Abstract

The electron spin resonance studies by Galeener et al. on bulk-quenched non-crystalline (nc-) silica glasses, nc-SiO$_2$, have distinguished between pre-existing defects formed during quenching and annealing of glasses, and X-ray and g-ray radiation induced defects. This article shows similar defects in plasma-deposited thin films and thermally-grown nc-SiO$_2$ and nc-GeO$_2$. Pre-existing defect densities increase exponentially with increasing quenching and annealing temperatures and in “dry silicas” with no detectable Si-OH vibrations are assigned to E’ centers or singly occupied Si atom dangling bonds. Non-bonding O-hole centers, or NBOHCs are also detected in dry silicas, but only after significant X-ray or g-ray irradiation. Pre-existing defect are also detected by 2nd derivative O K pre-edge X-ray absorption spectroscopy in remote plasma deposited/thermally grown nc-SiO$_2$ and nc-GeO$_2$ thin films. These spectra display singlet and triplet features labeled according to Tanabe-Sugano (T-S) diagrams. It is demonstrated by ab initio theory and experiment that pre-existing defects in thin film nc-SiO$_2$ and nc-GeO$_2$ are vacated O-atom sites in which an O-atom has never resided.

Keywords: non-crystalline SiO$_2$, remote plasma processing, X-ray absorption spectroscopy, vacated O-atoms sites, pre-edge O K edge XAS, medium range order, non-crystalline GeO$_2$

1. Introduction

ESR active pre-existing defects detected in nc-SiO$_2$ and in nc-GeO$_2$ and Se-rich Ge$_{1-x}$Se$_x$ alloys are qualitatively different. This is associated with qualitative differences in medium range order (MRO) between oxides and chalcogenides: S-atoms and Se-atoms for S-S and Se-Se bonds, where O-atoms do not except in peroxides. This difference, in the context of electronic spectroscopy and theory, is based on d-state ligand field splittings, $\Delta$LF, associated with molecular orbital theory descriptions of valence band states [1]. $\Delta$LF, in eV at Si, Ge and As cation sites in oxides and chalcogenides can be determined from analysis of X-ray absorption and electron energy loss spectroscopies, XAS and EELS, respectively, and from reflectivity (R), and spectroscopic ellipsometry (SE) spectra. $\Delta$LF is local symmetry, atomic
coordination, and atom specific. A non-vanishing value requires a scale of coherent order extending up to and generally beyond, 3rd next-nearest-neighbors. This medium range order (MRO) regime includes discrete values of dihedral angles [1]. As such, a non-vanishing \( \Delta L \) is a spectroscopic indicator for 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 the connection with detection of pre-existing ESR active defects in nc-SiO

2. Medium range order

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, \( \lambda_{corr} \), are 0.4 nm in SiO\(_2\), [4] and extend to \(~0.65\) nm in GeSe\(_2\) [2,3], and are associated with 3rd and 4th nearest-neighbor (NN) distances. The coherence length, \( \lambda_{coh} \), for molecular cluster formation is obtained from the FSDP width beyond the 3MRO regime. e.g., \( \lambda_{coh} \approx ~1\) nm in Si(Ge)O\(_2\), [3] and increases to 2.9 nm in GeSe\(_2\) [4]. The clusters are non-periodically-distributed, and contribute to macroscopic strain relief. However, they are more constrained than the network in which they are immersed, and therefore are the regions in which pre-existing, locally strain-reducing defects are formed.

Ab-initio calculations on terminated small clusters demonstrate that \( \lambda_{corr} \) in nc-SiO\(_2\), and also in crystalline SiO\(_2\) is derived from the back-donation of electrons from occupied O 2p non-bonding orbitals into empty Si atom 3d orbitals. This and facilitated by of the large Si-O-Si bond angle of \(~150\) degrees [5]. It is necessary to describe these atomic states using representations that are non-spherical. Proceeding in this way the 2p\(_\pi\) states have a T1u character, and the Si 3d states, a T2g character [5].

The concept of a continuous random network (CRN) description of non-crystalline glasses and thin films derives from a paper published by Zacharaisen in 1932 [6]. His definition of a CRN includes only 1st and 2nd nearest neighbors correlations, equivalently, bond-lengths and bond-angles, respectively [7, 8, 9]. This definition was supported by studies of a group in the UK which demonstrated that nc-SiO\(_2\) glass was not microcrystalline [10]. Zacharaisen did not reference a second paper by the authors of Ref. 10, [11] in which they found what is now designated as the FSDP. They assigned this feature in nc-SiO\(_2\) to an inter-atomic spacing of 0.43 nm, essentially the same as that reported in nc-SiO\(_2\) [2,3].

3. Experimental procedures

Nc-SiO\(_2\) films were prepared by remote plasma enhanced chemical-vapor-deposition (RPECVD) onto Hf-last cleaned Si substrates at a temperature of 300°C, and subsequently annealed to temperatures up to 950°C in an inert Ar environment [12]. These films and nc-GeO\(_2\) films will be designated as remote plasma deposited, RPD 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 spectroscopically from RPD nc-SiO\(_2\) films annealed to the same temperatures.

RPD nc-GeO\(_2\) films were deposited onto Ge substrates, rinsed in NH\(_4\)OH at 300°C, using down-stream injected 2% GeH\(_4\) in He, and activating deposition with O-species from an up-stream localized O\(_2–\)He plasma [12]. Depositions were on (i) chemically cleaned Ge surfaces, and (ii) Ge surfaces subjected to either (a) remote plasma-assisted oxidation, RPO, (b) remote plasma-assisted nitridation, RPN, or (c) 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 this method, the photoelectron yield vs. X-ray photon energy is determined by measuring the current necessary to return
the sample to neutral. In these XAS studies, and those performed on Beam-Line 10, samples are mounted on an Al metal support, with stretched Ta wire in contact with the top surface of the sample. The current measured relative to ground is a measure of the linear absorption coefficient with a precision of a few percent [13].

4. XAS Results

Figure 1 is XAS O K edge spectrum for an RPD nc-SiO₂ annealed at 950°C in an Ar ambient. TEY is plotted for X-ray photon energies between 520 and 570 eV. This spectrum is marked to indicate three spectral domains of interest: (a) 525 to 532 eV, O K pre-edge that includes mid-band-gap pre-existing defect state shake-up features; (b) 532 to ~550 eV, the O K edge that includes intrinsic virtual bound or 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 O and Si core levels.

Spectra in the pre-edge region complemented by 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 from which one of the Si-O-atom bonds has been broken, but in which that Si-O group remains within the network. As such vacancy defects contain one Si-atom dangling bond and one NBOHC with an Si-O terminal bond, and the vacated sites of this paper contain two Si-atom dangling bonds.

A relationship between pre-existing defects in RPD nc-SiO₂ and MRO results from 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 \( \lambda_{\text{corr}} \) in SiO₂ of ~0.4 to 0.5 nm corresponding to discrete dihedral angles bridging Si-O-Si bonds, and a larger coherence length, \( \lambda_{\text{coh}} \) 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 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) 3 negative ion singlet states, (iv) inter-connected triplet, and singlet terms, and (v) singlet and triplet ground states. The effective resolution in this spectral regime is ~0.1 eV; however, data are obtained continuously with an sampling rate spectral width of 0.025 to 0.30 eV. This allows 2 and 3 point smoothing of the data prior to differentiation.
Fermion wave functions for electrons in the Si-atom dangling bonds are anti-symmetric and include 4-vector spin states (see Fig. 2). Labeling of features in Fig. 1 is from the $d^2$ Tanabe-Sugano (T-S) diagram for tetrahedrally-bonded Si, and for intermediate values of DLF [1]. The T-S diagrams were developed for occupied d-states on single TM-atom, however, the same group theoretically-allowed transitions also apply to two occupied d-states on different atoms, e.g., $n = 3$, in close proximity, e.g., up to 0.3 to 0.5 nm. This is a regime in which their respective radial wave-functions overlap in a weak Si-Si bond. This is equivalent to defining this a chemical bond in terms of Pauli Exclusion. The relative strengths of defect terms in SiO$_2$ films, as function of temperature display about the same dependence as the D$_2$ Raman peak [14,15].

Figure 2 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 are 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.
The Raman and IR frequencies for 4-symmetric Si-O bonds are 800 cm\textsuperscript{-1} [14] Scaled to 3-symmetric Si-O bonds as in a dangling bond defects, this yields a frequency of ~600 cm\textsuperscript{-1}, thereby providing a new assignment for the Raman D\textsubscript{2} feature [15]. 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. The vacated site is a relaxed state in which the two dangling bonds are linear rather than at an angle of ~145°. 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, the dependence of ground state energies is the essentially same for both orbital geometries. The DFT studies of the Robertson and Shlugger groups for one-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 have a singlet character [16,17].

![Energy (eV) vs Si-Si distance](image)

Fig. 5. Plot of the variation of the single and triplet ground state energies as function of the distance between the Si atoms for a vacated O-atom site, and an O-vacancy created by X-ray or g-ray radiation resulting in ejection of a neutral O-atom.

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 studies of the Lucovsky group which yield both singlet and triplet features in pre edge O K XAS spectra for nc-SiO\textsubscript{2} and nc-GeO\textsubscript{2} as well as TM oxides [18]. The ground state energies of the singlet ground states calculated by the Robertson group are generally >3 eV above the valence band edge. This estimate is in good agreement with one electron calculations, as well other studies [19]. 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. The energy separation between these states and negatively charged O-vacancies is significantly smaller in the Robertson and Shugger group calculations then what has been reported by the Lucovsky group, because the DFT calculations are not based on molecular orbital ground states that inherently include d-state ΔLF splittings [1,12].
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 \[1,18,20\]. In summary above, XAS studies on SiO$_2$ 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 7 is a comparison of the second derivatives of O K edge spectra of RPD nc-SiO$_2$ and RPD nc-GeO$_2$ \[12\]. Each spectral trace indicates a singlet band gap feature, at 8.9±0.1 eV in nc-SiO$_2$ and 9.7±0.1 eV in nc-GeO$_2$. Each band gap features is followed by exitonic triplet features beginning about 0.5 below the respective band gap and spanning approximately 0.5 eV. The same band gap and excitonic features are observed in transmission spectra of thick bulk silica (nc-SiO$_2$ \[19\]).

![Figure 7](image)

**Fig. 6** Comparison of O K edge spectra of ~5 nm thick films of nc-SiO$_2$ and nc-GeO$_2$ remote plasma deposited at 300°C onto plasma nitrided SiON surfaces of Si. The nc-SiO$_2$ film was annealed in Ar at 900°C, and the nc-GeO$_2$ was not annealed after deposition.

![Figure 7(a)](image)

**Figure 7 (a)** Comparison between O K edge spectra for two GeO$_2$ films of different thickness, 2 nm and 5 nm, deposited on chemically-cleaned Ge, and annealed at 400°C. Figure 7(b) Changes in spectra between the 5 nm film of Fig. 8(a) annealed at 400°C and 700°C brought about by release of interfacial O-atoms forming gaseous GeO for release from the film.
Figure 7 is a comparison between O K edge spectra of 2 nm thick and 5 nm thick films of nc-GeO₂ annealed at 400°C. The spectral features are essentially the same as are second derivation O K pre-edge defects features (not shown). Figure (7) presents a comparison between Comparison between low-resolution O K pre-edge spectra for the 5 nm thick GeO₂ film deposited on chemically-cleaned Ge at 300°C, 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 GeO₂ and creates Ge suboxide bonding throughout the Ge film. This reaction leads to the differences in the spectra in this figure [19]. 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, 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 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 [15,19].

In summary, 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 [15] Pre-existing defect densities increase exponentially with increasing quenching and annealing temperatures and in “dry siliconas” 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. 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 [18].

It is also important to differentiate between (i) pre-existing and (ii) radiation, electron and neutron induced defects in “wet” and “dry” silica, [15,19] since this differentiation is also important in understanding differences between ESR defects in nc-GeS(Se)₂ [20,21,22]. The “dry-silica” results also apply to with pre-existing defects in plasma-deposited and annealed thin films of nc-GeO₂ and nc-SiO₂, and nc-GeS₂ as well, whereas, ESR defects in S-rich nc-Ge₁₋ₓSₓ alloys are similar to “wet-silica” results. The pre-existing “wet silica” defects are NBOHC’s indicating qualitatively different defects when compared with pre-existing defects in “dry silicas” [15]. In each instance these require activation, for example 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.

The results reported above in this section of the article, as well as the comments made in Section 4 relative to an new interpretation of the origin of the D₂ feature are consistent with the results presented for nc-GeS₂ and S-rich nc-Ge₁₋ₓSₓ alloys. The conclusion as that vacated sites are responsible for pre-existing defects in nc-GeO₂ and nc-SiO₂, and nc-GeS₂ as well.

As already noted above, 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 a non-bridging S-atom hole center (NBSHC) center on the S 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 As$_{1-x}$(S,Se)$_x$ alloys [23,24]. Local strain in SiO$_2$ and GeO$_2$ 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 not reports of pre-existing defects in these alloys, or in stoichiometric compounds as well.

Complementary studies of amorphous As and Se, and As$_2$Se$_3$ were performed by the NRL group of Bishop, Taylor and Strom [16,17]. These studies performed at low temperatures, demonstrated an optically induced ESR signal in As$_2$Se$_3$ 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 As$_2$S$_3$ and As$_2$Se$_3$, respectively, to a single electron occupancy in non-bonding S 2p and Se 3p lone pair orbitals, that is to NBS(Se)HCs [23,24]. The ESR “dry-silica” glasses spectral functions are qualitatively similar to the NBOHC ESR in SiO$_2$. Finally, the Xerox PARC group of Biegelsen and Street demonstrated qualitatively different ESR signals for optically induced ESR in As$_2$Se$_3$ in the Urbach tail, and at higher photon energy as which photo-darkening 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

(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 coupled phase relationships between these discrete dihedral angles [9].

(ii) MRO has also been detected by spectroscopic identifications of d-state ligand field splittings, $\Delta$LF’s, that derive from the valence band states comprised of symmetry-adapted linear combinations (SALC’s) of atomic states [1,18]. These splittings are detected in Si and L$_{2,3}$ and Ge M$_{2,3}$ spectra, respectively, for nc-SiO$_2$ and nc-GeO$_2$, UPS and XPS valence band spectra, conduction band spectra obtained by spectroscopic ellipsometry and reflectivity, as well as O K edge XAS spectra.

(iii) $\Delta$LF’s, and hence MRO are also obtained from analysis of O K pre-edge defect spectra. This approach treats the two 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 T-S diagrams as the basis for extracting values of $\Delta$LF’s [1,18].

(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-SiO$_2$, and nc-GeO$_2$.

(v) The vacated O-atom site model has been extended to a vacated S (Se)-atom model for nc-GeS(Se)$_2$. Due to catenation of S- and Se-atoms in S(Se)-rich nc-Ge$_{1-x}$S(Se)$_x$ and also in nc-As$_{1-x}$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-SiO$_2$ and nc-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-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-Si(H) alloys [27].
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References