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Strain-eliminating chemical bonding self-organizations within intermediate phase (IP) windows in chalcogenide, oxide and nitride non-crystalline bulk glasses and deposited thin film binary, ternary and quaternary alloys

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ABSTRACT

Transitions into, and out of intermediate phases (IPs) with minimal strain have been identified to date by Boolchand and co-workers, in bulk glasses, primarily by the extraordinary low values of the change in enthalpy, ΔH_{nr} , associated with non-reversible heat flow, and by Lucovsky and coworkers in deposited thin films, and at dielectric–semiconductor interfaces by combining spectrographic characterizations, primarily synchrotron X-ray absorption and X-ray photoemission, and electrical measurements. This paper emphasizes chemical bonding self-organizations that minimize macroscopic strain within the IP windows, and identifies for the first time the necessary and sufficient conditions for IP windows to open, and to close, as a function of changes in the alloy composition. Percolation theory, and in particular competitive and synergistic double percolation provide a quantification of IP window first and second transition compositions that account for many of the experimentally determined IP window threshold transitions and IP window widths identified to date.

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1. Introduction

A significant number of important research results over the past 20–25 years 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. Significant new ideas were introduced more than 25 years ago by Jim Phillips [1,2]. These referenced papers proposed a semi-empirical bond constraint theory, SE BCT, based on a mean-field description of average atomic bond coordination, and bond constraints. The theory was used to explain the ease of glass formation in several well-known and technologically important compounds including As_2S_3 and SiO_2 . In particular SE BCT demonstrated that descriptions of non-crystalline solids using the mean-field atomic coordination or average number of bonds/atom, $r_c(N_{av}, \langle r \rangle)$, and the average number of valence bonding

stretching and bending constraints/atom, $n_c(C_{av})$ provided a simple and elegant way to separate compound compositions and/or binary alloy compositions in general, into good, and marginally poor glass formers.

A value of n_c equal to the network dimensionality of three provides a criterion for ideal and relatively easy glass formation, and the basis for separating chalcogenide alloy compositions for bulk glasses into three different groups. Based on 2-body bond-stretching forces and 3-body bond-bending forces there is a linear relationship between r_c and n_c , such that a value of $n_c = 3$ occurs when $r_c = 2.4$ [1,2]. Alloy compositions with $r_c < 2.4$ and $n_c < 3$ have been designated as floppy, whilst alloys compositions with $r_c > 2.4$ and $n_c > 3$ have been designated as stressed-rigid. Ideal, or optimally-coordinated displayed values of $r_c = 2.4$ and $n_c = 3$. The only system for which this description applies without modification is the Ge_xSe_{1-x} alloy system. However, this system does not display a single transition between floppy and stressed-rigid bonding, but instead displays a composition range in which mean-field theory does not apply. This alloy regime is characterized/identified by

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very low values of ΔH_{nr} that have been found in composition range between $x_c(1) = 0.2$, and $x_c(2) = 0.26$ that has been labelled an intermediate phase or simply an IP. Boolchand, using SE BCT, noted that the first transition into the IP occurred a composition $x_c(1) = 0.2$, corresponding to $n_c(1) = 3$, and $r_c(2) = 2.4$ [3]. However, it was noted further that a mean-field theory did not apply within the IP window, but that this region was instead characterized by unspecified chemical bonding self-organizations (CBSO's). No attempt was made to explain why the IP window terminated abruptly at $x_c(2) = 0.26$. It was further suggested that $n_c = 3$ throughout the entire extent of the IP window, but this was not demonstrated by a model or simulation, and is inappropriate to apply it to a region in which there are departures from mean-field bonding, which instead are associated with non-statistical CBSO's. This paper addresses these issues head-on, and provides a simple and elegant way to (i) understand the nature of the CBSO's that minimize macroscopic strain, and (ii) predict the IP window boundaries and widths for a majority of the alloy systems studied by Boolchand and coworkers, as well as in other IP windows that have identified through electronic property studies that have identified windows in which defect densities are low, thereby reflecting an addition manifestation of macroscopic stress relief [4].

2. Modifications and additions to SE BCT

2.1. Broken bond-bending constraints

The concept of broken bond-bending constraints for tetrahedrally coordinated Si with two O and two Si bonding neighbors was first addressed by Lucovsky and Phillips [5]. Symmetric three atom bonding arrangements such as Si–Si–Si, and O–Si–O have are constrained at the tetrahedral angle of $\sim 110^\circ$. On the other hand, it is unlikely that the asymmetric O–Si–Si bond angles will be constrained to the same degree because the *local energy* gaps are associated with O–Si and Si–Si bonds are different. If these gaps are sufficiently different then the Pauling bonding resonance responsible for bond-bending forces is expected to be negligibly weak compared to the resonances responsible for the bond-bending forces associated with the symmetric Si–Si–Si and O–Si–O bond angles. Under these conditions it is appropriate to remove the constraints for the asymmetric bond angles from constraint counting, and characterize these removed constraints as *broken constraints*. In general, this reduces the number of bond-bending constraints/tetrahedrally coordinated Si or Ge from 5 to 2.5 [6,7]. Stated differently five of the six bonding angles associated with tetrahedral bonding are constrained, but the sixth is simply determined by noting that sum of these six angles equals 360° . For an asymmetric tetrahedral arrangement, Ge–Ge–Se₃, three bond angles are symmetrical, Se–Ge–Se and, three are asymmetrical, Ge–Ge–Se. Since there are only at most 5 constraints possible, it is reasonable to assume that on average the number of constraints is reduced by 50% and is equal to 2.5.

2.2. Repulsive bonding constraints

Additional constraints are associated with the relatively strong repulsive forces between the electrons in (i) lone-pair orbitals on nearest and second neighbor network As and Se-atoms in As–Se and Ge–As–Se alloys, and (ii) lone pair Se orbitals and terminal I atoms in Ge–Se–I alloys as discussed in Refs. [6,7]. One additional constraint/atom will be added to each pair of like atoms involved in a lone pair repulsion as for example pairs of As atoms separated by one Se (or S) atom. Because of the higher density of non-bonding electrons on halogen atoms compared with As, the number of constraints for each halogen atom will be increased as the square

root of the number of non-bonding pairs, or from 1 to 1.5 constraints/halogen atom.

3. Chemical bonding self-organizations

It has been noted above that mean-field theory does not apply within the IP window, and instead this region has been characterized as having as yet unspecified CBSOs [3]. It was further suggested that $n_c = 3$ throughout the entire extent of the IP window, but this was not demonstrated by a model or simulation, and in point of fact is not applicable because it is a mean-field average. This paper develops a simple and elegant way to (i) understand the nature of the chemical bonding self-organizations that minimize macroscopic strain, and (ii) to predict the IP window boundaries and widths for a majority of the alloy systems studied by Boolchand and coworkers ([3], and Refs. therein [8]).

The basis for the model derives from chemical phase separation (CPS), or equivalently a CBSO, that has been reported for Zr and Hf silicate alloys [9,10]. The predominantly ionic Zr–O and Hf–O bonds and +4 formal valence states of Zr and Hf induces a significant disruption of the SiO₂ continuous random network. Following an anneal at 900°C, there is a CPS in which locally-rigid ZrO₂ or HfO₂ nano-crystallites with an approximately 2 nm grain sized are encapsulated by locally-compliant SiO₂. At higher concentrations there is increased nano-grain growth, and insufficient SiO₂ to encapsulate the larger-sized nano-grains, and these CPS compositions are no longer within an IP window. A model that includes this type of CBSO is now applied to representative IP phases identified by Boolchand et al. [3], as well as others that we have identified in electronic chalcogenide, oxide, and nitride materials [4,11]. This model correctly describes IP window widths in chalcogenide binary, and pseudo-binary alloys with examples given below, as well as those in the thin film electronic materials. However, for the thin films, care must be taken to distinguish between bonding in as-deposited films, and films that have been subjected to annealing at temperatures that are functionally equivalent to cycling bulk glasses by cycling bulk glasses through their glass transition temperature, T_g , during scanning calorimetry studies.

4. Application to chalcogenide bulk glasses

Table 1 includes the IP windows for three chalcogenide alloy systems: (i) Ge_xSe_{1-x}; (ii) As_xSe_{1-x}; and (iii) As_xS_{1-x}. Note that the windows for the As alloys are shifted to lower values of x , relative to Ge_xSe_{1-x}, and therefore cannot be described by the original SE BCT that was based on 2-body and 3-body valence forces [6,7]. This is a direct result of the additional bonding constraints associated with repulsions between non-bonding pairs of the As and/or Se and S atoms. The difference between As_xSe_{1-x} and As_xS_{1-x} is consistent with the bond-chemistry of the compliant local bonding groups; i.e. a propensity for S-atoms to display increased catenation, i.e. SS–S bonding, more easily than Se-atoms [8]. For each alloy system, we first identify necessary and sufficient conditions, based on percolation theory and the relaxation of macroscopic strain, and the identification of the locally-compliant, and locally-rigid bonding groups that apply. The assignment of these groups includes the additional lone pair atom bonding constraints for the As alloys.

4.1. Ge_xSe_{1-x}

The IP window extends from a first transition at $x = 0.20$ to a second transition at $x = 0.26$. Looking into the IP window from the respective floppy and stressed rigid alloy regimes wherein

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