) the infrared effective charges for the normal mode infrared vibrations [10].

![Diagram](attachment:image.png)

Fig. 1. (a) Schematic representation of the Si-O-Si terminated cluster used for the ab-initio calculations of this paper. The Si-O-Si bond angle, \( \alpha \), is 180° in this diagram, and will be varied from 120° to 150° for the calculations. The Si* represent an embedding potential that Si core eigenvalues are correct. (b) Normal mode motions in non-crystalline SiO₂.

The electronic structure calculations employ variational methods in which an exact Hamiltonian is used, and are done initially at a self-consistent field (SCF) Hartree-Fock level with a single determinant wave function that does not include electron correlation. Following this, there is a configuration interaction (CI) refinement of the molecular orbitals based on a multi-determinant expansion of the wave function including electron correlation [1]. Based on the variational principle any increase in binding energy based on the CI refinement provides an improved solution to the calculation.

Fig. 2 presents the dependence of the total energy for SiO₂ as a function of the bond angle of the two-fold coordinated O-atom for a constant Si-Si distance of ~0.31 nm [11]. The ground state energy distribution is relatively insensitive to the dihedral angles that define the orientation of the terminating groups. More importantly, the results emphasize the importance of contributions with d-like symmetries to the Si basis set. These are equally important for Ge, S, and F, and have been included in the respective calculations [10]. It significant to note that the calculated minimum in total energy occurs at a Si-O-Si bond angle of 148±2° and is different than the 144° bond angle in Ref. 6 and 7, but approximately equal to the average bond angle determined for SiO₂ in Refs. 8 and 9.
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The IR effective charges, $e_{\text{IR}}$, $j = \text{AS, SS and R}$, have been calculated for the asymmetric bond-stretching (AS), $v_{\sigma}$, symmetric bond-stretching or (bond-bending) (SS or B), $v_{\pi}$, and out-of-plane bond-rocking (R), $v_{\nu}$, infrared active vibrations of non-crystalline SiO$_2$ [10]. Similar calculations have been made for the GeO$_2$, BeF$_2$, GeS$_2$, as well as As$_2$S$_3$, $\Delta_{\text{eff}} = \Delta_{\text{d}}/\Delta_{\text{s}}$, where $\Delta_{\text{d}}$ the change in the dipole moment for the $i^\text{th}$ normal mode displacement $\Delta_{\text{d}} \Delta_{\text{s}}$. The three orthogonal normal modes motions of O-atoms are defined with respect to the coordinate system displayed in Fig. 1(b). The normal coordinate is $y$ for the asymmetric (AS) bond-stretching vibration, and the relative motion of the O-atom is parallel to a line joining the neighboring Si-atom. The normal coordinate is $z$ for the symmetric (SS) bond-stretching vibration, and the relative motion of the O-atom is in the direction of the bisector of the Si-O-Si bond angle, $\alpha$. Finally, the normal coordinate is $x$ bond-rocking (R) vibration, and is perpendicular to the plane of the Si-O-Si bonding group. The IR effective charges have been calculated from SCF and CI calculations as a function of $\alpha$. The displacements $\Delta x$, $\Delta y$ and $\Delta z$ for the calculations were <5% of a nominal Si-O bond length of 0.16 nm. There are two contributions to the effective charges, one from the equilibrium charge distribution, $e_b$, and the second from dynamic charge redistributions, $e_{\text{CR}}$, that occur during the normal mode motions [11,12]; total effective charge, $e_{\text{eff}} = e_b + e_{\text{CR}}$ [1,10]. These $e_{\text{eff}}$ values are approximately the same for SiO$_2$ and GeO$_2$, and for GeS$_2$ and As$_2$S$_3$, and agreement with experiment is excellent for SiO$_2$, GeS$_2$ and As$_2$S$_3$. Additionally, i) the ratios of the IR dielectric functions for GeO$_2$ are also in agreement with the calculated effective charges [13], and ii) the effective charge for the symmetric stretching mode in BeF$_2$ cannot be detected by reflectivity in agreement with its very low value [14].

The same method has been applied to transition metal (TM) elemental oxides that have been proposed as alternative gate dielectrics for advanced Si devices [15]. These calculations have focused primarily on the TM d-states that contribute to the lowest energy conduction band electronic structure. Figure 3 summarizes the results of these calculations, indicating the evolution of these d-state term splittings for a i) centro-symmetry bonding environment, as in a non-crystalline thin film, ii) distorted bonding as in tetragonal and orthorhombic crystalline phases, and iii) at grain boundaries in nanocrystalline thin films. Changes in band edge states have been used to detect the transition from non-crystalline Zr-O bonding in silicate alloy to crystalline bonding in a chemically separated ZrO$_2$ phase [16].

3. Bond constraint theory (BCT)

Three aspects of BCT are summarized: i) the determination of mean field coordination, $n_c$, and bonding constraints per atom, $r_{\text{c}}$, initially also designated as $N_{\text{av}}$ and $C_{\text{av}}$, respectively [2,3], ii) the intermediate phase as applied to continuous random network structures, CRNs [4,5], and iii) the extension of bond-constraint theory to silicate and chalcogenide alloys in which the introduction of ionic alloy constituents promotes network disruption and modification [17].
Consider first $n_c$ and $r_c$. These concepts were first applied to covalent-bonded continuous random networks, CRNs in which the constituent atoms are two-, three- or four-fold coordinated, and the three- and four-fold coordinated atoms were in non-planar arrangements [2,3]. The mean-field coordination, or equivalently the number of bonds per atom was obtained by applying the 8-N rule for bonding counting, and proceeding accordingly [17]. The number of bond-stretching constraints/atom $n_{c_{\text{stretch}}}$ is given by $m/2$ where $m$ is the bonding coordination, and the number of bending constraints/atom, $n_{c_{\text{bend}}}$ is given by $2m-3$. This leads to the first important result regarding the number of bonding constraints/atom:

$$r_c(C_{\text{av}}) = 2.5 n_c(N_{\text{av}}) - 3. \quad [1]$$

Bonding of in planar arrangements reduces the number of bond bending constraints/atom to $m-1$, so that $r_c$ is modified accordingly. Applied to Si$_3$N$_4$, in which $N$ is three-fold coordinated and in a planar bonding arrangement. This reduces the number of bond bending constraints from $2m-3 = 3$ to $m-1 = 2$. Since the number of planar $N$ atoms is $n = 4$, and the total number of atoms in the molecular representation is $N_T = 7$, $r_c$ is given by

$$r_c = 2.5 n_c - 3 \cdot 0.4 n/N_T. \quad [2]$$

The number of bonding constraints, $r_c$ is then equal to 5.35, and is reduced from 5.58 before this correction was made. For two fold coordinated atoms, $2m-3 = m-1$, so that the counting is unchanged. Finally for terminal atoms, $m-1 = 0$, and there are no bond bending constraints [4,5].

For all of the examples that follow the mean field condition for the onset of stressed-rigid networks is $r_c = 2.4$, corresponding to a value of $n_c = 3$, the dimensionality of the network. In the mean-field approximation this value of $r_c$ separates a floppy or under-constrained alloy composition range, as in Ge$_x$Se$_{1-x}$, with $x = 0.2$ from an over-constrained or stressed-rigid regime of alloy compositions [4,5]. However, as has been demonstrated in Refs. 4, 5 and 18 that there is generally an intermediate phase regime that delays the onset of global rigidity through a chemical bonding self-organization [4,5]. This prevents the percolation of bond-strain until $r_c \approx 2.52$, so that there are two-transitions, instead of one as predicted by Maxwellian or mean-field theory. The first transition marks the onset of local bonding rigidity, and the percolation of bonding rigidity. The intermediate phase regime displays some remarkable properties with regard to glasses, and/or thin films in the floppy and stressed-rigid regimes that bracket it. For example, there is reversibility of heat flow as contrasted with irreversible heat flow in the both the floppy and stressed-rigid regimes [4,5].
4. Ab Initio and bond constraint theory and vibrational spectroscopy

The fundamental absorption features in the infra-red spectrum of SiO$_2$ thin films and bulk glasses are similar, and a spectrum is included in Fig. 4(a) for a thin film subjected to annealing at 900 °C in an inert gas ambient, and thereby densified [19]. The features at 450 cm$^{-1}$, 810 cm$^{-1}$ and 1075 cm$^{-1}$ are respectively the bond-rocking (R), symmetric stretching (SS) or bond-bending (B), and asymmetric stretching modes (AS) for which IR effective charges have been determined in Section 3. The Si and O terminating atoms to the cluster in Fig. 1(a) do not contribute directly to the IR effective charges or the displacements of the O-atoms and the effective or renormalized valence forces that have been applied to the model calculation [1]. The spectrum shows an additional feature that appears as a prominent shoulder on the high energy side of the AS feature and indicated by the arrow in Fig. 4(a). This was erroneously assigned to a longitudinal optical mode feature in Ref. 13; this assignment has been corrected [20]. This spectral feature is a direct result of network connectivity and is implicit in BCT, i.e., a network connectivity feature, NCF.

![Absorption spectra for as-deposited and annealed SiO$_2$](image)

Fig. 4. (a) Upper trace: infrared absorption spectra for as-deposited (300°C) SiO$_2$, and lower trace: the same spectrum after annealing at 900 °C in an inert ambient. The absorptions associated with normal mode oxygen atom motions are label AS, SS and R following the notations in the text. The feature introduced by network connectivity is labeled NCF. (b) In phase and out of phase of phase atomic motions for the SA and NCF modes in (a).

The local bonding environment in Fig. 1(b) is connected to the network through four-fold coordinated Si atoms, and these are terminated by O-atoms and Si pseudo-atoms. The atomic displacements of this additional feature have been identified in Ref. 20 which employed a Cluster Bethe Lattice (CBL) method to couple local bonding displacements of the O-atom normal modes to the rest of the network structure, emulated in this example by the CBL termination. Analysis of the results for the vibrational spectrum of GeO$_2$ that is essentially the same as SiO$_2$ with respect to the normal mode motions of the O-atoms. The CBL density of state features for the O-atom motions include in-phase and out-of-phase motions. This is illustrated in Fig. 4(b) for the SS vibration, where the O-atoms move in the same directions for the in-phase motions, and the Si-atoms are oppositely direction. In contrast, two pairs of O-atoms move in opposite directions for the out-of-phase motion, and because of the random character of the network, there are small displacements of the Si-atoms that provide the dipole moment changes for IR activity. These motions are anticipated in BCT by the constraint counting procedure that includes two bond-stretching and five bond-bending constraints for each Si atom neighbors to the O atom at the center of the cluster. In this context, BCT plays the same role in non-crystalline network solids that periodicity plays in crystals.

The vibrational spectra for Ge$_2$ and GeSe$_2$ display three features for the R, SS and AS modes have been assigned to the corresponding S- and Se-atom motions as for O-atoms in SiO$_2$. However, the ratio of the atomic displacements for S- and Se-atoms relative to Ge-atom displacements is different because of atomic mass ratios. In addition, the Raman spectrum of GeSe$_2$ indicates an additional IR feature that has been assigned to edge connectivity of GeSe$_4$ tetrahedra [20]. The SiO$_4$ tetrahedra are corner connected in non-crystalline and crystalline SiO$_2$, while the SiSe$_4$ tetrahedra of non-crystalline and crystalline SiSe$_2$ are edge-connected [4,5]. This deviation
from the edge connectivity is not anticipated in BCT, and must be addressed through calculations that address both bonding environments as in Ref. 20. This aspect of chalcogenide atom bonding is not addressed in any of the examples addressed in the remainder of this article and the reader is referred to review papers by Boolchand and coworkers for more detailed discussions [4,5].

5. Photo-darkening and photo-structural changes

The ab initio calculations have been used to determine the ground state energy, and the lowest excited singlet state for band edge transitions in As$_2$S$_3$, GeS$_2$, and GeO$_2$ that are important in reversible photo-darkening and photo-structural changes [21,22,23] The CI refinements give better solutions for the electronic structure, and this is particularly important for the lowest excited states where there are significant changes in the local bonding, e.g., bond angle increases at the S-sites ~5-10° in As$_2$S$_3$ and GeS$_2$ [24].

Fig. 5 is molecular orbital energy diagram for As$_2$S$_3$ that includes the energy of the singlet band gap transition in the annealed state, and after a photo-darkening light exposure. The minima in the ground and excited singlet states for As$_2$S$_3$ are displaced by approximately 7° in the As-S-As bond-angle. In addition, and not shown in the Fig. 5, there is rotation of the AsS$_2$ terminal cluster groups in the excited state that is essentially the same as that described in Ref. 25, which models changes in local structure by EXAFS before and after photo-darkening. The displacement of the minima in the ground and excited states of GeS$_2$ is slightly larger, ~10°, but no change in the relative dihedral angles for the orientation of the GeS$_3$ terminal cluster groups is required to optimize final state energies. The calculated singlet excitation energy for the As$_2$S$_3$ cluster differs by less than 0.5 eV from the experimental defined E$_{ab}$ band gap (energy at which the absorption constant, $\alpha = 10^4$ cm$^{-1}$), and the agreement between the energy difference of ~0.35 eV for the vertical transitions of the ground and photo-induced structurally-altered states in Fig. 5, and the photo-darkening band edge shift is also very good.

![Energy versus bond angle for the singlet ground state and first excited states for As$_2$S$_3$.](image)

The agreement between the calculated excitation energies, and their difference for GeS$_2$ is not as good as for As$_2$S$_3$, and this may be due in part to differences in local bond strain not specifically incorporated into the cluster model. As$_2$S$_3$ is an ideal glass former, or equivalently it is at the boundary for the onset of self-organization in the As-S binary alloy system, whilst the GeS$_2$ composition (33% Ge) is stressed-rigid and well removed from the Ge-Se alloy intermediate phase regime [5].

Finally, the bond angle variations for GeO$_2$ in the ground and excited states suggest a significantly reduced band edge difference of at most 0.1 eV, so that photo-darkening is not expected to be observable. Similar considerations apply to As$_2$O$_3$, where reversible photo-structural changes have not been reported [26].

For As$_2$S$_3$, the photo-structural changes following light-soaking [21] do not require intra-
molecular bond scission in agreement with the model of Ref. 22, and the bond and dihedral angle changes are effectively equivalent to the inter-molecular bond scission of Ref. 22. These elastic and completely reversible photo-structural changes are consistent with the ideality of the network structure of As$_2$S$_3$ as quantified by an average number of bonds/atom, \( n_c = 2.4 \), and more importantly by the average number of bonding constraints/atom, \( r_c = 3 \), equaling the dimensionality of the network, or atomic degrees of freedom [2-5]. As such As$_2$S$_3$ is in a regime of As-S alloy compositions in which self-organization after annealing produces strain free glasses or thin films, and aging, or equivalently photon induced intra-molecular bond scission does not occur [4,5].

The ab initio calculations for GeS$_2$ identify a similar initiating optical excitation for photodarkening, but the bond scission mechanism is qualitatively different as a result of significant local bond stress. This is consistent with an increased value of \( n_c \), 2.67 bonds/atom, and an average number of bonding constraints/atom, 3.67, that is greater than the network dimensionality of 3. Following the arguments of Refs. 4 and 5, this makes the GeS$_2$ network locally stressed-rigid, and qualitatively different than that of the unstressed or optimally constrained network of As$_2$S$_3$. It also makes it energetically favorable to relieve the additional bond strain associated with photo-induced bond angle changes through intra-molecular bond scission, rather than through elastic deformations as in As$_2$S$_3$, consistent the universal bond scission model [23].

6. Silicate and chalcogenide alloys

6.1 Zr silicate pseudo-binary and -ternary alloys

The first part of this section addresses Zr silicate pseudo-binary alloys, (ZrO$_2$)$_x$(SiO$_2$)$_{1-x}$, and the second Zr silicate pseudo-ternary alloys that include Si$_3$N$_4$ as well, i.e. (ZrO$_2$)$_y$(SiO$_2$)$_z$(Si$_3$N$_4$)$_{1-x-y-z}$. Figures 6(a) and (b) present FTIR results for Zr silicate alloys with ZrO$_2$ fractions, \( x \), equal to 0.23 and 0.5 [19]. The feature at \( \approx 950 \) cm$^{-1}$ in Fig. 6(a) for the as-deposited films is assigned to a terminal Si-O$^-$ group, an indicator of network disruption by addition of the ionic ZrO$_2$ elemental oxide into the SiO$_2$ host network. The broader Si-O bond-stretching feature in Fig. 6(b) is assigned to the SiO$_2$+ molecular ion, and indicates complete network disruption in the as-deposited film, and additionally in as-deposited Zr silicate films with higher ZrO$_2$ compositions, i.e., \( x > 0.5 \). There are significant changes in FTIR spectral features in Figs. 6(a) and (b) between the as-deposited films and films annealed at 900 °C, as well as continuous changes at intermediate annealing temperatures. The 900 °C changes are indicative of a chemical phase separation, CPS, into SiO$_2$ and ZrO$_2$. This separation has been confirmed by high-resolution transmission electron microscopy, HRTEM, imaging [27]. The FTIR spectral features change continuously over the entire range of annealing temperatures indicating bonding changes that are precursors to the CPS process that is evident after the 900 °C anneal.

![Fig. 6](image-url) Infrared absorption spectra for as-deposited and annealed Zr silicate thin films with ZrO$_2$ concentrations: (a) \( x = 0.23 \), and (b) \( x + 0.5 \).

There is no XRD detectable crystallization, except for the \( x = 0.5 \) sample after a 900 °C anneal; however, this is anticipated in alloys with \( x > 0.5 \) as well. For example, the FTIR spectra for a Zr silicate alloy with \( x = 0.61 \) in which there is network inversion with ZrO$_2$ being the major...
constituent instead of SiO$_2$, are consistent with the SiO$_2^+$ molecular ion in the as-deposited films, and CPS into non-crystalline SiO$_2$ and crystalline ZrO$_2$ after the 900 °C anneal.

Fig. 7. (a) and (c) Infrared absorption spectra of as-deposited annealed thin film Zr Si oxynitride alloys, and (b) and (d) derivative x-ray photoelectron spectra for the same as - alloys. The approximate alloy constituent compositions for (a) and (b) are (SiO$_2$)$_{0.3}$,(Si$_3$N$_4$)$_{0.4}$,(ZrO$_2$)$_{0.3}$. and for (c) and (d), (SiO$_2$)$_{0.45}$(Si$_3$N$_4$)$_{0.45}$(ZrO$_2$)$_{0.1}$.

Figs. 7(a) and (c) display FTIR spectra for two pseudo-ternary Zr(Hf)O$_2$-SiO$_2$-Si$_3$N$_4$ alloys, and Figs. 7(b) and (d) include derivative XPS O 1s core level spectra for these same alloys [28]. Spectra in Figs. 7(a) and (b) are those of an alloy with ~8.8±1% Si$_3$N$_4$, 43.8±2% SiO$_2$ and ~47.4±2% ZrO$_2$. This alloy is in effect a Zr silicate alloy, with a relatively small concentration of Si$_3$N$_4$. It displays qualitatively similar behavior to Zr silicate alloys. The FTIR and XPS spectra indicate CPS at annealing temperatures greater than 900 °C, as well as continuous changes in bonding at lower annealing temperatures. After the 900 °C anneal, there are non-crystalline SiO$_2$ features at ~1050 cm$^{-1}$ and 800 cm$^{-1}$, and a nano-crystalline ZrO$_2$ feature at ~450 cm$^{-1}$ in the FTIR spectrum. In the XPS there are two distinct spectral features after a 1000 °C anneal, indicative, respectively of SiO$_2$ and ZrO$_2$ bonding. In addition, bonding changes at intermediate temperatures have been detected in studies of the soft x-ray absorption near edge structure (XANES) of these same alloy films [29]. These indicate relatively small bonding changes for annealing temperatures to about 750 °C with no evidence for CPS, and then a significantly larger change between 750 °C and 1000 °C, with unambiguous evidence for CPS.

Spectra in Figs. 7(c) and (d) are for an alloy with approximately equal concentrations of Si$_3$N$_4$ and SiO$_2$, ~45±1% and a significantly reduced concentration of ZrO$_2$, 10±2%. This alloy is in effect a Si oxynitride alloy with equal concentrations of SiO$_2$ and Si$_3$N$_4$, and smaller ZrO$_2$ alloy fraction. After annealing, the FTIR indicates weak Si-O features which are more SiO$_2^+$-ion-like than SiO$_2$ network-like and a non-crystalline ZrO$_2$ feature. This is supported by derivative XPS that shows a single dominant feature at an energy that is significantly different from either non-crystalline SiO$_2$ or ZrO$_2$, and closer in energy to the feature in as-deposited Zr silicate with 50% ZrO$_2$, with no detectable evidence for CPS that includes SiO$_2$ and ZrO$_2$.

The data presented above can be understood in terms of i) the general concepts of BCT, cast in terms of the average number of bonds/atom, $n_b$, and the average number of bonding constraints/atom, $r_c$ [2,3], ii) the extension of BCT from continuous random networks (CRN) to disrupted networks with silicates being the prototypical examples [30], and iii) the competing factors
of bond energy (enthalpy) and configurational entropy that determine local atomic bonding, and morphology of multi-component oxides.

These three concepts are described in three theorems, and associated corollaries, and build on the ideas developed in Section 3.

I: A value of $r_0 = 3.0$ equal to network dimensionality separates an alloy system into 2 regimes: (a) a floppy, or compliant regime for $r_0 < 3$, (b) an over-constrained or stress-rigid for $r_0 > 3$, $r_0 \sim 2.5 n_0 - 3$, with minor changes that reduce the bond-bending constraints at planar bonding sites such as N-atoms as in Si$_3$N$_4$ [2,3].

Corollary I(a): The density of bonding defects over-constrained networks is proportional to $[r_0 - 3]^2$, where the bond-bending constraints are broken by bond-strain [31].

Corollary I(b): Bond-strain is relieved by formation of chemically-ordered intermediate phases [4,5], which can occur over limited ranges of alloy compositions, or at buried interfaces.

II: For silicates with ionic oxides, e.g., Na$_2$O and ZrO$_2$, $n_{metal}$ is equal to the number of Pauling resonating single bonds/atom or chemical valence, 1 for Na and 4 for Zr, and not the actual coordination of 4 for Na, or 8 for Zr [30].

Corollary II(a): In low concentration silicates, where there is not significant network disruption, dative bonds are formed between the metal atoms, and non-bonding pairs on bridging O-atoms of the host SiO$_2$ CRN, restoring the bond-bending constraint of the O-atoms of an ideal SiO$_2$ CRN [32].

III: Network disruption is described in terms of the concentration of corner-shared SiO$_{4/2}$ tetrahedra. It is dependent on the concentration and primary valence of the ionic oxide additive(s) to the SiO$_2$ network [33].

Corollary III(a): The distribution of different corner-shared SiO$_{4/2}$ tetrahedra is statistical.

Fig. 8(a) describes network break-up in terms of shared corners/Si atom, C$_s$, versus metal oxide concentration; the oxide formula in one metal atom representation, e.g., Na$_2$O, is given by NaO$_{1.5}$. $C_{ox}$ equals 2[$C_{ox} - C_{MRB}$], $C_{ox}$ is the oxygen atom concentration, and $C_{MRB}$ is the concentration of resonating single bonds/metal atom. For (ZrO$_2$)$_x$(SiO$_2$)$_{1-x}$, $C_{ox}$ = 2, and $C_{MRB}$ = 4$x$, so that $C_s$ = [2 - 4$x$]. For $x = 0$, $C_s$ = 4, for the ideal corner-connected SiO$_2$ CRN, and for $C_s$ = 0.5, $C_s = 0$ for the completely disrupted network of Zr$^{4+}$ ions and SiO$_{4+}$ molecular ions. (NaO$_{1/2}$)$_x$(SiO$_2$)$_{1/2}$ corresponds to Na$^{+}$ ions and SiO$^{5-}$ molecular ions, fully ionized limits for Ca$^{3+}$ and Y$^{3+}$ follow similar patterns [33].

The conclusions to be drawn from Fig. 8(a) are: i) metal atoms of ionic oxides disrupt or break-up the network connectivity, by converting bridging O-atoms in Si-O-Si arrangements to terminal ionic groups, SiO$^{1+}$; ii) number of terminal groups equals the valence of metal ion, 1 for Na, 2 for Ca, 3 for Y and 4 for Zr; iii) the connectivity of the SiO$_2$ host network is defined by shared corners, $C_s$ between SiO$_{4/2}$ units [33]; so that iv) $C_s = 4$ for a totally connected CNR network, and $C_s = 1.0$ completely disrupted network - a mixture of Si-O molecular ions and metal ions. Intermediate values of $C_s$ give different degrees of network break-up. Alloys with metal atom concentrations greater than the x for which $C_s = 0$, are inverted, with the metal oxide phase dominant, and with an increasing concentration of O$^{2-}$ ions as well Si-O molecular ions.

Fig. 8. (a) The mean-field concentration of corners, 0, 1, 2, 3, and 4, shared per tetrahedral SiO$_{4/2}$ arrangement for silicate alloys with +1, +2, +3 and +4 ionic oxide silicate additives. (b) The mean - field number of terminal SiO$^{5-}$ groups per tetrahedron as a function of alloy composition.
Fig. 8(b) indicates the statistical distribution of SiO\textsubscript{x2} units in ZrO\textsubscript{2}-SiO\textsubscript{2} alloys as a function of alloy composition, x, where 4, 3, 2, 1, or 0, is equal to C\textsubscript{x}. Results presented in Figs. 6(a) and (b) for as-deposited films are consistent with Figs. 8(a) and (b). The low concentration alloy, x = 0.23, has a terminal SiO\textsuperscript{3+} group, the ~950 cm\textsuperscript{-1} FTIR feature, whilst, the higher concentration alloy, x = 0.5 has a SiO\textsuperscript{2+} spectral feature.

Since Zr(H) silicate alloys are i) over-constrained or stressed-rigid on deposition; i.e., \( r_c > 3 \), and ii) CPS into SiO\textsubscript{2}, and Zr(H)\textsubscript{2}O\textsubscript{3} is not blocked by a congruently-melting silicate phase. CPS is determined by kinetics, and increases as the temperature passes through 900 °C, a temperature at which Si-O bond-breaking becomes increasing probable. Additionally, it is not possible to prepare Zr(H) silicate bulk glasses by quenching from a melt.

There are two ways to suppress CPS, and crystallization of the Zr(H)\textsubscript{2}O\textsubscript{3} component completely. The first method has been by post-deposition nitridation of Zr or Hf silicate alloys, but the mechanism has not been explained, nor have conditions for complete suppression been identified [34]. The spectra in Figs. 7(a) and (b) provide the critical experimental data, and help to identify the mechanism that is an extension of the model pseudo-binary silicate alloys. Consider first (Si\textsubscript{x}N\textsubscript{y})(SiO\textsubscript{2})\textsubscript{3}, pseudo-binary alloys, where Fig. 9 gives the statistical distribution of Si atoms with different combinations of O and N atom nearest neighbors. The x = 0.5 composition is optimum for gate stack applications. At this composition the majority of the Si atoms, ~42%, have 1 O and three N neighbors. There is also a chemically-ordered phase, Si\textsubscript{2}ON\textsubscript{2}, in which each Si has 3 N and 1 O neighbor.

Fig. 9. The statistical distribution of Si atom neighbors in Si oxynitride alloys, (Si\textsubscript{x}N\textsubscript{y})(SiO\textsubscript{2})\textsubscript{3}, as a function of alloy composition. These groups include 4O, 3O and 1N, 2O and 2N, 1O and 3N and 4N neighbors.

A pseudo-ternary with approximately equal concentrations Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2}, ~45%, and a significantly lower concentration of ZrO\textsubscript{2}, ~10%, shows a bonding change by FTIR and XPS between the as-deposited state, and after a 1000 to 1100 °C anneal that is clearly not a chemical separation into SiO\textsubscript{2} and ZrO\textsubscript{2}. Based on the FTIR measurements, after annealing the local bonding can no longer be described as a Si oxynitride alloy with a small ZrO\textsubscript{2} alloy content. It is better described having a Si\textsubscript{3}N\textsubscript{4} rich Si nitride alloy back-bone in which stress is relieved locally by chemical ordering at internal void surfaces which encapsulate Zr\textsuperscript{4+} ions by two Si-O\textsuperscript{2-} terminations/Si as in crystalline ZrSiO\textsubscript{3}. CPS into SiO\textsubscript{2} and ZrO\textsubscript{2} is hindered by the Si\textsubscript{3}N\textsubscript{4} rich Si nitride alloy back-bone. In contrast, the lower Si\textsubscript{3}N\textsubscript{4} content alloy, ~10%, with approximately equal SiO\textsubscript{2} and ZrO\textsubscript{2} concentrations of ~45% displays CPS into SiO\textsubscript{2} and ZrO\textsubscript{2} because the Si\textsubscript{3}N\textsubscript{4} content is insufficient to isolate the Zr\textsuperscript{4+} ions. These distinctions are supported by studies of other alloy compositions in the pseudo-ternary Zr(H)\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-Si\textsubscript{3}N\textsubscript{4} alloy systems.

6.1 Chalcogenide pseudo-silicate alloys

Pseudo-binary glasses and thin film alloys such Ag\textsubscript{5}Se\textsubscript{5}-As\textsubscript{2}Se\textsubscript{3}, and GeTe-Sb\textsubscript{2}Te\textsubscript{3}, are of interest for applications in photolithography, and read/write optical memories, respectively. BCT describes network strain, and its role in irreversible and/or reversible transitions that can be application enabling. These applications require either chemical stability, or intentional CPS. These
differences have been addressed above, focusing on applications as high-k dielectric thin films for advanced Si devices where atomically-engineered ZrO$_2$-SiO$_2$-Si$_3$N$_4$ alloys with low ZrO$_2$ concentrations are over-constrained, yet display self-organization, rather than CPS during annealing at temperatures required for process integration. As noted above, thin film chalcogenides can be i) optimally constrained CRNs with $n_c = 2.4$ and $r_c = 3$ as in As$_2$Ge$_2$-As$_2$S$_3$, As$_2$S(Se)$_2$-GeS(Se)$_2$; ii) over-constrained CRNs with $n_c > 2.5$, and with defect densities $10^{17}$ to $10^{19}$ cm$^{-3}$ as in As$_2$S(S)$_2$-GeS(Se)$_2$, GeSe(Se)$_2$-Sb$_2$Se(Se)$_2$; or iii) disrupted by ionic additions as in Ag(Na,Cu)$_2$Se-GeSe$_2$ or Ag(Na,Cu)$_2$Se-As$_2$Se$_3$, with the extent of disruption being critical for specific applications. Specific examples addressed in this article include i) comparisons of network disruption based on Na$_2$O in SiO$_2$ as a point of reference for Na$_2$S in GeS$_2$ and As$_2$S$_3$ [35,36], and ii) the effects of bond strain in the over-constrained alloys, GeTe-Sb$_2$Te$_3$, and the like, that underpin their device functionality in DVD players [37,38].

Pseudo-binary alloys of SiO$_2$ and covalent or ionic metal oxides fall into two distinct classes differentiated by i) bond ionicity, and ii) bond-constraint counting. These distinctions are based on extension of BCT from i) continuous random networks, CRNs, e.g., solid solutions of SiO$_2$ and B$_2$O$_3$, to ii) disrupted and modified silicate networks, SiO$_2$ mixed with ionic oxides (network additives) including Na$_2$O, CaO, Al$_2$O$_3$ and ZrO$_2$ [17]. CRN thin films formed by deposition and melt-quenched bulk glasses display the same local bonding and network structure, whereas for silicates, the situation is markedly different. Photo- or thermal-driven changes in thin film bonding that are device enabling are related to the state of bond-strain inherent in deposition kinetics, whereas properties of quenched-glasses may be different. The driving forces for these differences are qualitatively the same for i) SiO$_2$-ionic oxide silicates, and ii) chalcogenide alloys where As/Ge sulfide/selenide CRNs are substituted for SiO$_2$ CRNs.

Pseudo-binary SiO$_2$ CRN glasses and thin films with covalent bonding obey the 8-N rule for coordination [17]. These oxides are either optimally constrained or floppy with mean-field bond coordinations, $r_c$, of 2.4 or below. In contrast, and depending on the valence of metal, Na (+1), Ca (+2), Al (+3) and Zr (+4), thin film silicates vary systematically from floppy to over-constrained. This is reflected in the degree of network disruption and modification, and has been quantified accordingly. This has been introduced in the last section of this article in the context of trivalent and tetravalent transition metal oxide additives to an SiO$_2$ host CRN. The same approach is now applied for the first time to binary chalcogenide alloys, and the same systematics apply. It is therefore equally important to separate these alloys into different classes, based on bond-strain, combined with the degree of network disruption and/or modification.

Fig. 10 describes network break-up by the addition of the univalent metal sulfides (or selenides) such as Na$_2$S(Se)$_2$, Ag$_2$S(Se)$_2$ and Cu$_2$S(Se)$_2$ into GeS(Se)$_2$ and As$_2$S(Se)$_2$ host CRNs. Values of $C_c$, corners shared per Ge(As) atom of 2(1.5) represent significantly disrupted networks, whilst values of 1(0.75) represent completely disrupted networks with no percolation of network conductivity. The model calculation for As$_2$S(Se)$_2$ host CRN neglects S(Se) to As bonding, and which would require a significant charge redistribution as well.

Fig. 10. The mean-field concentration of Ge atom corners, $C_c$, per tetrahedral GeS(Se)$_2$ arrangement for GeS$_2$ alloys with Cu(Na,Ag)$_2$S(Se)$_2$ ionic chalcogenide additives. The mean-field concentration of As atom corners, 0, 1, 2, and 3 shared, $C_c$, per pyramidal As$_2$S(Se)$_3$ arrangement for As$_2$S$_3$ alloys with Cu(Na,Ag)$_2$S(Se)$_2$ ionic chalcogenide additives. The calculation for the As$_2$S(Se)$_2$ CRN host does not include the bonding of S(Se) atoms that can increase the coordination of As to four.
The As$_2$S(Se)$_3$ host CRN is not stressed-rigid, and the same also applies at all alloy compositions. This observation is consistent with the experimental EXAFS studies on As-Cu-Se glasses [39,40]. In marked contrast, glass formation has not been observed in GeSe$_2$-Ag$_2$Se alloys with up to ~20% Ag$_2$Se [35,36,41]. However, good glass formation has been found in this alloy system in two other composition regimes. The first includes alloys along the GeSe$_2$-Ag$_2$Se join line with Ag$_2$Se compositions <20% Ag$_2$Se. This observation is consistent with the host CRN composition i) marking the onset of local bond-rigidity and ii) defining the beginning of an intermediate phase. The GeSe$_2$-Ag$_2$Se alloys of interest are in a floppy regime, with $n_r$~2.5, and $r_c$~0.2. The second regime of good glass formation in the Ge-S(Se) system as at compositions close to Ge$_2$S(Se)$_3$. This corresponds to a second intermediate phase regime; e.g., for Ag$_2$Se ~0.1 to 0.2, $r_c$~2.6, and $n_r$~3.0.

The non-crystalline ternary alloy Ge$_2$Sb$_2$Te$_3$ has been found to give reversible changes in optical transmission, and has become the preferred materials for use in DVD read-write (R-W) optical disk applications [37,38]. Changes in local bonding associated with optical laser light pulse produce changes in transmission that are read with a weaker laser pulse [37]. Studies have explored the properties of these non-crystalline thin films by extended x-ray absorption fine structure spectroscopy, EXAFS, and x-ray absorption near edge spectroscopy, XANES, and have determined the bonding coordination and nearest neighbor bond lengths in the as-deposited and laser written films [38]. Recent, and as yet unpublished XANES data presented in this paper confirm previously published results [42], but have additionally addressed the bond-coordination in greater detail. These results have provided the basis for an analysis of thin film bonding in the context of bond constraint theory, BCT, which provides a new interpretation of the local atomic structure in the amorphous phase. This approach has been extended to other alloy compositions that are also of technological interest including the compositions, GeSb$_2$Te$_4$ and GeSb$_2$Te$_5$ that also fall on a tie-line between GeTe and Sb$_2$Te$_3$ in a compositional phase diagram. An analysis of bonding in the context of BCT, and the interpretation of our XANES data has raised significant issues relative to the short range order in non-crystalline films, and this tie-line representation [37,38].

Based on the new XANES results, bonding changes in optical memory applications have been referenced to an amorphous state including Ge$_2$Te$_3$ and Sb$_2$Te$_3$, units as well as a small fraction of three-fold coordinated Te atoms. Ge has 3.9±0.15 nearest neighbors: 3.3±0.1 Te and 0.6±0.1 Ge. In this model, three-fold Te atoms act as nucleating sites for the transition from an amorphous to nanocrystalline state, and changes in transmissivity are shown to scale directly with the fraction of these nucleation sites. The transition is less abrupt in alloys with a higher fraction of 4-fold Sb nucleation sites [37].

![Fig. 11. Reduction of transmissivity as a function of the fraction of three-fold coordinated Te atoms in the amorphous to crystalline transition in "GST" alloys along the tie-line from GeTe to Sb$_2$Te$_3".](image-url)

Based on the new XANES studies, bond-counting algorithms have been developed that apply to continuous random networks as well as non-crystalline solids in which the coordination is greater than the 8-N rule. The mean coordination, $r_c$, for Ge$_2$Sb$_2$Te$_3$ is 2.93. Based on the GeTe-Sb$_2$Te$_3$ tie-line model of Ref. 38, this composition is stressed-rigid with a mean-field number of bond-constraints/atom, $n_r$ = -4.3. An alternative model associated with a change in the local bonding of Ge from a Ge-Te$_{6/2}$ arrangement of Ge-Te, to a Ge-Ge-Te$_{6/2}$ arrangement of Ge$_2$Te$_3$ gives a
significant reduction of \( n_c \). This composition is stressed-rigid in the alternative model, but with a mean-field number of bond-constraints/atom, \( n_c = \sim 3.4 \). This includes a reduction of Ge atom bond-bending constraints associated with a change in symmetry from Ge-Te(12) to a Ge-Ge-Te(12) arrangement. In this model, \( r_{\text{eff}} \) is reduced to a value of 2.54, accounting for the ease of glass formation. In the context of the new bonding model, other GST alloys considered for optical memory applications, GeSbTe4 and GeSb2Te5, are also stressed-rigid, but reduced values of \( r_{\text{eff}} \) were applied. The three alloys discussed above contain significant concentrations of three-fold Te, ranging from 16.7% for GeSb2Te5 to 12.5% and 7.1% for GeSbTe4 and GeSb2Te5, respectively.

The most important result of the new model is addressed in Fig. 11 that contains a plot of the normalized reduction in transmissivity as a function of the fraction of three fold Te bonding sites. This plot for the amorphous to crystalline transition as determined from the results presented in Ref. 37, and is consistent with a model in which these sites act as nucleation centers for this transition.

The stressed-rigid nature of the GST films in the plot suggests that bonding changes induced by the write pulse relieve bond-stress by converting the bond-strain energy into increases in the coordination for both Ge and Te. The Ge coordination increases from 4 to 6 neighbors, and the Te coordination and bond-lengths change accordingly. In effect the transition trades configuration entropy in the amorphous state for an increase in bond enthalpy in the crystalline state.

The model proposed above is being tested by performing XANES studies for GST alloy compositions that lie on the tie line from Sb to GeSb2Te5. Determination of the number of Ge-Te, Sb-Te and Ge-Ge neighbors, as well as the number of bonds/Te and Sb atoms being made. These will then be correlated with optical transmissivity results of Ref. 37. These samples contain Sb-Sb bonds as well, and it is important to test the scaling relationship between these homopolar bond concentrations, and the crystallization kinetics.

7. Self-organization: A pathway to device applications

Thin films prepared by plasma CVD at 300 °C are addressed with respect to this issue. It will be demonstrated that in Si,NxH1-x-y alloys self-organization occurs during deposition [43], but in (SiO2)(Si,N)x/2(ZrO2)y/2 it occurs during or after high-temperature anneals at temperatures \( \geq 900^\circ \text{C} \) [28]. Thin films in the self-organized intermediate phases are used as gate dielectrics in a-Si:H TFTs and crystalline (c-) Si FETs so that it is important to address this issue.

In plasma-deposited a-Si,NxH1-x-y alloys, the source gas ratio, R = NH3/SiH4. R = 2.7 gives sub-nitride films with y/x < 1.3 and H in Si-H groups, R = 12-15 gives films with y/x values > 1.6 and H in Si-NH2 groups. There is a narrow range of gas ratios, R = 10±0.5, with y/x ≈ 1.5±0.05. This regime defines an intermediate phase between a floppy regime for R > 11, and stressed-rigid regime for R < 9.5. Minimization of bonding defects in this intermediate phase has been detected by the variation of TFT channel mobility, \( \mu \), with R. \( \mu < 0.5 \text{ cm}^2\text{V}^{-1}\text{cm}^{-1} \) for R < 8 and R > 11, but for R in a narrow regime between 9.5 and 1 \( \text{cm}^2\text{V}^{-1}\text{cm}^{-1} \), for an alloy with a composition \( \sim \text{Si}_{0.7}\text{N}_{0.3}\text{H}_{0.3} \). In this alloy \( n_c = 2.7 \), and the average number of bonding constraints/atom, \( r_c = 3.0±0.1 \). This value of \( r_c \) is an indicator of a self-organization that suppresses percolation of network rigidity, thereby reducing defects that trap channel electrons during TFT operation. The plot in Fig. 12 represents the first electrical detection of an intermediate phase.

![Fig. 12. Channel mobility of electrons in a-Si:H TFTs as a function of the source gas ratio, R = NH3/SiH4. Based on determinations of H, Si and N atom concentrations as function of, the diagram includes the identification of stressed-rigid, intermediate phase and floppy SiNH concentrations.](image-url)
Similar behavior occurs in (SiO)\(_2\)(Si\(_3\)N\(_4\))(ZrO)\(_2\) alloys deposited at 300°C and then annealed at high temperatures \(\geq 900\) °C. Alloys with approximately equal concentrations of SiO\(_2\) and ZrO\(_2\) (x~1-1-x-y), but with smaller concentrations of Si\(_3\)N\(_4\), y < x, display chemical phase separation (CPS) into non-crystalline (nc-) SiO\(_2\) and crystalline ZrO\(_2\) after annealing to 900°C, whereas alloys with approximately equal concentrations of SiO\(_2\) and Si\(_3\)N\(_4\), x-y, with x > 35%, display spectroscopic evidence for bonding changes for annealing temperatures up to 900°C, but the absence of CPS into SiO\(_2\) and ZrO\(_2\) for annealing at temperatures >900°C. These as-deposited films have mean-field values of \(n_c > 3.1\) and \(r_c > 3.85\). After 900°C annealing, alloys display chemical ordering with non-crystalline (n-c) Zr silicate groups encapsulated within a non-crystalline Si\(_3\)N\(_4\) back-bone with \(n_c = 2.77\) and \(r_c = 3.2 \pm 0.1\). These values of \(n_c\) are close to those, \(r_c = 3.0\) to 3.3, of glasses and films within the intermediate phase of Ge\(_x\)Se\(_{1-x}\) where x~0.2. Finally, it is significant to note that concurrent with CPS in the low Si\(_3\)N\(_4\) content films, there is a release of N at temperatures at which the CPS occurs. This has been detected by XAS, as well as XPS and FTIR.

![Fig. 13. Schematic representation of the bonding of Zr\(^{4+}\) ions in a “cavity” region of the Si-N backbone structure. Ionic bonds are formed with two terminal SiO\(^6\) states that are at the boundary of the cavity. Four additional bonds are made to other terminal O atom groups reducing the bond order to 0.5, and increasing the O atom coordination to three as in stoichiometric ZrSiO\(_3\).](image)

The bonding of terminal O-atoms in the (SiO)\(_2\)(Si\(_3\)N\(_4\))(ZrO)\(_2\) alloys, and terminal SiN-H and Si-H groups in the SiO\(_2\)(Si\(_3\)N\(_4\))(H)\(_2\) alloys in the intermediate phase regime are responsible for the low values of \(r_c\). A schematic representation of this bonding is displayed in Fig. 13. Low \(r_c\) is the result of functionally equivalent chemical self-organizations that prevent percolation of network stress, thereby avoiding formation of defects that would degrade TFT and FET performance.

8. Conclusions

The ab initio calculations highlighted in this article were first applied to SiO\(_2\), using a central cluster that includes the Si-O, and Si-Si and O-O bond lengths (or equivalently the Si-O-Si and O-Si-O bond angles) obtained from diffraction studies. The Si atoms at the boundaries of these central clusters were terminated by O atoms attached to pseudo-Si atoms or H-atoms. Similar clusters were constructed for As- and Ge-chalcogenides as well. After configuration interaction refinements these calculations gave an excellent description of i) the local atomic structure, ii) the infrared effective charges that are associated with the normal mode motions of the O and chalcogen atoms, and ii) band edge optical transitions before, and after light-soaking.

The effects of more distant neighbors, or equivalently the coupling between the central clusters and the CRNs in which they have been embedded has been described in terms of bond constraint theory. BCT. This formalism is based on the number of bonds/atom or mean-field coordination, \(n_c\), and the number of valence force field bonding constraints/atom, \(r_c\). This formulation provides a basis for dividing an alloy system, e.g., Ge\(_x\)Se\(_{1-x}\) into three distinct regimes with different properties: i) a floppy regime, in which \(r_c < 3\), ii) a stress free or intermediate phase regime in which \(r_c > 3\), and iii) a stressed-rigid or over constrained regime in which \(r_c > 3\). One of the most significant results of this approach has been the detection of the intermediate phase regime. This regime is bounded by two transitions: i) the first marks the onset of mean-field bond rigidity, and the ii) the second the percolation of bond-strain or rigidity throughout the entire network. Percolation of strain in the intermediate phase regime is prevented by chemical self-organization
into non-statistical bonding groups.

One of the most important contributions of this paper is related to the application of BCT for i) describing significant features in the IR spectra, and vibrational density of states determined by inelastic neutron scattering, that are not associated with oxygen or chalcogen normal mode motions, and ii) distinguishing between elastic and inelastic photo-structural changes following light-soaking. A second contribution is related to the extension of BCT to silicate and pseudo-silicate chalcogenides in which there significant network disruption and modification associated with the incorporation of ionic alloy constituents.

The second contribution quantifies network disruption in silicates and chalcogenide analogues, and then applies this approach to several important classes of thin film materials, including chalcogenides alloys for photolithographic and reversible optical memory applications, and hydrogenated silicon nitride and Zr Si oxynitride films for gate dielectric applications in amorphous Si TFTs and crystalline Si and other semiconductor FETs. In all of these applications, intermediate phases play a significant role in the functionality required for the specific applications.

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