Process induced pre-existing defects in non-crystalline SiO$_2$ and GeO$_2$ at vacated O-atom bonding sites and comparisons with Ge-S(Se) alloy bonding sites

Gerald Lucovsky*, Daniel Zeller, JinWoo Kim, and Kun Wu
North Carolina State University, Raleigh NC, USA
*e-mail: lucovsky@ncsu.edu

Abstract: Three related topics are addressed in this article: (i) X-ray spectroscopy (XAS) studies of remote plasma deposited (RPD) nc-SiO$_2$ and nc-GeO$_2$ emphasizing (a) band-edge states and (b) pre-existing bonding defects; (ii) interpretation of X-ray absorption and photoemission spectra based on many electron theory, and in particular charge transfer multiplets (CTs); and (iii) band-edge electronic structure and intrinsic defects in nc-SiO$_2$ and nc-GeO$_2$ thin films and their interfaces with Si and Ge substrates. The most significant result is the identification of local atomic structure in medium range order (MRO) clusters in which the pre-existing defects are embedded. These defects are vacated O-atom sites in which O-atoms have never been resident. They are confined to 1 nm scale chemically-ordered clusters distributed non-periodically with quartz-structured 4-fold coordinated Si(Ge) and 2-fold coordinated O bonding in 12-atom regular rings. Vacated O-atom sites defects are formed during processing and annealing, and reducing macroscopic as well as local bond-strain strain. They are qualitatively different, and readily distinguished from defects introduced by electrical, and by X-ray, $\gamma$-ray or high energy electron stressing of nc-SiO$_2$ and nc-GeO$_2$.

1. Introduction
It is significant to note that ESR-active pre-existing defects detected in nc-SiO$_2$ and nc-GeO$_2$, and in Se-rich Ge$_{1-x}$Se$_x$ alloys are qualitatively different. This is due quantitative differences in medium range order (MRO) between oxides and chalcogenides. MRO is order by definition beyond the regimes of (i) bond-lengths or 2-atom atom distances, and (iii) 3-atom correlated bond-angles. S-atoms and Se-atoms form S-S and Se-Se bonds, where O-atoms do not except in peroxides which have not been detected in irradiated SiO$_2$ bulk glasses or films. MRO is correlated with d-state ligand field splittings, $\Delta$LF. These are non-zero when molecular orbital theory descriptions of valence band states in which case the number of valence band features is either 3 or more in compound and alloy oxides and chalcogenides [1]. The $\Delta$LF are energy differences in 5-fold degenerate atomic core level d-states induced by non-spherical local symmetry in the valence band structure, or in virtual bound states in the conduction band regime as well. Of particular importance are the values of $\Delta$LF associated with O-vacancy defect sites. These are split into 2-fold degenerate eg states and 3-fold degenerate t$_{2g}$ spectral regimes. This splitting is a direct consequence the non-spherical local symmetry and the medium range order (MRO) at the vacated O-atom sites [1].

Values of $\Delta$LF, in electron volts (eV), are obtained by X-ray absorption (XAS) and electron energy loss spectroscopy (EELS). The same values can also be extracted from dielectric constants obtained from a dispersion analysis of (i) reflectivity (R), and (ii) spectroscopic ellipsometry (SE) spectral data. $\Delta$LF is local symmetry, atomic coordination, and atom specific. It is equally important to distinguish the spin-orbit splitting, $\Delta$SO of the centro-symmetric core states from the final state values of $\Delta$SO' in O K edge spectra. Additionally, and of particular importance for nc-SiO$_2$, GeO$_2$, and Ge(S,Se)$_2$, a non-zero value of $\Delta$LF requires a scale of coherent-order extending up to, and generally beyond, 3rd
next-nearest-neighbors, NN. Medium range order (MRO) regime includes discrete values of dihedral angles, and correlated/symmetric dihedral angle arrangements as well. Therefore, a non-vanishing ΔLF is a spectroscopic indicator of MRO, complementing X-ray and neutron diffraction determinations of the position, and width of the first sharp diffraction peak (FSDP) in reciprocal space [2]. This approach to MRO provides a significant and direct connection with the existence of pre-existing ESR active defects in nc-SiO₂ and nc-GeO₂ as well.

2. Medium Range Order in Non-crystalline Oxides

MRO regime bonding correlations are obtained from the position FSDP in the structure factor from X-ray or neutron diffraction [2,3]. MRO correlation lengths, λcorr, are 0.4 nm in SiO₂ and GeO₂ [2,3] and extend to ~0.65 nm in GeSe₂ [2,3,4]. These are in the nm-regimes of 3rd and 4th NN distances. The coherence length, λcoh, for molecular cluster formation is calculated from the width of FSDP and is beyond the MRO regime. For example, λcoh, is ~1 nm in Si(Ge)O₂ [3] and increases to ~2.9 nm in GeSe₂ [4]. These clusters are non-periodically-distributed in both oxides and chalcogenides, contributing to macroscopic strain relief. These clusters are more constrained locally than the non-crystalline networks in which they are immersed. It is therefore not surprising that the nm-scale regions in which pre-existing, locally strain-reducing vacated O-bonding site defects are created. Ab-initio calculations on terminated small O-Si-O-Si-O clusters with 0.5 nm dimensions demonstrate, that MPO is derived from back-donation of electrons from occupied O 2pπ non-bonding orbitals into empty Si atom 3d orbitals [5]. The back-donation also reduced bond-ionicity and is common in when bond-ionicities exceed 50%, The back-donation is facilitated by the large Si-O-Si bond angle of ~150 degrees [5]. The local bonding is qualitatively different in chalcogenides. Bond angles centered on S or Se sites are between ~95 and ~105 degrees, and significant back-donation as described above is not present.

However, it is mandatory to describe the atomic states of atoms in both nc-oxides and nc-chalcogenides in the same way using representations that are non-spherical. Proceeding in this way the 2pπ states of Si in nc-SiO₂ have a T1u character, and the Si 3d states on Si, a T2g character [5].

The continuous random network (CRN) description for glasses and nc-thin films was first proposed in a paper published by Zacharaisen in 1932 [6]. Since that time it has generally been accepted as being a good model for non-crystalline glasses and then films, being extended to chalcogenides as well. Zacharaisen’s description of a CRN includes only 1st and 2nd NN correlations, or equivalently, bond-lengths and bond-angles, respectively [7, 8, 9]. This definition was initially supported by X-ray studies of a group in the UK, who demonstrated that nc-SiO₂ glass was not microcrystalline [10]. However, Zacharaisen did not reference a second paper by the same authors in which they observed what is now designated as the FSDP [11]. They assigned this X-ray diffraction feature in nc-SiO₂ to an inter-atomic spacing of 0.43 nm, essentially the same as that more recently reported in nc-SiO₂ by similar X-ray diffraction, including the Fourier transformed structures factor [2,3]. The detection of MRO in nc-Si(Ge)O₂, and nc-Ge(S,S) and As(S,Se) compound phases and alloys, combined with local-strain reduction in clustered regions is what reduces total strain, both local- and macroscopic in the inhomogeneous networks in which they are immersed. This non-periodic nano-scale hard-soft mixtures is the mechanism for total strain-relief rather than an average bond-coordination number matched to the degrees of vibrational disorder [7].
3. Experimental Procedures

The nc-SiO$_2$ films of this chapter have been prepared by remote plasma enhanced chemical-vapor-deposition (RPECVD) or simply RPD, onto HF-last rinsed Si substrates. The depositions were made with a substrate temperature of 300°C. Thin films were then annealed in Ar to temperatures up to 950°C. [12]. These films and nc-GeO$_2$ films will henceforth be designated as remote plasma deposited nc-Si(GeO$_2$). Nc-SiO$_2$ films formed by oxidation of Si in dry-O$_2$ ambients at temperatures to 900°C and subsequently annealed at higher temperatures cannot be distinguished by spectroscopic methods from 300°C RPD nc-SiO$_2$ films annealed to the same temperatures.

RPD nc-GeO$_2$ films were deposited onto Ge substrates at 300°C, after a rinse in NH$_4$OH. RPECVD depositions used down-stream injected 2% GeH$_4$ in He. Deposition was activated by O-species from an up-stream localized O$_2$–He plasma [12]. Reactive deposition was on either:(i) chemically cleaned Ge surfaces, and (ii) Ge surfaces subjected to either: (a) a remote plasma-assisted oxidation, RPO, (b) a remote plasma-assisted nitridation, RPN, or (c) an RPO followed by RPN [12].

Si and Ge L$_{2,3}$ soft X-ray XAS spectra were obtained using total electron yield (TEY) data acquisition on Beam-Line 8-1 at the Stanford Synchrotron Research Lightsource (SSRL). In the TEY approach, the photoelectron yield vs. X-ray photon energy is determined by measuring the current necessary to return the sample to neutral. The current is proportional to the linear absorption coefficient with a precision of a few percent [13]. Finally, in these XAS studies, and also the XAS studies performed on Beam-Line 10, the nc-SiO$_2$/GeO$_2$ thin films are deposited on Si or Ge substrates, and these are mounted on an Al metal support with stretched Ta wire in contact with the top surface of the sample.

Fig. 1. OK pre-edge, conduction band and O K post edge spectral regimes identified for nc-SiO$_2$ formed by RPD and annealed at 950°C for 1 minute in Ar.
4. Experimental Results and Analysis of Spectral Data

Figure 1 is XAS O K edge spectrum for an RPD nc-SiO₂ annealed at 950°C in an Ar ambient. TEY absorption is plotted for X-ray photon energies between 520 eV and 570 eV. This spectrum is marked to indicate 3 spectral domains of spectroscopic significance: (a) 525 to 532 eV, O K pre-edge that includes mid-band-gap pre-existing, shake-up defect state features; (b) 532 to ~550 eV, this so-called O K edge includes intrinsic virtual bound states above the O-atom ionization (IP) energy and generally referred to as conduction band final-states; and (c) 550 to 570-80 eV, the O K post-edge, or ZANES region that includes shake-up features associated with localized O and Si core states with symmetric closed shell bonding arrangements [14]. These are local resonances in the a continuum regime above the ionization limit and require a three-electron state charge transfer multiplet (CTM) description.

Spectra in the pre-edge region combined with ab initio theory calculations indicate that (i) pre-existing defects in thin film SiO₂ are vacated O-atom sites, rather than bona-fide O-vacancies in which only one of the SiO-atom bonds has been broken with an Si-O terminal group attached to the network structure. As such O-vacancy defects contain one Si-atom dangling bond and one non-bonding O-hole center (NBOHC) with a terminal Si-O neutral bond. In contrast, the O-vacated site defects of this chapter contain two Si-atom strongly-correlated dangling bonds. This pair of state with overlapping radial wave-function requires X-ray activation for detection in electron spin resonance (ESR) measurements [14].

A relationship between pre-existing defects in RPD nc-SiO₂ and MRO results in discrete dihedral angles extending to 3rd and generally 4th nearest-neighbors [9]. This scale of MRO is established by position of the FSDP in the structure factor from X-ray or neutron diffraction [2,3]. Analysis of the FSDP yields a $\lambda_{corr}$ in SiO₂ of ~0.4 to 0.5 nm corresponding to discrete dihedral angles bridging Si-O-Si bonds, and a larger coherence length, $\lambda_{coh}$ identifies non-periodically organized clusters with dimensions ~1 nm. As such, nc-SiO₂ is not a CRN according to Zacharaisen which is by definition has no MRO [6].

Figure 2(a) is a high resolution 2nd derivative O K pre-edge X-ray absorption spectra for an SiO₂ film annealed in Ar at 950°C: (i) the band-gap, (ii) 3 band edge excitons, (iii) singlet
states *inter-mixed* and separated from triplet terms, and (iv) singlet and triplet ground states. Fig. 2(b) is a similar plot for REPCVD GeO$_2$ with the post-deposition, pre-metallization anneal at a lower temperature of 700°C.

Returning to Fig. 2(a), the effective resolution in this spectral regime of the excited defect states, is ~0.1 eV; however, the data are obtained continuously with sampling rate spectral widths of 0.025 to 0.30 eV. This allows 2- and 3-point smoothing of the data prior to differentiation, as well as 2- and 3-point smoothing of differentiated TEY spectra. Fermion wave functions for electrons in the Si-atom dangling bonds are anti-symmetric and include 4-vector spin states (see Figs. 2(a) and 2(b)). The symmetry labeling of features in Fig. 2 is from the d$^8$ Tanabe-Sugano (T-S) diagram for tetrahedral-bonded Si at intermediate values of Δ$\text{LF}$ [1]. The intermediate value is an indicator of partially covalent bonding, as contrasted with the definition of crystal field splitting which assumed 100% ionic bonding. The T-S diagrams were developed for occupied d-states on single transition metal (TM)- and rare-earth (RE) atom, however, the same group theoretically-allowed transitions also apply to 2-occupied d-states on different atoms, e.g., n = 3, in close proximity, e.g., up to 0.3 to 0.5 nm. In nc-SiO$_2$, this is a regime in which the respective radial Si-atom wave-functions overlap forming relatively weak Si-Si bond insuring strong-correlation. This observation is equivalent to an extension of the Pauli Exclusion principle from single atoms to pairs of inter-acting atoms with strongly-correlated Fermion states. More importantly, the relative strengths of defect terms in SiO$_2$ films display approximately the same temperature dependence for films annealed at ~875° to 900°C and 950°C as the D2 Raman peak recorded by Galeener [15,16].

Figures 2(a) and 2(b) includes the symmetries of the radial spatial and spin contributions to the singlet and triplet two electron Fermion wave functions. The important differences in orbital geometries between process-induced vacated O-bonding sites and O-vacancies created by stress are indicated in Fig. 3. The orbital geometry for the O-vacancy has the same Si-O-Si bond-angle as in SiO$_2$, 148 degrees and the Si orbitals are not co-linear as they shown symbolically for the vacated O-site [5]. When the distance between two Si atoms bordering the vacancy is increased, the 3-fold symmetry is maintained for Si-atoms back-bonded to the network.
Figures 2(a) and 2(b) indicate O pre-edge spectra respectively for nc-SiO\(_2\) and GeO\(_2\). Values of \(\Delta LF\) have been extracted from the analysis of these spectra, and are respectively 1.7 eV and 1.3 eV, each with an experimental uncertainty of 0.15 eV. The respective values are derived from the 4th NN local molecular orbital bonding at the defect sites. This is sensitive to the formal ionic charge of the atomic dangling bonds extending into the vacated sites, and the bonding coordination of the dangling bond atom. These charges are 4+ for Si and Ge in the respective oxides. Each of these dangling bond atoms is 4-fold coordinated with 3 equivalent O-atoms back-bonded the dangling bonds. The respective 4+ ionic radii are 0.40 nm for Si\(^{4+}\) and 0.53 nm for Ge\(^{4+}\). Based on electrostatics, the ratio of values (SiO\(_2\)/GeO\(_2\)) = 1.31, and is expected to be equal to the inverse ratio of the respective +4 ionic radii (Ge/Si) = 1.32. This demonstrates that values for the \(\Delta LF\) extracted from O pre-K edge spectra are localized at the defect site, and include: (i) the two dangling bonds projected in the site, (ii) the vacated O-atom site, and finally (iii) the three equivalent O-atoms back-bonded to the dangling bonds, thereby making a total of 5-atoms. This local group has MRO, and therefore a localized molecular orbital. The same values of the \(\Delta LF\) are extracted from Si and Ge, 2p and 3d core state excitations and the O K-edge, as well. This leads to an interesting and significant connection between the values of \(\Delta LF\) and Madelung constant truncated at 5 atom nm-scale clusters. This truncation is the same as in a primitive unit cell in the crystalline forms of SiO\(_2\) and GeO\(_2\). This equivalence of local \(\Delta LF\) values at defects and in nm-scale clusters, with Madelung constants at third and fourth NN’s has important implications for the validity of one-electron band structures. It effectively invalidates the almost universally-accepted concept of determining an empty structure, filling it available electrons, and using this as a basis to identify un-occupied conduction band states. In the ab-initio calculations the conduction band state are virtual, and qualitatively the same as virtual molecular orbital final states for optical and thermal excitations. Further discussions of his flawed concept are clearly beyond the scope of this chapter. As such, the text below continues a critique of the assignments made by the Galeener group for the pre-existing defect state geometries.

![Fig. 5. Variation of single and triplet ground state energies as function of the distance between Si atoms for a vacated O-atom site, and an O-vacancy created by X-ray, \(\gamma\)-ray or high energy electron irradiation.](image-url)
The Raman and IR frequencies for 4-symmetric Si-O bond-stretching vibrations are 800 cm\(^{-1}\). Scaled to 3-symmetric Si-O bonds, and localized at the Si-dangling bond O-vacated defects yields a frequency of \(\sim 600\) cm\(^{-1}\), thereby providing a new assignment for the Raman D2 feature [16]. The results of ab-initio calculations based on two electron wave functions for the two geometries in Fig. 4 are included in Fig. 5, which displays the variation of the single and triplet ground state energies as function of the distance between the Si atoms. As expected, both the exchange energy and the radial wave function, \(F(r)\) overlap are larger for the vacated site for the smallest spacing. However, for Si-Si distances >3.6 Å and extending to 4.5 to 5.0 Å, the ground state energies are essentially the same for singlet and triplet state spin occupancy. The density functional theory (DFT) studies of the Robertson and Slugger groups based on 1-electron states indicate that TM atoms bordering a vacancy show relatively small relaxations of order 0.1-0.2 Å, and as such the only possible ground state and excited states in their respective DFT studies must have a singlet character [17,18].

The results in Fig. 5 explain the fundamental differences and similarities between ab initio calculations and the DFT results. First, the only possible ground states in DFT calculations are singlet states, so that they cannot explain all of the spectroscopic study results of the Lucovsky group which yield both singlet and triplet features in O pre-K-edge XAS shake-up spectra for nc-SiO\(_2\) and nc-GeO\(_2\), and additionally for TM elemental and composite or mixed oxides as well [19]. The ground state energies of the singlet ground states calculated by the Robertson group are \(>3\) eV above the valence band edge and have only a singlet character. Their estimate is in agreement with other one-electron calculations in Ref. 20. However, it is not consistent with electrical measurements, which indicate the singly-occupied ESR active states of states prior to post-metal annealing are significantly closer to the valence band edge, < 0.3 eV.

In marked contrast, ab initio quantum chemistry calculations yield both singlet and triplet features for pre-existing defects in TM oxides and SiO\(_2\) consistent with Fig. 4 and T-S
diagrams [1,19,20]. In summary above, XAS studies on SiO₂ films as-deposited and annealed at different temperatures establish (i) as-deposited films display both singlet and triplet features, and (ii) singlet features increase in strength as annealing temperatures are increased consistent with the new proposed interpretation for D2. Figure 6(b) conduction and valence band offset energies for Si-SiO₂ and Ge-GeO₂ interfaces.

Figure 7(a) is a comparison between O K edge spectra of 5 nm thick films of nc-GeO₂ annealed at 400°C. The spectral features at the band edge and above the respective threshold energies for the transition from "s-like" to "d-like" features are the same. This is consistent with the nm-dimensions of the embedded clusters. Figure 7(b) presents a comparison between O K pre-edge spectra for the 5 nm thick GeO₂ film deposited on chemically-cleaned Ge, and annealed for one minute in Ar at 400°C and 700°C. Decomposition reactions between nc-GeO₂ and c-Ge substrates at c-Ge/nc-GeO₂ interfaces at temperatures of 700°C release gaseous GeO, and create Ge suboxide bonding throughout the Ge film. This reaction leads to the differences in the spectra in this figure. Combined with other experiments the maximum processing temperatures for nc-GeO₂ (i) at nitrided c-Ge surfaces is between 550° and 600°C, and (ii) increases to about 700°C an c-Si surfaces interfacial layers formed by sequential remote plasma oxidations and nitridations with a total interfacial layer thickness no more than 0.7 to 0.8 nm.

5. Discussion

ESR features in SiO₂ films exposed to X-rays and γ-rays, and high energy electrons have been interpreted with an O-vacancy mechanism in which one of two Si-O bands at an Si-O-Si bonding site has been broken [19] The ESR E’ center is a singly occupied dangling bond attached to three-fold Si, requiring activation by high-energy electrons, X-rays or γ-rays. The
second ESR signal is a non-bonding O-associated hole center (NBOHC) defect. Therefore in irradiated films or glasses a pair of neutral defects comprised of an E' center and a NBOHC is created [16,19,20].

ESR studies by Galeener and co-workers on bulk-quenched silica (nc-SiO₂) have distinguished between pre-existing, and X-ray and γ-ray radiation induced defects [16] Pre-existing defect densities increase exponentially with increasing quenching and annealing temperatures and in “dry silicas” these are assigned to E’ centers which are singly occupied Si-atom dangling bonds. NBOHC defects are detected in “dry silicas”, but only after X-ray or γ-ray irradiation, and also reported in “wet silicas” with detectable Si-OH bonding [13]. Pre-existing defects have also been detected by 2nd derivative O K pre-edge X-ray absorption spectroscopy in remote plasma deposited and thermally grown nc-SiO₂ and nc-GeO₂ thin films [19,20].

It is important to re-emphasize the differences between (i) pre-existing and (ii) radiation, electron and neutron induced defects in “wet” and “dry” silica, [16,20] since this differentiation is important for understanding differences between ESR defects in nc-GeS(Se)₂ [20,21,22]. The “dry-silica” results also apply to pre-existing defects in plasma-deposited and annealed thin films of nc-GeO₂ and nc-SiO₂ and nc-GeS₂ bulk and thin film samples as well. In contrast, ESR defects in S-rich nc-Ge₁ₓSₓ alloys are similar to “wet-silica” results. The pre-existing “wet silica” defects are NBOHC’s and have qualitatively different properties when compared with pre-existing defects in “dry silicas” [16]. These defects always require activation with optical or UV radiation for ESR detection. They are present in the S-rich alloys because the S-S bond energy is less than the Ge-S bond energy. This means that it costs more energy to break a Ge-S-Ge bonding arrangement that a Ge-S-S-Ge arrangement. This bond cleave gives a pair of non-bridging S-hole centers (NBSHC’s), the S (and also Se) analog of NBOHC’s.

The results reported this section, as well as the comments made in Section 4 relative to a new interpretation of the origin of the D2 feature are consistent with the results presented for nc-GeS₂ and S-rich nc-Ge₁ₓSₓ alloys. The conclusion as that vacated sites are responsible for pre-existing defects in nc-GeO₂ and nc-SiO₂, and nc-GeS₂ as well, and not planar small ring structure.

As already noted above, and similar to plasma-deposited SiO₂ and GeO₂, the stoichiometric GeS₂ compositions contain small concentrations of detectable pre-existing ESR defects [20,21,22]. However, for Ge concentrations between about 20 at. % and about 31.5 at. %, two defect signatures are evident, one characteristic of an E’ center on the Ge atoms, and the second is an NBSHC local terminal group on one of the Ge-atoms. These conjugate defects result from local strain induced breaking a Ge-S bond, into a Ge dangling bond back-bonded to the three S-atoms of the network, and a terminal and neutral singly occupied S dangling bond. Paired pre-existing defects of this sort have not been reported in non-crystalline S-rich concentrations As₁ₓ(S,Se)ₘ alloys [23,24]. Local strain in SiO₂ and GeO₂ is relieved by vacating bridging O-atoms, whereas the lower average coordination in chalcogenide rich As-S and As-Se alloys is insufficient to force defect formation by vacating or bond-breaking mechanisms, and as such there are no reports of pre-existing defects in these alloys, or in stoichiometric compounds as well.

Complementary studies of amorphous As and Se, and As₂Se₃ were performed by the NRL group [23,24]. These studies performed at low temperatures, demonstrated an optically induced ESR signal in As₂Se₃ by excitation in the Urbach tail, absorption constant ~100 cm⁻¹, and accompanied by mid-band gap absorption. The NRL group has attributed the ESR
response in $\text{As}_2\text{S}_3$ and $\text{As}_2\text{Se}_3$, respectively, to a single electron occupancy in non-bonding S $2p\pi$ and Se $3p\pi$ lone pair orbitals, that is to NBS(Se)HCS [23,24]. Finally, the Xerox PARC group of Biegelsen and Street demonstrated qualitatively different ESR signals for optically induced ESR in $\text{As}_2\text{Se}_3$ in the Urbach tail, and at higher photon energy as which photodarkening occurred, [25] confirming significant SRO and MRO scale bonding changes in the photo-darkened state. These local changes in SRO and MRO have identified in EXAFS studies, [20] and ab-initio calculations [26].

6. Summary and Conclusions

(i) Quantification of MRO has been achieved by analysis of the FSDP in the structure factor obtained from analysis of X-ray and neutron [2,3]. This extends to 3rd and 4th NN's and as such includes discrete values of dihedral angles, and in many instances it also includes constant and coupled phase relationships between the discrete dihedral angles [9].

(ii) MRO has also been detected by spectroscopic determinations of d-state ligand field splittings, $\Delta\text{LF}$’s, that derive from the valence band states comprised of symmetry-adapted linear combinations (SALC’s) of atomic states [1,19]. These splittings are detected in (i) Si L2,3 and Ge M3,4 spectra, respectively, for nc-$\text{SiO}_2$ and nc-$\text{GeO}_2$, (ii) UPS and XPS valence band spectra, and in (iii) conduction band virtual bound state spectra obtained by spectroscopic ellipsometry and reflectivity, as well as the analysis of O K edge XAS spectra.

(iii) $\Delta\text{LF}$’s, and evidence for MRO are also obtained from analysis of O K pre-edge defect spectra. This approach treats the 2-electrons localized at an O-vacancy, or in a vacated O-atom site as a strongly-correlated pair on two different atoms, and then applies the appropriate T-S diagrams for assigning symmetries and ordering of the excited states, thereby extracting values of $\Delta\text{LF}$’s [1,19].

(iv) Proceeding in this the vacated O-atom site model has been verified by a combination of ab-initio quantum chemistry calculations and the O K pre-edge spectra for nc-$\text{SiO}_2$ and nc-$\text{GeO}_2$.

(v) The vacated O-atom site model has been extended to a vacated S (Se)-atom model for nc-$\text{GeS(Se)}_2$. Due to catenation of S- and Se-atoms in S(Se)-rich nc-$\text{Ge}_1-x\text{S(Se)}_x$, and also in nc-$\text{As}_1-x\text{S(Se)}_x$ alloys, the vacated S(Se)-atom site models do not apply.

Finally, (vi) it is significant to note that pre-existing defects in nc-$\text{SiO}_2$ and nc-$\text{GeO}_2$ are thermally-activated by removal of O-atoms from Si-O-Si and Ge-O-Ge bonding sites within chemically self-organized cluster geometries obtained from the analysis of the width of FSDP in reciprocal space. In a similar way, the limiting defect densities in a-$\text{Si(H)}$ with 10 at.% H are associated with thermal activation of Si-H vibrations at the perimeter of the self-organized clusters in a-$\text{Si(H)}$ alloys [27].

Acknowledgements

The authors acknowledge support from the National Science Foundation, NSF, and from the Defense Threat Reduction Agency, DTRA. They also acknowledge the contribution of Cheng Cheng and Brian Papas at NC State University. The authors acknowledge helpful discussions with Professors David Aspens Jerry Whitten at NC State University. Lastly the authors acknowledge the use of the Beam-lines 10-1 and 8-1 at the Stanford Synchrotron Research Lightsource, SSRL, in Menlo Park CA, and assistance of Dr. Dennis Norland, a beam-line scientist.
[1] F.A. Cotton, Chemical Applications of Group Theory, 2nd Ed. (Wiley Nescience, New York, 1963) Chapter 8.
[2] J. Du, R.L Corrales, Phys. Rev. B 72, 092201 (2005).
[3] S.C. Moss and D.L. Price: in Physics of Disordered Materials, edited b. D. Adler and H. Fritsch and S.R. Vishinski (Plenum Press, New York, 1985), p. 77; D.L. Price et al., J. Phys. Condense. Matter 1, 1005 (1989).
[4] N.R. Rae, et al., J. Non-Cryst. Solids 240, 221 (1998).
[5] J. L. Whitten, et al., J. Vac. Sci..Technol. B 20 (2002) 1710.
[6] W.H. Zachariasen, J. Am. Chem. Soc. 54, 3341 (1932).
[7] G. Lucovsky and J.C. Phillips, J. Phys.: Condens. Mater. 19 455218 (2007), and references therein.
[8] B. Kramer, K. Maschke and P. Thomas, phys. stat. sol. (b) 49, 525 (1972).
[9] G. Lucovsky and F.L. Galeener, J. of Non-Cryst. Solids 35 & 36 (1980) 1209.
[10] J.T. Randall, H.P. Rooksby, B.S. Cooper, Z. Krist, 75, 196 (1930).
[11] J.T. Randall, H.P. Rooksby, B.S. Cooper, Nature (supplement), 458 (1930).
[12] G. Lucovsky and D. Zeller, J. Nanoscience and Nanotechnology, 11, 7974-7981 (2011).
[13] Owens, S.C. Bayliss, G.W. Fraser, S.J. Gurman, Nucl. Instrum. Methods Phys. 280 Res. Sect. A 385, 556 (1997).
[14]. 25. F. deGroot and A. Kotani, Core Level Spectroscopy of Solids (CRC Press, Boca Raton, 2008).
[15] F.L. Galeener and G. Lucovsky, Phys. Rev. Lett. 37, 1474 (1976).
[16] F.L. Galeener, J. Non-Cryst. Solids 71, 373 (1985); Phys. Rev. B 47, 7760 (1993).
[17] K. Xiong, et al., Appl. Phys. Lett. 87, 183505 (2005).
[18] L. Gavartin, et al., Appl. Phys. Lett. 89, 082908 (2006).
[19] G. Lucovsky, Japan J. Appl. Phys. 50, 04DC09 (2011).
[20] D.L. Griscom, Ceramic Soc. Jap. 90, 823 (1981), and Refs. therein.
[21] R.A. Street and D.J. Biegelsen, J. of Non-Cryst. Solids 32 (1979) 339.
[22] K. Arai and H Namikawa, Solid State Commun. 13, 1167 (1973)/
[23] S.G. Bishop et al., Phys. Rev. Lett. 21, 1346 (1975).
[24] S.G. Bishop et al., Phys. Rev. B 15, 2294 (1977).
[25] J. M. Lee, M.A. Paesler, D.E. Sayers, A. Fontaine, J. of Non-Cryst. Solids 123, 295 (1990).
[26] R. Mowrer, G. Lucovsky, L.S. Sremaniak, J.L. Whitten, J. of Non-Cryst. Solids 338-340, 543 (1994), and Refs. therein.
[27] G. Lucovsky and H. Yang, Jpn. J. Appl. Phys. 37, 1082 (1998).